

ENHANCED SURFACE DYNAMICS AND PROPAGATION IN MOLECULAR
GLASSES

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ABSTRACT

ENHANCED SURFACE DYNAMICS AND PROPAGATION IN MOLECULAR GLASSES

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Nanometer-sized thin films of small organic molecules are widely used in applications ranging from organic electronics and pharmaceuticals to coatings and nano-imprint lithography. Studies show that properties of these nanometer-sized thin films deviate strongly from their bulk counterparts, possibly due to enhanced surface dynamics and increased surface-to-volume ratio. Developing new techniques that can readily measure the surface dynamics of an organic glass can help understand such phenomena. In this thesis, I will first introduce a novel technique that uses tobacco mosaic virus as the probe particle to directly measure surface diffusion on molecular glasses. The surface diffusion is measured to be greatly enhanced compared to bulk counterpart. The surface diffusion is also investigated on ultra-stable glasses and aged glasses with suppressed relaxation dynamics and ultrathin glasses with overall enhanced dynamics. The surface diffusion is found to stay fast and invariant on molecular glasses with varying bulk relaxation dynamics, suggesting that the surface diffusion is decoupled from bulk relaxation dynamics and is only a purely free surface motion. Further, I combine a morphological probe tracking the isothermal dewetting process in ultrathin molecular glasses with cooling-rate dependent glass transition temperature measurements to study the propagation length scale of the surface enhancement effect. Results show that organic glass films with thicknesses of 30 nm or less have dynamics significantly enhanced relative to bulk, induced by the free surface. Furthermore, there is a sharp glass to liquid transition observed around 30 nm, indicating long-range correlated dynamics in ultrathin molecular glasses. While these studies are important for a host of applications, they can also help elucidate the fundamentals of interfacial effects in thin film systems.

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CHAPTER 1 : Introduction

Amorphous materials, or glasses, are everywhere around us and have been widely used since ancient times. They can be made from metallic atoms and alloys, inorganic materials, polymers, small organic molecules and colloids. Glassy materials have many emerging applications in industries, including but not limited to windows and displays, optical fibers, electronics[131, 146, 139], pharmaceuticals[153, 28, 63], coatings[85], data storage[148] and nuclear waste storage[110]. Thus a good understanding of the formation and properties of glassy materials is imperative to address the needs in such wide areas of applications.

1.1. Introduction to Glass Transition

1.1.1. Overview

As schematically shown in Figure 1.1, the easiest and most common way of making a glass is by cooling a material in its liquid state rapidly enough below the melting point temperature (T_m) to avoid crystallization. When the phase transition from liquid to crystal is avoided, the system will enter a metastable equilibrium regime named supercooled liquid. In the supercooled liquid state, the molecular motions slow down dramatically with any further cooling. Figure 1.2 shows the rapid increase of viscosities (η) and structural relaxation times (τ_α) for two materials (inorganic SiO_2 [98] and small organic molecule o-terphenyl[113]) in the supercooled regime as the temperature is further decreased. Upon further cooling, at some temperature the dynamics of the system becomes so slow that it falls out of equilibrium and forms a glass, this temperature is what is called the glass transition temperature, T_g . Glasses are out-of-equilibrium materials and the glass transition is path dependent. As shown in Figure 1.1 if a slower cooling rate is used, path 2 will be taken to form a glass from the supercooled liquid state where the glass transition temperature would be slightly lower than that of path 1. As glasses are in out-of-equilibrium states, if held at some temperatures below its T_g for some time, as a result of thermodynamic driving force towards the equilibrium supercooled liquid state, the enthalpy or volume will decrease in

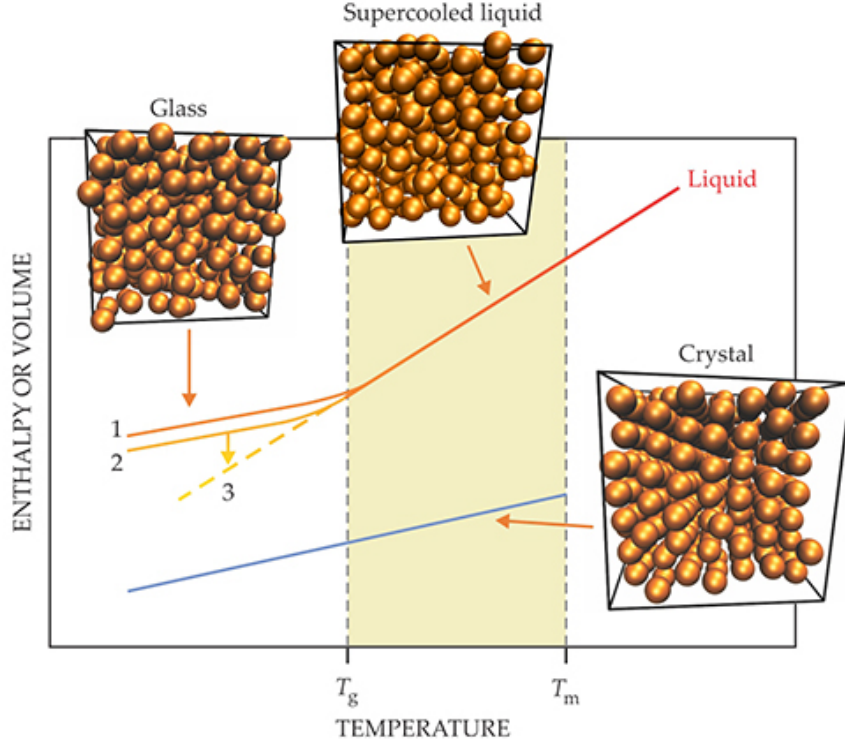


Figure 1.1: Schematic of enthalpy or volume as a function of temperature for liquid, glass and crystal. Reproduced from [11], with the permission of the American Institute of Physics.

a nonlinear way as a function of isothermal holding time. This process, called physical aging, is illustrated as route 3 in Figure 1.1. Due to extremely slow relaxation times in glassy state, the aging process is very slow and takes exponentially longer time with further cooling below T_g .

Insets in Figure 1.1 also shows typical configurations for crystal, supercooled liquid and glass. Different from the unique energy minimum state of perfectly ordered configuration of crystals, glasses have disordered configurations similar to supercooled liquids and they can rearrange and explore other possible configurations, but due to their kinetically slow relaxations such exploration of configurations can be very slow and they can get trapped in local-energy minimum configurations.

Although glasses are everywhere around us and they have been used in various applications, the fundamentals of glass transition have long been a research challenge and there are many

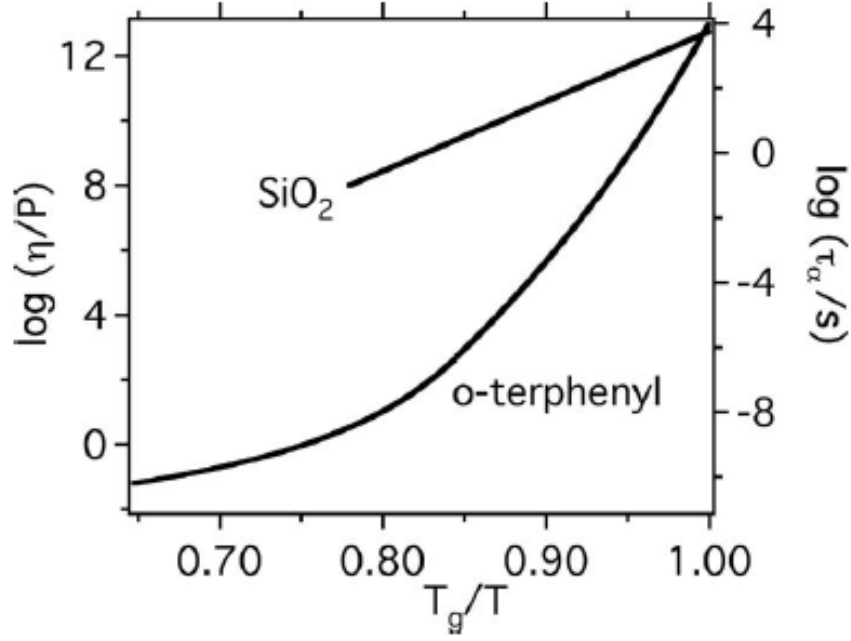


Figure 1.2: Viscosity and relaxation time as a function of inverse temperature for SiO₂ and o-terphenyl. Reprinted from [37], with the permission of AIP Publishing. Data from References [98] and [113].

unresolved questions associated with the glass transition phenomenon. It is imperative to facilitate the understanding of glass transition and guide for better glassy material design for industrial applications.

1.1.2. Theories

Many theories have been developed to describe the glass transition phenomenon, here we briefly introduce few of these theories in the field.

The Adam-Gibbs (AG) model[2] is a molecular-kinetic theory that describes the glass transition from an entropy approach based on the size of cooperatively rearranging regions (CRRs). In AG model, the total entropy of the system can be written as a sum of vibrational entropy and configurational entropy (S_{conf}). CRR defines the region within which the molecules relax to a new configuration in a cooperative manner and CRRs are assumed to be independent of each other. Theories based on AG entropy model include but not

limited to Random First Order Theory (RFOT)[84, 149] and models proposing string-like CRRs[36, 62]. The size of CRR is highly dependent on temperature, AG model and other similar models predict that as the temperature is decreased, the system will have a smaller configurational S_{conf} and thus the number of CRRs has to decrease, which will result in an increase in the size of CRRs or more molecules are required to move cooperatively as a distinct configurational state as the temperature is decreased. AG model can successfully connect the relaxation time and the configurational entropy of the system[2] and can describe the phonemically observed Vogel-Fulcher-Tammann (VFT) behavior of glassy systems. However, the exact physics of CRRs is not very well defined from an experimental point of view.

Mode coupling theory (MCT)[9, 80] provides a statistical mechanical description of the glass transition phenomenon. It considers a time dependent density correlation function in Fourier domain. MCT predicts a critical temperature T_c where the correlation time diverges, and the slowing down of the time correlation function or the glassy behavior would be observed. In MCT model, rich dynamical behaviors of the glassy system can be predicted at different time scales.

Activated barrier-hopping model developed recently by Schweizer *et al.*[90, 92, 91, 93] introduced a force-level theory to predict glass transition that is based on MCT framework, where they refer as Elastically Collective Nonlinear Langevin Theory (ECNLE). The ECNLE model considers a force field consisting a local cage hopping barrier that evolves nearest neighbors and a long-range collective elastic barrier where the two are distinct but coupled. This recent developed ECNLE model has been shown to be successful in predicting various types of supercooled liquids relaxations[90, 92] and in confined thin film relaxation dynamics[91, 93].

Other glass transition theories, include but not limited to coupling theory[100], facilitation models[22, 18] are also successful in predicting some of the observed experimental glass transition phenomena, yet each has their own limitations in directly comparison with ex-

periments or fails to describe all experimental observations.

1.2. Glassy Thin Film and Interfacial Dynamics

1.2.1. Overview

The very initial motivation of studies on nano-sized thin glassy films was attempting to probe the size of the cooperative rearranging regions. Over the past few decades, there have been many studies focused on the studies of properties of nano-sized thin glass films and there is growing evidence suggesting that when confined into nanometer scales, the dynamics of thin glass films can be greatly perturbed by the existence of interfaces. Many studies in polymeric glasses have shown the properties including glass transition temperature[76, 52, 122, 43, 117, 55], effective viscosity[152, 21], mechanical modulus[133, 102], fragility[46, 55, 56, 45] and physical aging rates[41, 114, 118] in nanometer-sized thin polymer glass films can strongly deviate from those of bulk properties. Similar observations have also been reported in small molecule organic glasses[70, 156, 128, 161, 160]. Although still under debates, it is widely accepted that the deviations in thin glass films from their bulk counterparts are due to the existence and perturbing roles of interfaces. For free standing thin glass films, the existence of film/air interfaces is reported to enhance the overall dynamics[51, 104]. For supported thin glass films the overall dynamics are determined by the interplay between film/air interface and film/substrate interface, a weakly adsorbing substrate could enhance the dynamics while a strongly adsorbing substrate could slow down the dynamics[122, 55, 58]. Many experimental efforts have been focused on investigating the interfacial effects on the thin glass film dynamics. Glass transition temperature measurements have been the most widely used approach. Film thickness dependent T_g measurements[76, 122, 52, 55, 58], local T_g measurements via fluorescence doping layers[41, 42, 115], and cooling-rate dependent T_g measurements[46, 55, 56, 58, 161] have provided great opportunities in understanding the size effects in the glass dynamics. Other important techniques include but not limited to dielectric measurements, effective viscosity measurements through monitoring capillary induced flow[152], fluorescence probe reorientation measurements[104, 106] as well

as physical aging experiments[41, 115, 118], they have also provided important insights into the understanding of the glass transition and interfacial effects in glass dynamics.

Despite the studies on learning interfacial effects from overall thin film properties or dynamics, there have been great efforts to develop experimental techniques to directly probe the dynamics at the interface. So far, most of the available techniques have focused on air/film interface or what we call the free surface. On the free surfaces of polymer glasses, nanoparticle embedding[140, 69, 119], nanohole relaxation[47] and stepped film decay techniques[21] have directly probed the surface dynamics on polymers. The results suggest that the dynamics at or near the free surface are greatly enhanced compared to the bulk dynamics with weaker temperature dependences. More recently, techniques have also been developed to probe the surface dynamics on small molecule organic glasses. Surface grating decay technique[163, 13, 86, 157, 125, 23] developed by Yu *et al.* uses a mask to pattern periodic gratings on the surface of molecular glasses in the liquid state and then monitors the decay of the surface grating at various temperatures above or below T_g . Very interestingly, they observed a transition from bulk viscosity to surface diffusion controlled flow at temperatures below around $T_g + 10$ K and the surface diffusion is measured to be orders of magnitude faster than the bulk diffusion with a weaker temperature dependence. The surface grating decay method has been applied to investigate several other small organic molecules and the surface diffusion is found to have a strong dependence on the molecular size and intermolecular interactions[157, 23]. A larger molecular size would slow down the enhancement of the surface diffusion and in the extreme case no surface diffusion is observed on polystyrene glasses with molecular weight larger than 1.7 kg/mol[157]. The existence of hydrogen bonding intermolecular interactions would also slow down or even erase the surface diffusion enhancement[23]. In contrast, such molecular size and intermolecular interaction dependences are not observed in bulk diffusion or relaxation dynamics. These observations request further investigation on the fundamentals of physical nature of the observed enhanced surface diffusion on molecular glasses.

1.2.2. Open Questions

Despite many progresses on understanding the thin film dynamics and surface dynamics in polymeric and molecular glasses in recent years, there are still many unresolved questions in the field. One of the ongoing investigation is about the dynamics of interface induced dynamical gradients and the length scales of such interfacial perturbations. Studies from fluorescence reorientation[104, 39] and nanoparticle embedding[140, 69, 119] have reported the thickness of the enhanced mobile layer near free surface can be a few nanometers thick and is dependent on temperature. Studies that investigated the local layer glass transition temperatures[42, 7, 8], thickness dependent effective viscosity or activation barrier for molecular rearrangement[161, 55, 56] suggest that the propagation length scale of interfacial effect can be 30-50 nm long. The relationship between the direct measure of surface dynamics and their propagation depth is still lacking. Further, after several decades of researches in nanoconfinement effect on the glass transitions, whether or how the knowledge we learn from thin film dynamics would benefit our understanding of the glass transition phenomena is not very clear yet. A collaborative investigation and understanding of the glass transition and dynamics of thin film fundamentals is imperative for these unresolved questions.

1.3. Stable Molecular Glasses by Physical Vapor Deposition

In addition to the potential importance to the glass transition theory, the enhanced surface dynamics also contribute to a new type of glasses that were first reported in 2007[137]. Researchers found that physical vapor deposition (PVD) can generate molecular glasses with exceptionally thermodynamic and kinetic stabilities when the substrate temperature was held below T_g [137, 79, 25, 132, 48, 83]. Such stable glasses made from PVD exhibit many interesting properties that can not be easily accessed by conventional glasses prepared from liquid-quenching method. The properties of these PVD glasses can be tuned by the deposition temperatures and deposition rates[71, 83, 25, 75, 32]. Such stable glasses have lower enthalpy[137, 79], higher density[83, 71, 32], higher kinetic stability[137, 138, 73, 25], lower water uptake[35] and tunable optical properties[29, 33, 30]. These newly discovered

stable glasses can access much lower energy states within very short deposition times than aging liquid-quenched glasses and are promising candidates for achieving near equilibrium configurations that may shed light on the fundamental nature of glass transition. Thus it is also important to understand how exactly do these stable glass form during physical vapor deposition. It is hypothesized that the stable glass formation is highly related to the enhanced surface dynamics where the high mobility of molecules at the free surface allows for efficient packing during vapor deposition. It would be imperative to directly test this hypothesis and understand the exact mechanism for stable glass formation by PVD.

1.4. Summary

In this dissertation, I will discuss my PhD work on investigating the interfacial effects on thin molecular glass films. In Chapter 2-4, I will introduce a novel experimental approach developed that uses tobacco mosaic virus as a probe particle for direct measurements of the surface diffusion on molecular glasses. The surface diffusions on ultrastable glasses, physically aged glasses and ultrathin glasses are also investigated to understand the fundamentals of enhanced surface diffusion on molecular glasses. In Chapter 5-6, I will focus on investigating the propagation depth of the interfacial effects on thin molecular glass films using a combination of isothermal dewetting and cooling-rate dependent T_g measurements. The effect of substrate interface on the propagation length scale will also be studied and discussed. In Chapter 7, I will present some of the preliminary results and interesting observations on ultrathin stable molecular glasses by physical vapor deposition and their possible relations with stable glass formation mechanism. In Chapter 8, I will conclude my research on molecular glasses and propose possible future directions related to the work presented here.

CHAPTER 2 : Using Tobacco Mosaic Virus to Probe Enhanced Surface Diffusion of Molecular Glasses

Adapted from Ref. [162] with permission from The Royal Society of Chemistry. Yue Zhang, Richard Potter, William Zhang and Zahra Fakhraai Using Tobacco Mosaic Virus to Probe Enhanced Surface Diffusion of Molecular Glasses. *Soft Matter*, 23: 9115, 2016. Copyright 2016 Royal Society of Chemistry.

2.1. Abstract

Recent studies have shown that diffusion on the surface of organic glasses can be many orders of magnitude faster than bulk diffusion. Developing new probes that can readily measure surface diffusion can help study the effect of parameters such as chemical structure, intermolecular interaction, molecules' shape and size on the enhanced surface diffusion. In this study, we develop a novel probe that significantly simplifies these types of studies. Tobacco mosaic virus (TMV) is used as probe particle to measure surface diffusion coefficient of molecular glass N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD). The evolution of the meniscus formed around TMV is probed as a function of time at various temperatures. TMV has a well-defined, mono-disperse, cylindrical shape, with a large aspect-ratio (average diameter of 16.6 nm, length of 300 nm). As such, the shape of the meniscus around the center of TMV is semi-two dimensional, which compared to using a nanosphere as probe, increases the driving force for meniscus formation and simplifies the analysis of surface diffusion. We show that under these conditions, after a short transient time the shape of the meniscus is self-similar, allowing accurate determination of the surface diffusion coefficient. Measurements at various temperatures are then performed to investigate the temperature dependence of the surface diffusion coefficient. It is found that surface diffusion is greatly enhanced in TPD and has a lower activation barrier compared to the bulk counterpart. These observations are consistent with previous studies of surface diffusion on molecular glasses, demonstrating the accuracy of this method.

2.2. Introduction

Enhanced surface dynamics and surface diffusion in glassy systems have gained extensive research interest over the past few decades [76, 46, 105, 152, 21, 163, 34, 157, 154]. Since ultra-thin amorphous films are used in various applications including organic electronics [139, 131, 146], coatings [85], and pharmaceuticals [153, 28, 63], it is imperative to understand the surface properties of these films as they may affect thin film viscosity [152, 21, 161], glass transition temperature [42, 76, 46, 55], thin film failure [146], or fast surface crystal growth [60, 154]. In addition, the fast surface dynamics in molecular glasses have been hypothesized to play a critical role in the formation of ultra-stable glasses by physical vapor deposition (PVD) [137, 83, 48, 79, 132, 86, 154].

Various techniques have been developed to directly quantify the dynamics of glasses near their free surface. Most of these measurements have been focused on polymeric systems, where while the surface diffusion is suppressed by chain connectivity, the surface relaxation dynamics are enhanced below bulk T_g [47, 105, 152, 21, 50, 89, 14, 107]. In small molecule glass systems, grating decay experiments on the surface of liquid-quenched [163, 157, 125] and aged glasses [13] on a wide range of molecules have shown that surface diffusion is enhanced by a few orders of magnitude at T_g and has a lower activation barrier compared to the bulk diffusion. These studies showed that unlike bulk diffusion, the value and the activation barrier for surface diffusion strongly depend on the molecules' size [157]. Diffusive flow was also observed in low molecular weight polymer films [119, 157] and disappeared or became extremely slow with increasing molecular weight, possibly due to the fact that long polymer chains penetrate into the glassy matrix and suppress the surface diffusion process. While strongly informative, since they require annealing above T_g for patterning, grating decay experiments can not be adopted to directly study the surface diffusion of stable glasses as they may transform into ordinary glass during high temperature patterning. Furthermore, using grating decay experiments is nearly impossible on the surface of ultra-thin films, as the grating size is typically comparable to the film thickness (20 nm - 40 nm)

, which can result in dewetting during embossing. Thus in order to expand these studies to a broader range of glassy systems, it is imperative to develop new techniques that do not require annealing above T_g .

Nanoparticle probe techniques have been broadly used in studies of glass surface properties [140, 69, 119, 68]. On the surface of polymeric glasses, nanoparticles typically embed into the film, even when held below bulk T_g , indicative of the existence of a highly mobile layer at the free surface that relaxes in response to the nanoparticle perturbation [140, 69, 119]. Daley *et al.* used nanospheres as probes to measure diffusion on the surface of molecular glass tris-naphthyl benzene [34]. Interestingly, in this molecular glass systems, in the absence of chain connectivity, instead of segmental relaxation surface diffusion becomes the primary response to the perturbation induced by the nanospheres. This is observed as rapid formation of menisci around the nanospheres without embedding at short annealing times. Similar to grating decay studies, nanosphere probe experiments indicated lower activation energy for surface diffusion compared to bulk diffusion (weaker temperature dependence). However, these experiments failed to provide the exact value of the surface diffusion coefficient. This is primarily because the rigid sphere with a constant height placed on the rigid glass surface generates under-defined boundary conditions for the fourth order differential equation governing the surface diffusion process and without a well-defined bonding box the flow of the meniscus could not be solved analytically. As such, in their studies, Daley *et al.* [34] could only measure the temperature dependence of the surface diffusion and not the actual values. A recent work using grating decay method by Ruan *et al.* [125] has measured the absolute values of surface diffusion coefficients on tris-naphthyl benzene and the results were two orders of magnitude smaller than those estimated by Daley *et al.* [34] on the surface of the same molecule.

Inspired by the nanosphere probe experiments [34], in this work we develop a novel technique that greatly simplifies both experimental procedures and data analyses for nanoparticle probe experiments and is able to provide an accurate value for the surface diffusion

coefficient. We use tobacco mosaic virus (TMV) as long aspect-ratio rods that produce self-similar semi-two-dimensional flow, simplifying the analysis. We demonstrate how this technique can be adopted to measure the diffusion coefficient of the glass surface by tracking the response of the surface to TMV’s perturbation at various temperatures. We show that below T_g the flow is diffusive, and use the self-similar properties of the flow to determine the surface diffusion coefficient. The self-similar nature of the flow allows us to quantify the value of surface diffusion without the need to analytically solve the under-defined boundary problem. The measured surface diffusion coefficients are orders of magnitude faster than the bulk diffusion coefficients at the same temperature and have weak temperature dependences. At bulk T_g , surface diffusion of TPD is about 6 orders of magnitude faster than bulk diffusion.

2.3. Experimental Details

N,N’-Bis(3-methylphenyl)-N,N’-diphenylbenzidine (TPD, $T_g = 330$ K, molecular structure shown in inset of Figure 2.4) was purchased from Sigma-Aldrich and used without further purification. 400 nm TPD films were prepared by physical vapor deposition as described in our earlier publications [83, 161] and were annealed at $T_g + 10$ K in vacuum to remove any stability or roughness before measurements. Tobacco mosaic virus was purified from infected leaves, dialyzed and suspended in miliQ water. TMV was then introduced onto the surface of annealed TPD films by spin-coating, resulting in dilute and uniform distribution of TMV nanorods on the films’ surface. Isothermal annealing was performed with a custom thermoelectric heating-stage calibrated with melting point standards. Non-contact atomic force microscopy (AFM) imaging was performed to track the evolution of the surface response at various isothermal annealing temperatures ranging from $T_g - 34$ K to $T_g - 12$ K (296 K - 318 K). More details of sample preparation, virus purification, temperature calibration, and AFM imaging are provided in SI.

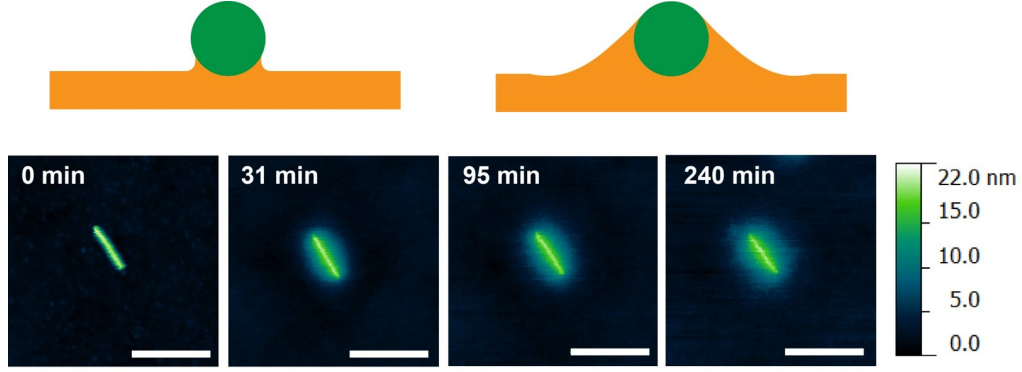


Figure 2.1: Top: Schematic illustration of the evolution of the meniscus in response to the perturbation induced by TMV curvature on the surface of a bulk film. Bottom: Representative AFM images obtained from the same TMV particle at various annealing times, demonstrating the temporal evolution of the meniscus around TMV. Film thickness 400 nm. Annealing temperature $T_g - 12$ K (318 K). Scale bar 500 nm.

2.4. Results

2.4.1. Fast meniscus formation mediated by surface diffusion

Tobacco mosaic virus (TMV) is an excellent candidate as probe particle for multiple reasons. TMV has a crystalline structure with well-regulated and mono-dispersed cylindrical shape resulting in easily reproducible measurements. As such, only one virus needs to be identified on a surface and statistics can be easily obtained by comparing line profiles at various distances from the virus' center as shown in SI Figure 2.6. When a TMV particle is placed on the TPD film surface, TPD molecules rapidly wet the particle, producing very sharp local curvatures around the TMV as schematically illustrated on the top panel of Figure 2.1. Such sharp local curvature induces a Laplace pressure gradient that drives the molecules to flow towards TMV and form a meniscus. Another important advantage of using TMV is that due to the long aspect-ratio of about 18 (average diameter of $\sim 16.6 \pm 0.2$ nm with a typical length of ~ 300 nm), the profiles around the center of TMV are semi-two-dimensional (2D) as evident in Figure 2.1. This simplifies both experimental procedures, by allowing enough statistics across the near-center of the virus for noise reduction (Figure 2.6), and

the mathematical modeling of the profiles' shape as detailed in the next section.

As shown in the AFM images presented in Figure 2.1, when held at a constant temperature below T_g ($T_g - 12$ K in this example), a bright halo grows around the virus, indicating meniscus formation. The size of the meniscus grows with annealing time. At relatively short time scales (less than 200 min in this case) no obvious embedding is observed and the height of TMV remains constant within instrumental error. As such, we attribute the growth of the meniscus at short times to the surface diffusion-mediated flow. At higher temperatures, or longer annealing times, the virus embeds into the film and is eventually engulfed by TPD, indicating zero final contact angle (SI Figure 2.7).

The 2D profiles, $h(x, t)$, perpendicular to the axis of TMV extracted from AFM images are plotted at various times for the example shown in Figure 2.1, as well as two other annealing temperatures in Figure 2.2. In order to reduce the random noise, each profile shown in these figures is the average of five line profiles near the center of the virus, recorded normal to its long axis as demonstrated in Figure 2.6. Since TMV has a mono-dispersed diameter to within a few angstroms, the growth profiles at various annealing temperatures can be directly compared with each other, without the need to consider the object's height variations, providing an additional advantage of using TMV as opposed to other types of nanorods.

Figure 2.2A shows that at each annealing temperature the width of the meniscus grows with time and a depletion zone with a depth of about 2 - 4 nm is observed outside of the meniscus, which also moves outwards as the width grows. While the rate of the meniscus growth slows down with decreasing temperature as seen in Figure 2.2A, the growth is still fairly rapid. For example, at the temperature of $T_g - 12$ K (318 K) the width of the meniscus reaches 500 nm (at least 30 times the diameter of TMV) only after about 30 minutes (red curve of Figure 2.2A(a)). This large length scale of material transport helps significantly reduce the noise from the tip convolution effect, and low lateral image resolution (~ 6 nm per pixel), allowing more accurate measurements compared to measurements on nanospheres,

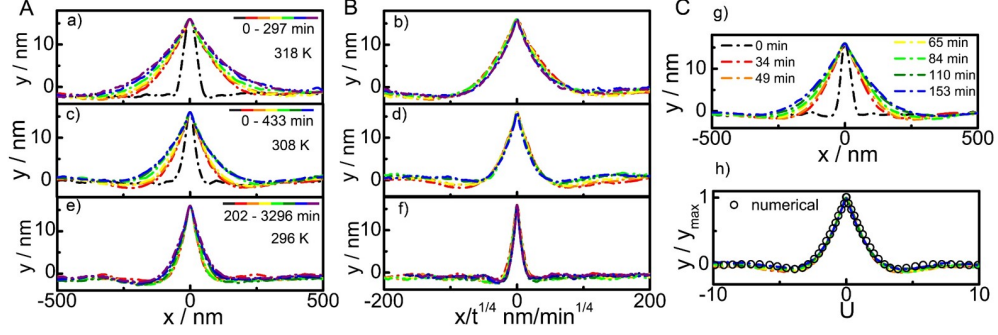


Figure 2.2: Panel A: Evolution of profiles around TMV at various temperatures, where y axis is the height of the profile at distance x from the center of TMV. Isothermal temperatures from top to bottom: 318 K ($T_g - 12$ K), 308 K ($T_g - 22$ K), and 296 K ($T_g - 34$ K). Panel B: Same profiles scaled by evolution time to the $1/4$ th power, $t^{1/4}$. Isothermal temperatures from top to bottom: 318 K ($T_g - 12$ K), 308 K ($T_g - 22$ K), and 296 K ($T_g - 34$ K). All profiles at each temperature collapse onto the same shape indicating the self-similar nature of the surface diffusion-mediated process. As the temperature is decreased, the evolution of the profile slows, resulting in narrower profile widths. Panel C: Example of fitting experimental profiles at the annealing temperature of 318 K to numerical solution [127]. Figure g) shows the experimental profiles used for fitting and the figure h) shows the numerical solution indicated by open black circles that fits the rescaled data at all time points very well. U is a scaled function of x and t , $U = \frac{x}{t^{1/4}} \left(\frac{kT}{D_s \gamma \Omega^2 \nu} \right)^{1/4}$. The only fitting parameter used is $A = \frac{D_s \gamma \Omega^2 \nu}{kT}$.

which have a smaller driving force for the same diameter particle. This is another important advantage of using TMV probe particles, resulting in faster characterization of the surface diffusion coefficient compared to existing methods that can take weeks of measurements at low annealing temperatures [163].

2.4.2. Self-similarity of the profiles produced by surface diffusion

To demonstrate that the growth of the menisci observed below T_g are mediated by surface diffusion, we can examine the flow in the region around the center of TMV. In this region, the flow induced by surface diffusion can be described as a 2D flow. We assume that at time scales much lower than the relaxation time of the bulk glass, the glass behaves as a rigid substrate, preventing TMV from embedding into the film. The constant height of the TMV as a function of time shown in Figure 2.2 (and Figures 2.9 and Figure 2.8) confirms

the validity of this assumption. At short times, the 2D growth of the meniscus due to the diffusion of molecules at the free surface can be described by the simplified Mullins model [95];

$$\frac{\partial h(x, t)}{\partial t} = -\frac{D_s \gamma \Omega^2 \nu}{kT} \frac{\partial^4 h(x, t)}{\partial x^4} \quad (2.1)$$

where $h(x, t)$ is the height of the profile at distance x from the center of TMV at time t , D_s is the surface diffusion coefficient, $\gamma = 72.3$ mN/m is the surface tension of TPD, $\Omega = 7.21 \times 10^{-28}$ m³ is the estimated volume of the molecule based on the molecular weight and relative density, $\nu = 2 \times 10^{18}$ m⁻² is the estimated number of atoms per unit area, and k is the Boltzmann constant. The only strong temperature-dependent parameter in the prefactor is the surface diffusion coefficient D_s . More discussion on the other terms of the Mullins model and the temperature-dependence of other relevant parameters can be found in SI.

One can easily demonstrate that after a transient time, the 2D profiles, $h(x, t)$, controlled by this equation would become self-similar, where they scale with time as $h(x, t) = h(x/t^{1/4})$ [95, 87]. Figure 2.2B shows the profiles, where x is scaled to $t^{1/4}$. For each annealing temperature, all profiles collapse onto the same curve, confirming the self-similarity of the process. After scaling, the narrower profiles at lower temperatures indicate that the pre-factor in equation 2.1, and therefore the surface diffusion is slower at lower temperatures.

In order to evaluate the absolute value of the surface diffusion coefficient based on the self-similar profiles, the experimental profiles at the temperature of 318 K were fit to a numerical solution of equation 2.1 developed under a slightly different context [10, 87, 127] but with mathematically identical boundary conditions (more details discussed in SI). As shown in Figure 2.2C, the numerical solution fits the experimental profile very well with a single fitting parameter, which is equal to the pre-factor in equation 2.1: $A = \frac{D_s \gamma \Omega^2 \nu}{kT}$. Based on this fit the surface diffusion coefficient is calculated to be $D_s = 2.7 \times 10^{-16}$ m²/s at 318 K.

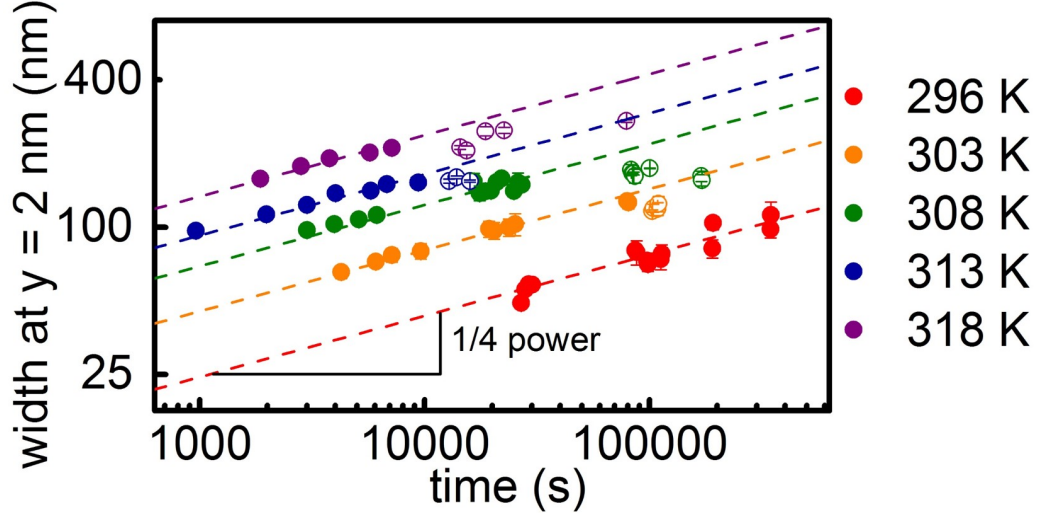


Figure 2.3: Half profile width as measured at a height of $h = 2$ nm from the bottom of TMV, $w(h = 2 \text{ nm})$, plotted as a function of time at various annealing temperatures in log-log scale. In the self-similar regime, the slope of the power-law should be $1/4$. The dashed lines are fits to the data with constant slope of $1/4$. The open symbols at longer times indicate deviations from $1/4$ power law, and therefore surface diffusion regime. This deviation coincides with the onset of embedding (Figure 2.9).

2.4.3. Temperature-dependence of the surface diffusion coefficients

In order to quantify the temperature-dependence of surface diffusion, we can plot the half width of the profile at a certain height ($h(x) = 2$ nm from the bottom of TMV was chosen here) as a function of time at various annealing temperatures as shown in Figure 2.3. Since the profiles are expected to be self-similar for the surface diffusion process, the width versus time should follow a power law with an exponent of $1/4$, and an intercept value that depends on $A = \frac{D_s \gamma \Omega^2 \nu}{kT}$. Figure 2.3 shows that at short time scales all the data follows the $1/4$ power-law very well, further confirming that the fast meniscus formation process is driven by surface diffusion. At longer times, the slope deviates from the $1/4$ power-law, and embedding of TMV into the film is observed (Figure 2.9). At this stage of the process, the measurement time is comparable to the onset time for embedding, which is a function of particle's shape, and the bulk relaxation response time of the system. At this time the film no longer behaves as a rigid substrate. Both surface diffusion and viscous flow processes

contribute to the evolution of the meniscus at these long time scales. Details of embedding have been studied in the past and won't be discussed here [34, 140, 69, 119, 68]. Since all profiles are self-similar, the value of D_s at all other temperatures can be obtained by calculating the relative width at each temperature compared with the reference temperature of 318 K, for which D_s was calculated to be $D_s = 2.7 \times 10^{-16} \text{ m}^2/\text{s}$.

2.5. Discussions

Surface diffusion coefficient of TPD at various temperatures are plotted in Figure 2.4 as a function of $1000/T$. In order to compare these results with bulk dynamics, alpha-relaxation times (τ_α) of TPD, measured from bulk viscosity [161] and bulk dielectric spectroscopy by Walters *et al.* [147] are replotted based on the empirical rule that the bulk diffusion coefficient of most organic glasses is approximately $10^{-20} \text{ m}^2/\text{s}$ at T_g [157], where the structural relaxation time is $\tau_\alpha = 100 \text{ s}$. Figure 2.4 shows that the surface diffusion coefficient on the surface of bulk TPD glass is greatly enhanced. The extrapolated value of D_s at T_g is $6.85 \times 10^{-15} \text{ m}^2/\text{s}$, which is roughly 6 orders of magnitude faster than the bulk dynamics at this temperature. Furthermore, the activation energy for D_s , as measured by the slope of the curve, is greatly reduced compared to the bulk. These observations are consistent with previous measurements on other molecular glass systems, which showed that compared to the bulk diffusion, surface diffusion is greatly enhanced, has weaker temperature dependence, and has an activation barrier that varies more strongly with the molecular weight of the molecule (Figure 2.10) [157]. This strong agreement with grating decay experiments confirms the validity of the assumptions used here to calculate D_s .

The low activation barrier for the surface diffusion, and therefore lower fragility, as well as faster surface diffusion is qualitatively consistent with the theoretical and modeling predictions [16, 130, 61, 62, 91, 93, 19, 134]. However, for the two cases where quantitative comparisons were possible [134, 19] the experimentally measured diffusion coefficients were faster than theoretical predictions, with deviation growing as the temperature is decreased below T_g . Both coupling model [19] and random first order transition theory [134] predict

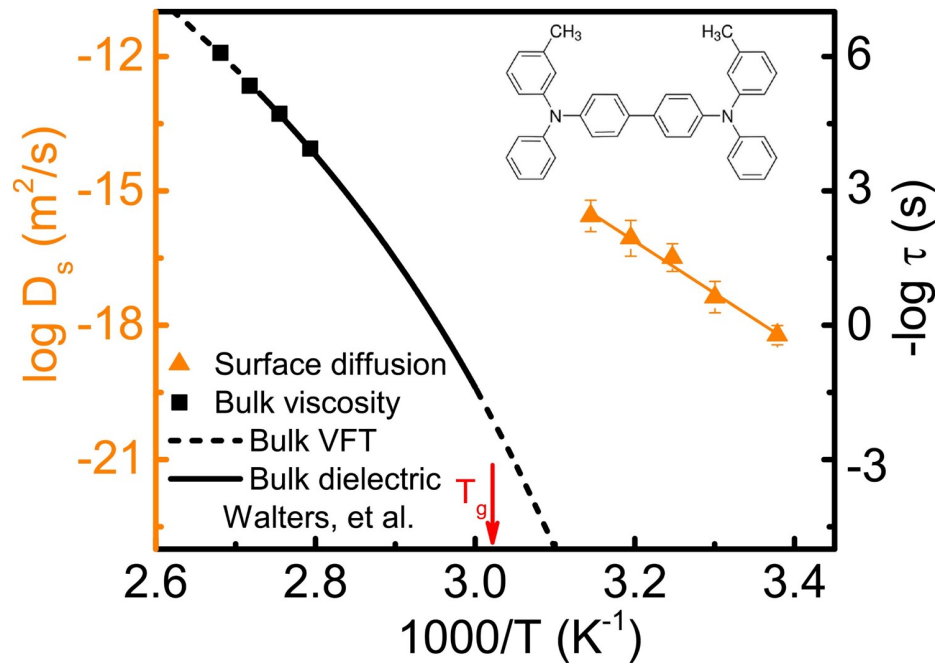


Figure 2.4: Surface diffusion coefficient, D_s , plotted with $1000/T$ (orange triangles, left axis). Data is compared with bulk relaxation times τ_α (solid line, right axis) measured from bulk viscosity[161] (closed black square) and bulk dielectric relaxation measurements (solid black line) [147] the the relative shift in the data is based on the empirical rule that the bulk diffusion coefficient at T_g is approximately $10^{-20} \text{ m}^2/\text{s}$, and τ_α is approximately 100 s. Error bars of surface diffusion coefficients were obtained from two repeating trials.

that the surface dynamics are faster due to lower interaction potentials at the free surface and remain faster on length scales that correspond to the length scales of cooperative motion. These types of models predict that the dynamics at the free surface should be a function of bulk relaxation dynamics. The faster than predicted surface diffusion indicates that the molecules at the free surface may be somewhat decoupled from the glassy alpha relaxation underneath, suggesting a hopping mechanism on the surface that allows the molecules to sample the potential landscape of the surface and move to reduce the surface energy.

The hypothesis that the surface diffusion may not be correlated with relaxation dynamics in these organic molecule glass systems is strengthened by the fact that surface diffusion is strongly dependent on the molecule’s size (Figure 2.10)[157] and it is expected to go to zero for large molecules such as long-chain polymers. While surface diffusion is zero in polymers, enhanced relaxation dynamics have been observed on polymer surfaces [46, 140] suggesting the decoupling between surface diffusion and relaxation dynamics.

The fast surface diffusion can be responsible for frequently observed fast crystallization on the surface of molecular glass films used as amorphous drugs or for OLEDs, which hinders the applications in drug delivery or organic electronic devices. On the other hand, the fast surface diffusion in molecular glasses may play an important role in producing ultra-stable glasses by physical vapor deposition. These stable glasses are reported to have exceptionally thermodynamic and kinetic stabilities [137, 72, 48] compared with conventional quenched ordinary glasses. Although the detailed mechanism behind the stable glass formation is still under investigation, it has been indicated both in experiments and simulations that the fast surface diffusion during vapor deposition plays an important role in their formation [24, 128, 132]. These studies hypothesize that due to the fast surface diffusion on molecular glass surfaces, during the deposition the molecules at the free surface have high mobility and can diffuse to find lower energy configurations before being buried by the incoming flux of molecules, resulting in a low energy, more equilibrated glass. Yet there has been no direct measurement

of surface diffusion on the surface of stable glasses. The method presented here can verify whether after a layer of stable glass has been formed the surface diffusion still remains high enough for the mechanism to carry on, as indirect measurements have indicated in the past [24], or whether or not the activation energy on the surface of stable glasses are the same as ordinary glasses. These questions will be explored in future publications.

2.6. Summary

In summary, we have demonstrated that Tobacco mosaic virus can serve as a very efficient probe allowing quick characterization of diffusion on the surface of molecular glasses. Using mono-dispersed TMV simplifies experimental procedures and data analyses for nanoparticle probe experiments and reduces the need for redundancy in measurements. Furthermore, TMV acts as a long aspect-ratio rod to produce semi-two-dimensional flow, simplifying the data analysis. The profiles produced in 2D are self-similar with a power-law of $1/4$. As such, hypothetically, by using the shape of the profile provided in this manuscript, a single AFM image taken at a time before the onset of embedding, suffices to measure the surface diffusion of an arbitrary molecular glassy system at a particular temperature. In practice, it would be easier to perform experiments at various time points to ensure that the $1/4$ power-law is accurate, and that the contact angle is such that TMV is wet by the molecule. This versatile method can readily provide an accurate value for the surface diffusion coefficient for various molecular systems, as well as various conditions such as ultra-thin films and stable glasses.

Using TMV probe experiments we showed that the diffusion coefficients measured on the surface of bulk TPD films are orders of magnitude enhanced compared to the bulk dynamics, along with a much weaker temperature dependence. The measured values of surface diffusion are much faster than theoretically predicted, indicating decoupling between surface diffusion and relaxation dynamics at the free surface. We hypothesize that surface diffusion is achieved through a hopping mechanism, which is consistent with the Mullins model [95]. This hypothesis will be explored in our future publications.

2.7. Acknowledgments

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2.8. Supplementary Material

Sample preparation and TMV deposition

N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) was purchased from Sigma-Aldrich and used without further purification. 400 nm films were prepared by physical vapor deposition (PVD) at a substrate temperature of bulk T_g ($T_g = 330$ K) with an average deposition rate of 0.2 nm/s. Details of the custom vacuum setup and procedures are published in our earlier work[83, 161]. Films were further annealed at $T_g + 10$ K (340 K) in vacuum oven overnight to anneal any stability or surface roughness. An AFM image of the surface of a typical sample is shown in Figure 2.5 that shows an initially flat morphology. The surface roughness is measured to be 0.91 nm.

TMV purification and deposition onto TPD films

Dried leaves infected by tobacco mosaic virus were purchased from ATCC (PV-598). Infected, dried leaves were pulverized into a grainy powder and was mixed with 3 mL of 0.2% -mercaptoethanol (Sigma-Aldrich) and 3 mL of 0.01 M phosphate buffer (pH 7.8) (Sigma-Aldrich). This solution was centrifuged for 15 minutes at 9,000 rpm and the resulting supernatant was saved, to which 80 μ L of 1-butanol (8 mL/100 mL extract) (Sigma-Aldrich) were added to coagulate chloroplasts and centrifuged again for 30 minutes at 9,700 rpm. The resulting aqueous supernatant was saved and dialyzed in miliQ water using mini-dialysis

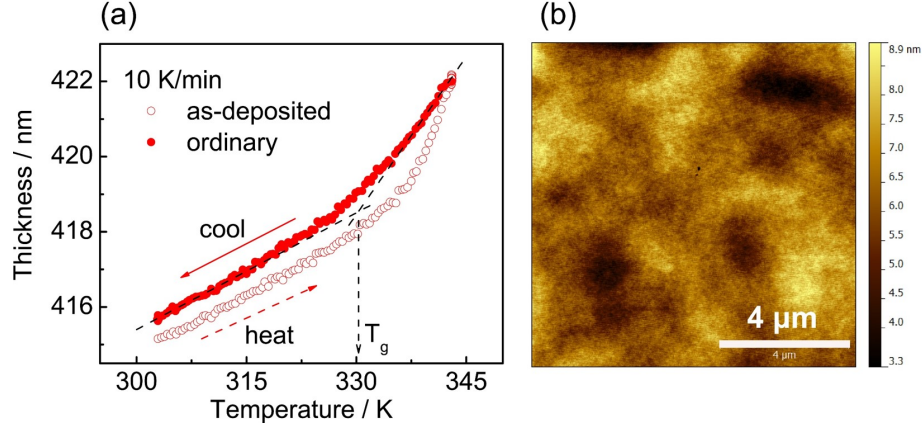


Figure 2.5: (a) As-deposited 400nm TPD films were heated well above its bulk T_g to anneal away any stability and transform into ordinary liquid cooled glass. Film thickness as measured by ellipsometry during heating and cooling at 10 K/min. (b) Initial morphology of 400 nm TPD films after annealing at $T_g + 10$ K in vacuum overnight. The surface roughness is measured to be 0.91 nm from AFM topography image.

devices (ThermoFisher Scientific, Slide-A-LyzerTM MINI Dialysis Device, 20K MWCO, 0.1 mL). 100 μL of the dialyzed TMV solution was pipetted onto the annealed TPD films, spin-coated for 3 minutes at 500 rpm and dried with nitrogen for further isothermal imaging measurements. On Si substrate, the height of TMV is measured to be 16.6 ± 0.2 nm with AFM. The process of spin-coating of TMV on TPD surface does not alter the surface morphology or the properties of the TPD film.

Isothermal annealing and AFM imaging

Isothermal annealing experiments were performed using a custom thermoelectric heating-stage, equipped with a thermoelectric module (Custom Thermoelectric TEC) and a thermistor (Oven industries TR91-170) to measure the value of the temperature, along with a DC power supply to control the temperature (Mastech HY3010E). The temperature of the heating-stage was calibrated with melting-point standards ($\text{C}_{13}\text{H}_{10}\text{O}$) $T_m = 48.0 \pm 0.3$ $^{\circ}\text{C}$ and ($\text{C}_{18}\text{H}_{36}\text{O}_2$) $T_m = 69.6 \pm 0.3$ $^{\circ}\text{C}$ (Sigma-Aldrich), the temperature fluctuations were within ± 2 K throughout the experiments in the temperature range used in this study. After identifying an isolated TMV particle, the sample temperature was brought to desired

annealing temperature (stabilize within a minute), the surface was then continuously imaged using non-contact atomic force microscopy (AFM, Agilent 5420). Non-contact AFM tips (Budget Sensors, Tap-300G, resonance frequency 300 kHz, tip radius of curvature <10 nm, force constant 40 N/m) were used for these measurements.

Extracting line profiles from AFM images

Here we show an example of how we extract line profiles from AFM topography images. Due to the large aspect ratio of TMV virus, enough statistics can be obtained from multiple line profiles near the center of the nanorod, resulting in very reproducible profiles. In top figure of 2.6, line 1 and line 3 defines the range of 2D flow without the effect from the two end regions of TMV. In the bottom panel, we show the line profiles from lines 1, 2 & 3, they overlap perfectly indicating the validity of 2D flow assumption across the virus.

Wettability of TPD on TMV

To demonstrate that TPD can completely wet the TMV virus, in 2.7 we show the spontaneous wetting and embedding of TMV on a bulk TPD film at an annealing temperature of 323 K ($T_g - 7$ K). The images shown in Figure S6 demonstrate that TPD can quickly and completely wet the TMV virus, reaching a zero final contact angle. As such, even at lower temperatures the zero contact angle implies that the virus is completely wet with a layer of TMV and the meniscus evolution after some transient time is independent of the contact angle, or interactions of TPD with TMV.

Additional profiles at all annealing temperatures studied

All the temporal profiles at five annealing temperatures surveyed in this study are shown in the left panel of 2.8. On the right panel, we show the self-similarity of the surface diffusion controlled process.

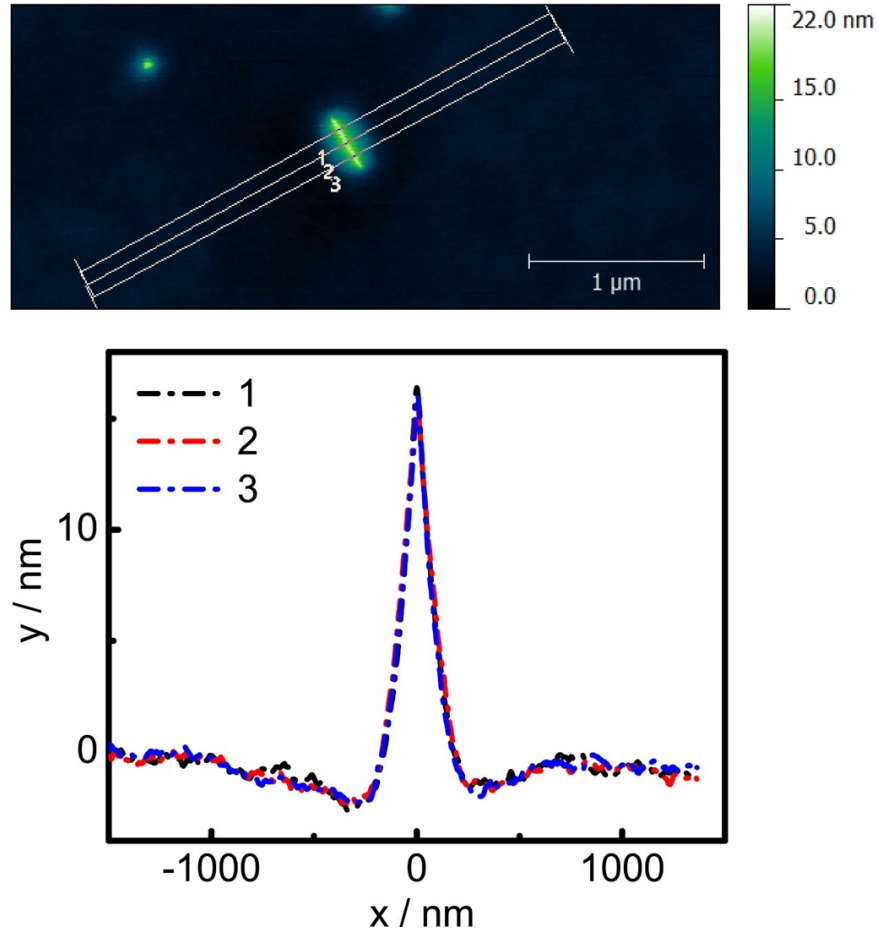


Figure 2.6: Typical line profiles obtained from AFM topography image. Top: AFM topography of a single TMV nanorod on TPD glass surface, line profiles were obtained from perpendicular lines across the TMV. From top to bottom: line 1, line 2 and line 3. Bottom: The three line profiles obtained from the top image, the profiles perfectly overlap within instrument noise, indicating the validity of two dimensional flow assumption.

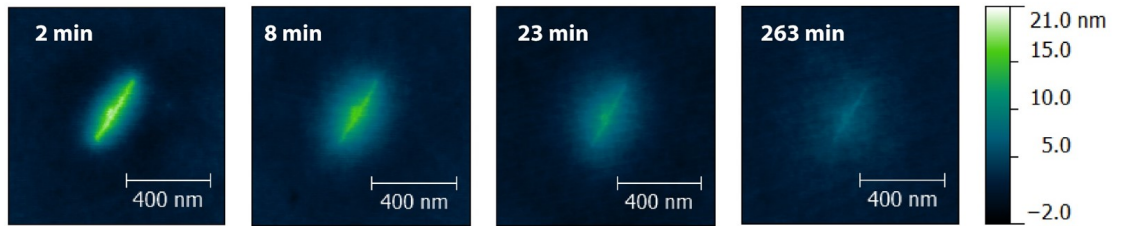


Figure 2.7: AFM images of rapid wetting and embedding of TMV on bulk TPD surface at the annealing temperature of 323 K.

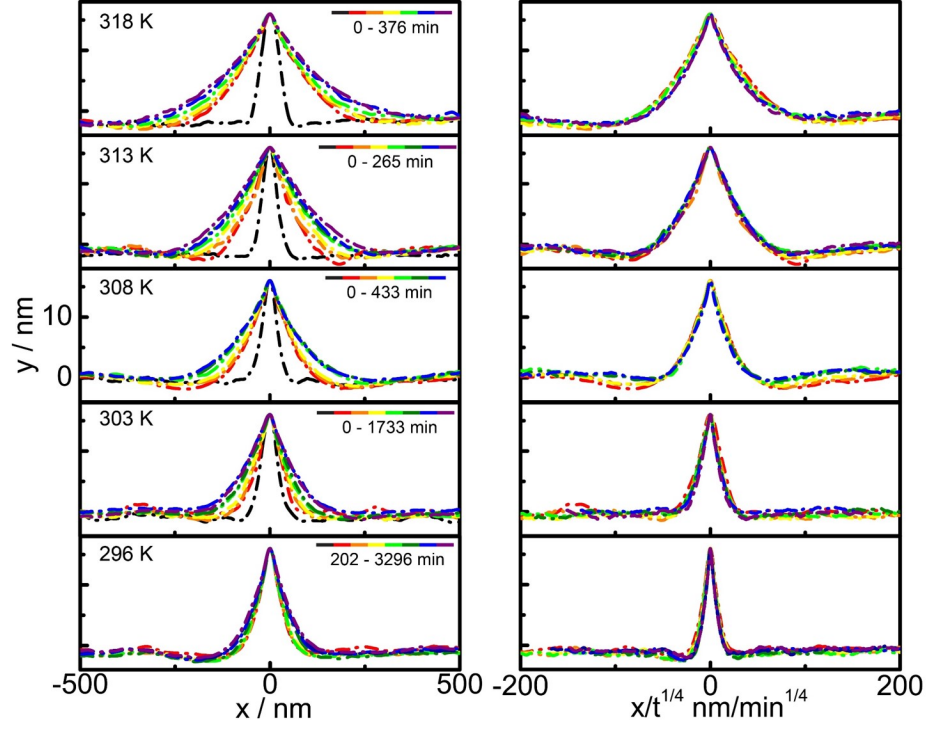


Figure 2.8: Temporal profile evolution at various annealing temperatures and self-similarity of surface diffusion controlled evolution. Left panel: time evolution of the profiles across TMV at five different annealing temperatures, from top to bottom: 318 K ($T_g - 12$ K), 313 K ($T_g - 17$ K), 308 K ($T_g - 22$ K), 303 K ($T_g - 27$ K), 296 K ($T_g - 34$ K); Right panel: scaled profiles with respect to $t^{1/4}$ collapse onto the same curve, indicative of self-similarity nature of the surface diffusion control process.

Experimental data fit to numerical solution

Since TPD completely wets the virus, it is reasonable to assume that the profile shape after some initial transient time is independent of the surface energy of the virus. However, the height of the profile remains constant, indicating that there is little accumulation of material on top of the virus. This is not surprising as there is little driving force directly on top of the virus for diffusion. As such, one can assume that the solution for this problem is mathematically identical to having a step function with a constant height towards which the molecules are attracted. Equation 1 has been solved for a constant step height boundary conditions [10, 127, 87]. Furthermore, in another work Benzaquen *et al.* numerically demonstrated that equation 1 would eventually evolve into the same universal curve even under a slightly different initial boundary condition[10]. The universal scaled profile can be written as $U = \frac{x}{t^{1/4}}(\frac{kT}{D_s\gamma\Omega^2\nu})^{1/4}$, where U is a scaled function of x and t. The experimental profiles were fit to the universal solution with a single fitting parameter $\frac{D_s\gamma\Omega^2\nu}{kT}$, where surface diffusion coefficient D_s can be evaluated.

TMV height versus time at annealing temperatures studied

We characterized the apparent height of the TMV virus versus annealing time at the five temperatures studied. As shown in Figure 2.9, at relative short time scales, the height of virus remains constant within the instrument error, and thus the surface diffusion mediates the surface flow at this short time window and results in meniscus formation as discussed in the main text. With the increase of annealing time and annealing temperatures, the virus starts to slowly embed into the film resulting in a decrease in apparent height. At this stage, the viscosity starts to drive the flow and the virus embeds into the film. The governing equation for embedding process is given by for surface viscosity control:

$$\frac{\partial h(x, t)}{\partial t} = -\frac{\gamma}{3\eta} \frac{\partial}{\partial x} [h^3(x, t) \frac{\partial^3 h(x, t)}{\partial x^3}] \quad (2.2)$$

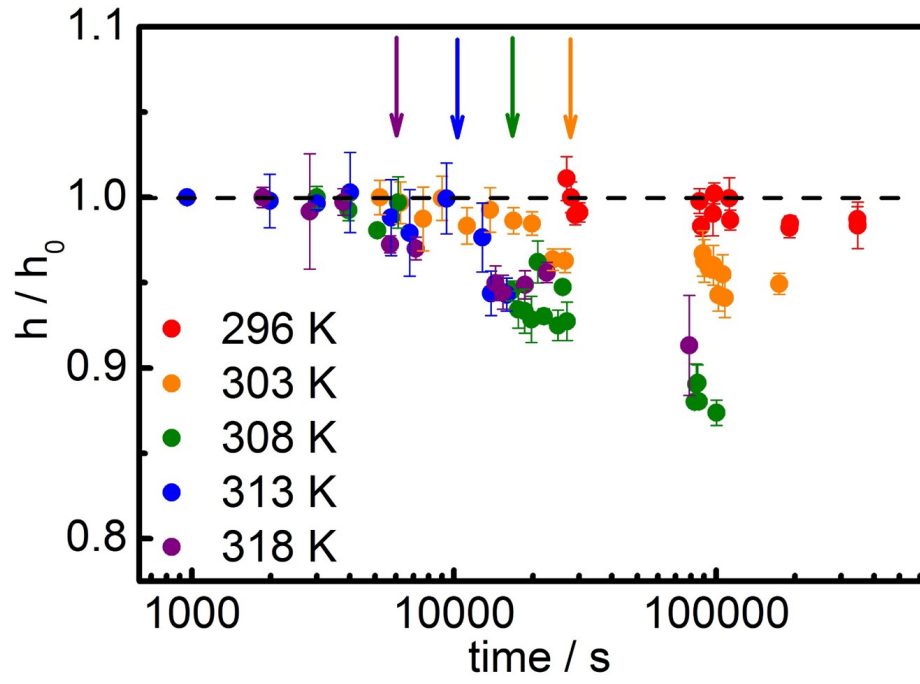


Figure 2.9: Normalized apparent height of the TMV virus versus annealing time at various annealing temperatures. Dashed line shows the TMV height before embedding and colored arrows show the time at which embedding becomes apparent beyond the noise in the measurement at each corresponding temperature.

or for bulk viscosity control:

$$\frac{\partial h(x, t)}{\partial t} = \frac{1}{2} \frac{\gamma}{\eta} \frac{\partial h(x, t)}{\partial x} \quad (2.3)$$

Mullins model and temperature dependence of relevant parameters

Here we present a brief discussion about the relevant driving forces for meniscus formation based on the Mullins model[95]. The full Mullins model includes the bulk viscosity, evaporation-condensation, bulk diffusion and surface diffusion as follows.

$$\frac{\partial h(x, t)}{\partial t} = A \frac{\partial h(x, t)}{\partial x} + B \frac{\partial^2 h(x, t)}{\partial x^2} + C \frac{\partial^3 h(x, t)}{\partial x^3} + D \frac{\partial^4 h(x, t)}{\partial x^4} \quad (2.4)$$

Where $A = \frac{1}{2} \frac{\gamma}{\eta}$, $B = \frac{p_0 \gamma \Omega^2}{(2\pi M)^{1/2} (kT)^{3/2}}$, $C = \frac{\rho_0 D_G \gamma \Omega^2}{kT} + \frac{D_v \gamma \Omega}{kT}$, and $D = \frac{D_s \gamma \Omega^2 \nu}{kT}$. Here γ is the surface tension, η is bulk viscosity, p_0 is the equilibrium vapor pressure, Ω is the molecular volume, ρ_0 is the equilibrium vapor density, D_G is diffusion coefficient of evaporated molecules in inert atmosphere, D_v is the bulk diffusion coefficient, ν is the number of atoms per unit area, and D_s is the surface diffusion coefficient. In this study, since the vapor pressure of TPD is very low at room temperature, there is no evaporation-condensation occurring during the course of this study. As such the evaporation-condensation term is negligible. Furthermore, at low temperatures used in this study the bulk diffusion is extremely slow (at least 4 orders of magnitude close to T_g , and decreasing rapidly with decreasing temperature). As such the bulk diffusion can also be assumed to be negligible. This was further confirmed by the grating decay studies where gratings of various sizes were used to verify the scaling factors for the important terms in the Mullins model[163, 157, 125]. This leaves the bulk viscosity and surface diffusion terms. The bulk viscosity becomes important at the onset of embedding. Before that, when the only important term in the model that governs the meniscus formation is the surface diffusion term. This is also confirmed in our studies with the fact that the profiles are self-similar with $h(x, t) = h(x/t^{1/4})$, which follows the scaling law for surface diffusion. This can only be true if all other terms are negligible and surface diffusion controls the flow. Bulk viscosity, evaporation-condensation,

and bulk diffusion follow different power-law and do not have the self-similar nature of $h(x, t) = h(x/t^{1/4})$. In addition, one can estimate the relative contribution from each term by estimating the prefactors order of magnitude and would find the other terms are much smaller ($< 1\%$ compared to surface diffusion term) and cannot contribute to such fast surface evolution and thus can be neglected. Similar discussions can also be found in grating decay measurements[163, 157, 125].

The approximation used by Mullins to obtain the linearized surface diffusion equation (Equation 2.1 in main text) is the small slope approximation. In our system, as can be seen in Figure 2.2, even for the earliest time point measured, the slope can be estimated from the height and the width of the profiles to be $h (17 \text{ nm}) / \text{width} (200 \text{ nm}) = 0.085$, which is much smaller than 1, fulfilling the small slope approximation. In addition, the self-similarity observed in the experimental data is a strong indication of the validity of the Mullins linearized model, which only the surface diffusion term present.

Temperature dependence of relevant parameters

The molecular volume of TPD, Ω , used in this study was estimated from the molecular weight and relative density at 295 K as $\Omega = MW/(\rho N_A)$. The change in relative density can be estimated from the thermal expansion coefficient measured from temperature ramp measurements by ellipsometry. As shown in Figure 2.5, the glassy thermal expansion coefficient of TPD can be fitted from the thickness change with temperature to be $2.1 * 10^{-4} K^{-1}$, in the temperature range performed in the experiment 296 K to 318 K, the change in relative density is therefore estimated to be $\sim 0.5\%$. Compared to a factor of 4 change in the value of the prefactor observed in Figure 2.3 of the main text, this can be considered a negligible density change. However, we note that this change is mainly the error in our estimation of volume based on density and the actual molecular volume is most likely constant in this modest temperature range.

Using the Eötvös rule[44], we can roughly estimate the temperature dependence of surface

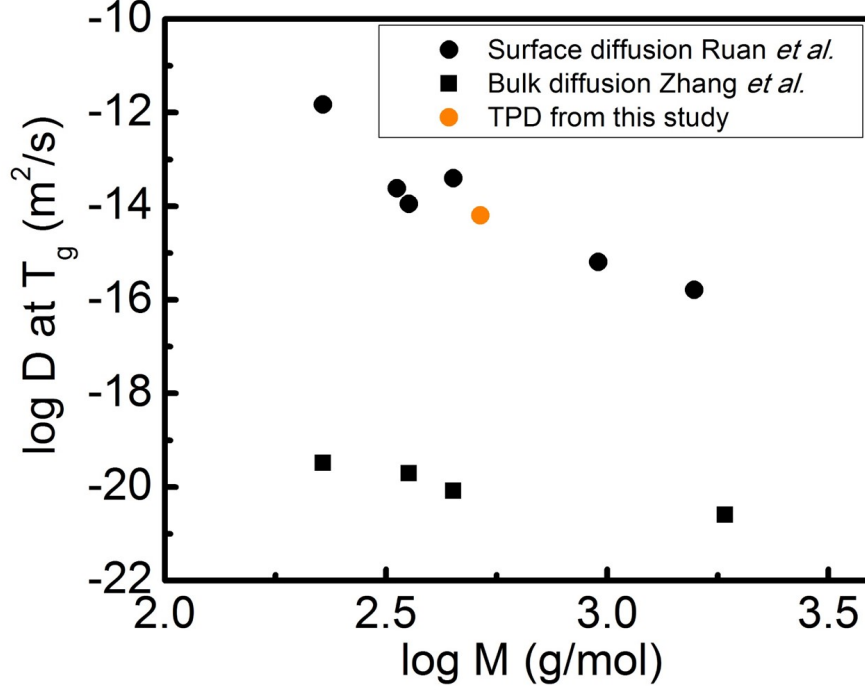


Figure 2.10: Surface diffusion coefficient of TPD measured in this study extrapolated to T_g (orange circle) and other organic molecules (black circle) from the grating decay studies by Zhang *et al.*[157], and bulk diffusion coefficients (black square) at the material's bulk T_g .

tension of TPD by $\frac{\partial\gamma}{\partial T} = \frac{-k}{V^{2/3}}$, where k is the Eötvös constant and has a value of $2.1 \times 10^{-7} \text{ J}/(\text{K} \cdot \text{mol}^{2/3})$, V is the molecular volume for TPD, which is calculated based on the molecular weight and relative density, to be $4.34 \times 10^{-4} \text{ m}^3/\text{mol}$. Thus $\frac{\partial\gamma}{\partial T}$ is calculated to be $-3.66 \times 10^{-5} \text{ N}/(\text{m} \cdot \text{K})$. Compared to the surface tension of TPD at 295 K, which is equal to $\gamma = 7.23 \times 10^{-2} \text{ N/m}$, the changes in γ are negligible in the temperature range of the experiments reported here.

Comparison with surface diffusion of other molecular glasses

In Figure 2.10, we compare the surface diffusion coefficient of TPD measured from TMV method in this study with other organic molecules measured using surface grating decay methods[157]. The surface diffusion coefficient of TPD at T_g is about 6 orders of magnitude

than the bulk diffusion coefficient and fits well with other organic molecules, indicating that the surface diffusion coefficient has a strong molecular weight dependence.

CHAPTER 3 : Invariant Fast Diffusion on Ultrastable and Aged Molecular Glasses

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3.1. Abstract

Surface diffusion of molecular glasses is found to be orders of magnitude faster than the bulk diffusion, with a stronger dependence on the molecular size and intermolecular interactions. In this study, we investigate the effect of variations in bulk dynamics on the surface diffusion of molecular glasses. Using tobacco mosaic virus as probe particle, we measure the surface diffusion on glasses of the same composition but with orders of magnitude of variations in bulk relaxation dynamics, produced by physical vapor deposition, physical aging and liquid-quenching. The bulk fictive temperatures of these glasses span over 35 K, indicating 13 to 20 orders of magnitude changes in bulk relaxation times. However, the surface diffusion coefficients on these glasses are measured to be identical at two temperatures below bulk glass transition temperature T_g . These results suggest that surface diffusion has no dependence on the bulk relaxation dynamics when measured below T_g .

3.2. Introduction

Molecular glasses have wide applications in organic electronics[139, 131, 146], coatings[85], pharmaceuticals[153, 28, 63], and nano-imprint lithography techniques[112]. Since the surface-to-volume ratio increases rapidly with the reduction in dimension as desired for these applications, understanding surface properties becomes increasingly important. Recent studies have aimed at developing efficient techniques to measure the surface mobilities on molecular glasses and have shown that surface diffusion can be orders of magnitude faster than bulk diffusion, with a lower activation barrier[163, 34, 13, 125, 162]. In addition, more recent studies reported that fast surface diffusion strongly depends on the molecular size

and intermolecular interactions[157, 125, 23].

Understanding fast surface diffusion on molecular glasses is highly relevant for understanding the formation of ultra-stable glasses[137]. Organic glasses prepared by physical vapor deposition (PVD) at substrate temperatures below bulk glass transition temperature, T_g , are found to have exceptional thermodynamic and kinetic stabilities[137, 72, 79, 83]. Glasses are out of equilibrium materials, therefore one can produce glasses with varying structures and properties by varying their states in the corresponding energy landscape. Physical aging is usually used to obtain glasses with varying properties by holding a glass below T_g . However, these changes in properties are typically small and take exponentially long times at lower temperatures. In contrast, within deposition time of minutes to hours, PVD can access states in the energy landscape that may take a liquid-quenched glass millions of years of aging to access[135, 137, 30, 83]. It has been proposed that due to the fast diffusion during PVD, molecules at the top surface have enough time to achieve a better configuration and thus a lower energy state before being buried by the next layer. Thus we call this process Surface-Mediated Equilibration (SME). Direct measurement of the surface diffusion on ultra-stable glasses is an important step in understanding the SME mechanism.

We have recently developed a new and efficient technique that uses tobacco mosaic virus (TMV) as probe particle for facile characterization of surface diffusion on ordinary glasses[162]. When TMV is introduced onto the surface, due to rapid wetting a sharp curvature appears around the virus and induces surface molecules to flow towards it and form a meniscus. Since the virus is semi one-dimensional, the flow around the center of the virus has reduced dimensionality and is self-similar, allowing for rapid characterization of surface diffusion by tracking the evolution of the meniscus shapes. This technique requires no modification of the sample surface, as long as the aqueous TMV solution does not disturb its properties.

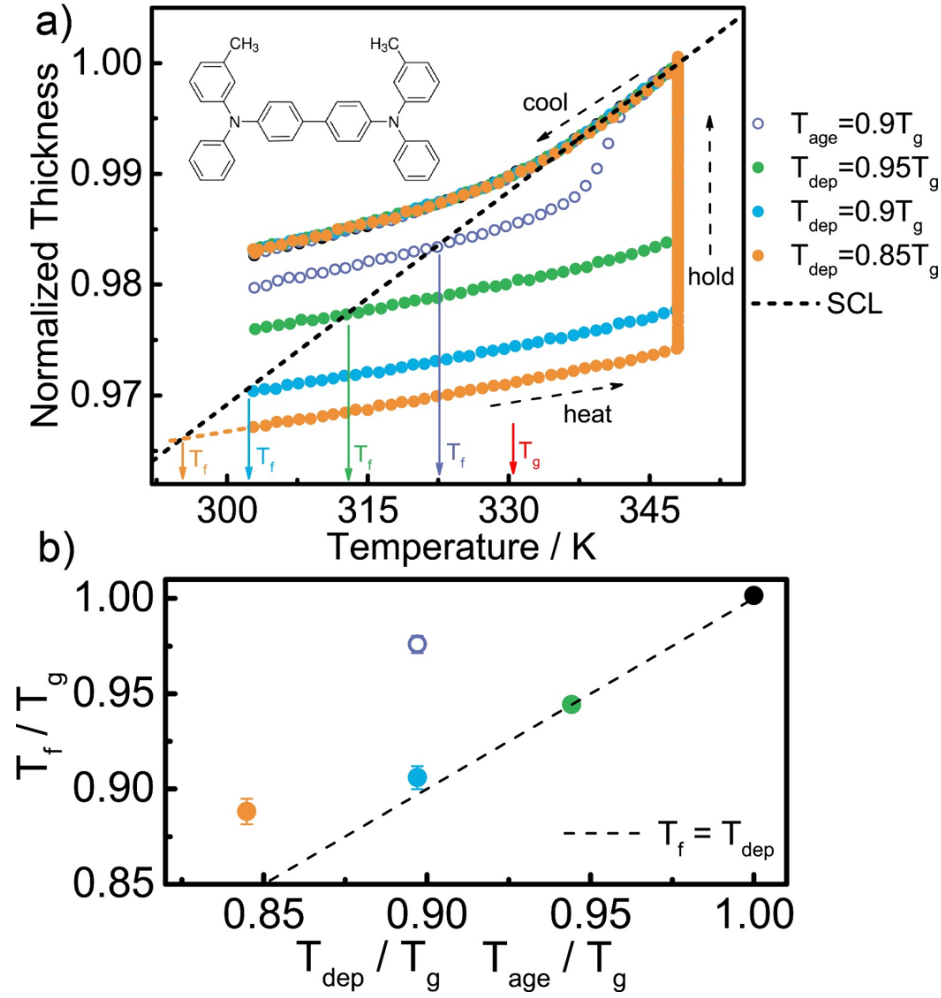


Figure 3.1: a) Thermal stabilities of PVD and aged glasses post TMV measurements. Thickness changes of PVD glasses deposited at $0.85 T_g$ (solid orange), $0.9 T_g$ (solid blue), $0.95 T_g$ (solid green) and glasses aged at $0.9 T_g$ (open purple) were monitored upon heating and cooling with ellipsometry. Black dashed line is the universal super-cooled line for TPD. Arrows indicate the fictive temperature for each glass and bulk T_g . Inset shows TPD molecular structure. b) Fictive temperatures versus deposition or aging temperatures.

3.3. Results and Discussion

In this study, the TMV-probe method is applied on the surfaces of ultra-stable PVD glasses to investigate the effect of variations in bulk dynamics on the surface diffusion for the first time. Surface diffusions on glasses prepared by physical aging and liquid-quenching are also studied for comparison. The fictive temperatures of PVD stable, aged, and liquid-quenched glasses span over 35 K, corresponding to 13-20 orders of magnitude change in the bulk structural relaxation time, τ_α . Measurements are performed at two temperatures well below bulk T_g ($T_g - 27$ K and $T_g - 34$ K). We find that the surface diffusion coefficients of all these glasses at each temperature remain invariant within half an order of magnitude (range of experimental error). No correlation between the fast surface diffusion and the bulk relaxation dynamics was found, suggesting that the fast surface diffusion is possibly decoupled from bulk molecular motions and only reflect free surface behavior.

To produce glasses with varying bulk relaxation dynamics, N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD, $T_g = 330$ K) films were prepared either by PVD at various substrate temperatures, or by physical aging at $0.9 T_g$ for a week. Fictive temperature, T_f , is used as a measure of glass stability and bulk relaxation dynamics[142, 94]. Figure 3.1 demonstrates how T_f was determined for each glass. Ellipsometry was used to measure the thickness of PVD or aged glasses as the films were heated at 10 K/min to 348 K and isothermally transformed into super-cooled liquid before being cooled back to glassy state at 10 K/min. Figure 3.1a) shows the normalized thickness for each film during and after transformation (detailed in SI). The excellent overlap in the super-cooled and ordinary glass states indicates that all glasses were transformed into a common super-cooled liquid state and had the same properties after transformation.

Fictive temperature is defined as the temperature where the extrapolated super-cooled liquid line intercepts the glassy line. Figure 3.1a) shows the extrapolation of the super-cooled liquid line of TPD and the different temperatures where it intercepts with the initial glass lines. The T_f value of each glass is indicated by colored arrow. Figure 3.1b) shows

the measured T_f versus T_{dep} or T_{age} . Figure 3.1 and Figure 3.8 show that PVD glasses have lower fictive temperatures and higher stabilities compared to aged or liquid-quenched glasses, with the most stable glass deposited around $0.85 T_g$, consistent with previous studies of PVD glasses[137, 72, 79, 48, 31, 147, 83].

The bulk τ_α of stable and aged glasses at a given temperature can be estimated based on Adam-Gibbs-Vogel (AGV) equation[2, 67]:

$$\ln \tau_\alpha(T, T_f) = \ln \tau_0 + \frac{DT_0}{T(1 - \frac{T_0}{T_f})} \quad (3.1)$$

where for TPD close to T_g , $D = 13.5$, $\tau_0 = 10^{-19.2}$ s, $T_0 = 258.9$ K[147, 161]. One can estimate that for the most stable glass with $T_{dep} = 0.85 T_g$ ($T_f = 293$ K) τ_α is about 20 orders of magnitude slower than that of the liquid-quenched glass where $T_f = T_g = 330$ K for both isothermal hold temperatures of 296 K and 303 K (Figure 3.10). A more conservative Arrhenius extrapolation, using the activation energy near T_g , shows that τ_α for this sample is at least 13 orders of magnitude slower than τ_α at $T_g = 330$ K (Figure 3.11). As such, the range of bulk relaxation explored here spans 13 to 20 orders of magnitude, corresponding to 35 K changes in T_f .

TMV-probe experiments were performed to measure the surface diffusion of glasses with varying T_f values. This method has been described in detail in our earlier publication[162]. Briefly, the semi-one dimensional TMV particle is introduced onto the surface of a glass. Due to rapid wetting of the material, a sharp local curvature is produced around TMV, resulting in a flux of surface molecules towards the virus and forming a meniscus around it. Atomic force microscopy (AFM) is used to monitor the temporal evolution of the meniscus shapes. The unique advantage of using semi-one dimensional TMV probe, with a large aspect ratio around 18, is that it simplifies the meniscus evolution into a two-dimensional flow and thus simplifies the analysis needed to define the surface diffusion coefficient[162].

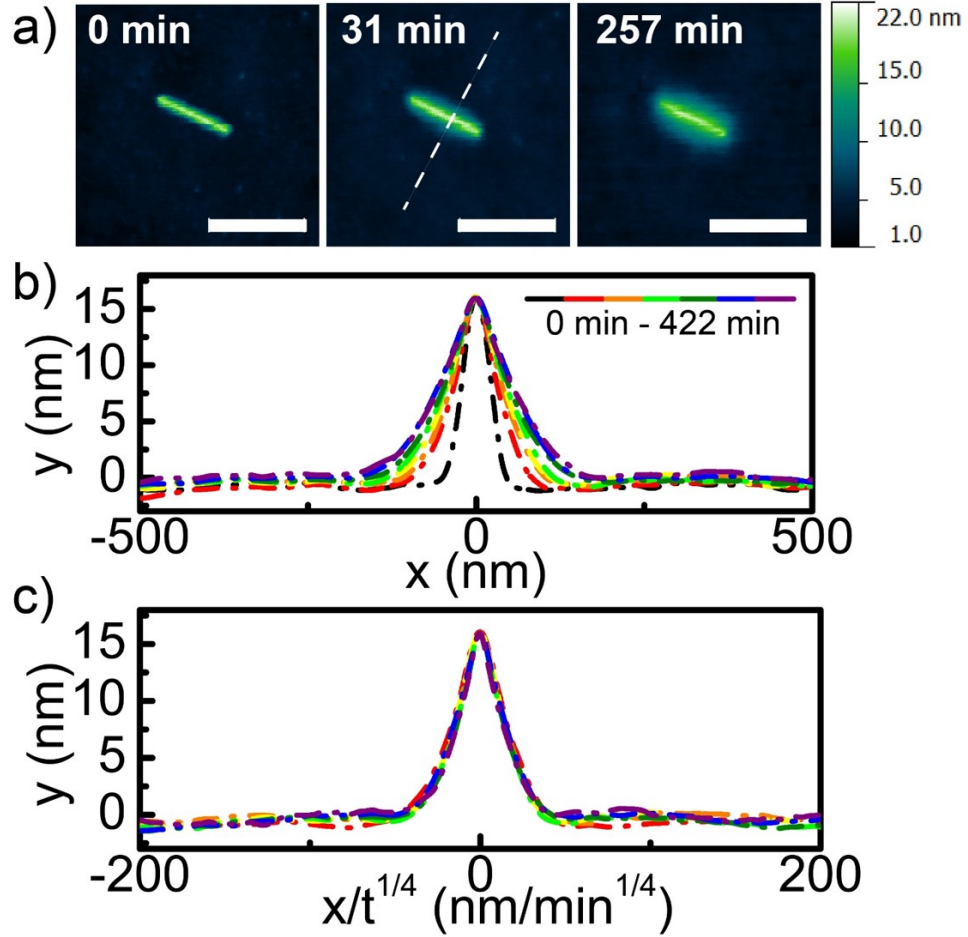


Figure 3.2: a) Representative AFM images of the surface response to TMV perturbation on a 400 nm stable glass ($T_{\text{dep}}=0.85 T_g$) held isothermally at 303 K ($T_g - 27$ K). Scale bars are 400 nm. b) Temporal evolution of the profiles across the center of TMV shown in a), each profile plotted was averaged from five near-center line profiles across the TMV. c) Profiles in b) collapse onto a universal curve after scaling x with $t^{1/4}$, indicating that the profiles are self-similar and follow surface diffusion-controlled flow.

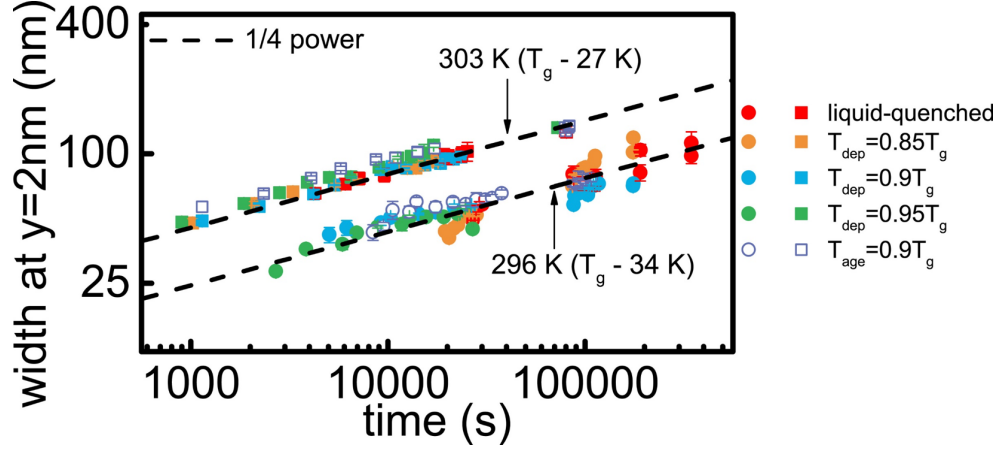


Figure 3.3: Half profile widths at a constant height $h = 2$ nm from the bottom of TMV plotted versus isothermal hold times at 296 K and 303 K for five TPD glasses. At each temperature, the profile evolutions on different glasses all follow the 1/4 power law indicated by black dashed lines.

Control experiments were performed to rule out the potential effect of TMV deposition on stable glass properties in Figure 3.9.

Figure 3.2a) shows representative AFM images of a meniscus evolution formed after TMV was placed on the surface of a 400 nm stable glass film deposited at $0.85 T_g$, held isothermally at 303 K. The meniscus around the TMV probe, observed as bright halo in the image, is formed by material accumulation due to curvature driven surface flow, and grows with isothermal holding time. Since the aspect-ratio is large, the flow around the center of TMV is semi two-dimensional. A line profile normal to the long axis near the center of TMV, as the example shown in Figure 3.2a), can be used to evaluate the evolution of the process shown in Figure 3.2b). Five line profiles near the center of TMV were averaged to produce the profiles shown in Figure 3.2b) at each given time for noise reduction. As seen in the plot, the cross-section profile widens with time as the sample is held at 303 K.

We note that in the time window of this measurement, no obvious embedding of TMV was observed, indicating that the meniscus formation is due to a diffusive process on the surface[162]. As demonstrated by Mullins[95], the governing equation for a flow solely driven

by surface diffusion in two dimensions can be described as:

$$\frac{\partial h(x, t)}{\partial t} = -\frac{D_s \gamma \Omega^2 \nu}{kT} \frac{\partial^4 h(x, t)}{\partial x^4} \quad (3.2)$$

where $h(x, t)$ is the height at distance x from the center of TMV at time t , D_s is surface diffusion coefficient, γ is surface tension, Ω is molecular volume, ν is number of atoms per unit area, and k is the Boltzmann constant. Previous studies have shown that profiles following equation 3.2 are self-similar after a transient time[95, 10, 87, 127, 162]. Figure 3.2c) shows that the profiles in Figure 3.2b) are indeed self-similar and collapse onto the same curve when x is scaled with $t^{1/4}$.

To further show that the meniscus evolution follows equation 3.2, the half profile widths at a constant height of 2 nm are plotted versus time in Figure 3.3. For the temperatures and time intervals studied, all profile evolutions follow the 1/4 power law scaling, further confirming that the flow of the molecules is governed by surface diffusion. Under these conditions the prefactor $\frac{D_s \gamma \Omega^2 \nu}{kT}$ can be used to compare the value of surface diffusion for glasses with different bulk relaxation dynamics or fictive temperatures[162]. Except for D_s and T , other parameters in this prefactor depend on the molecule used and should be roughly the same for films of the same chemical composition (detailed discussions in SI). It is interesting to observe from Figure 3.3 that at each temperature, the profile width evolutions and therefore the prefactors are very similar for all five glasses surveyed. At each temperature, the data fall on the same line within the range of experimental error, suggesting that surface diffusion coefficients are the same for all of these glasses, decreasing with decreasing temperature.

With the data in Figure 3.3, D_s for stable and aged glasses can be obtained by comparing the intercept value for each data set with that of liquid-quenched glass reported previously[162]. Figure 3.4 plots D_s for each glass measured at two different temperatures as a function of T_f . The error bars represent variations between two to three independent measurements on newly deposited or aged samples. Figure 3.4 shows that regardless of

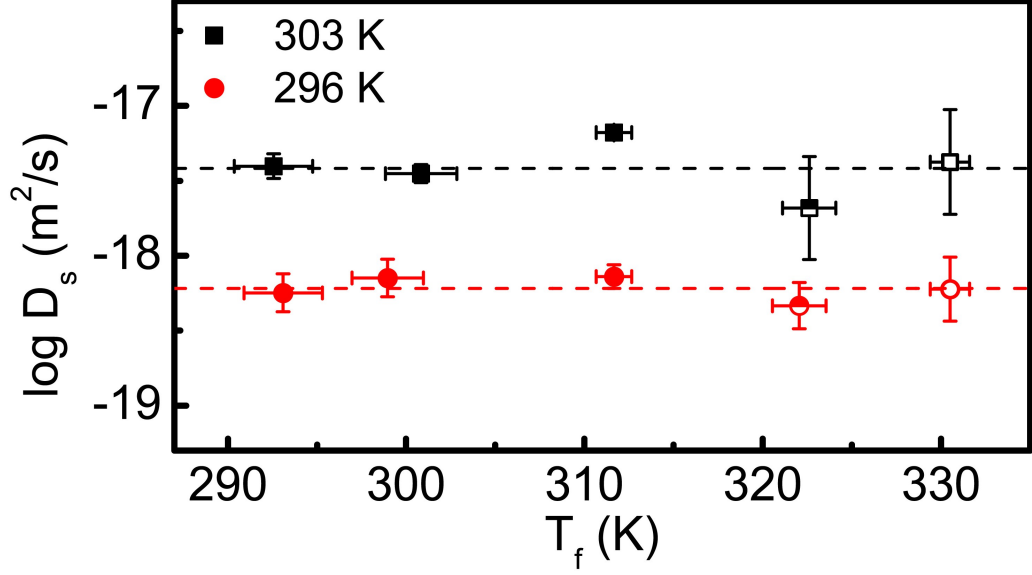


Figure 3.4: Surface diffusion coefficients on stable (filled), aged (half filled) and liquid-quenched glasses (open) measured at 303 K (black) and 296 K (red), plotted versus fictive temperature. Dashed lines are the average D_s at each temperature.

the preparation methods or T_f values, surface diffusion coefficients at each temperature remain the same within half an order of magnitude. The dashed lines show the average values of D_s at each temperature, where $D_s(303\text{K}) = (3.82 \pm 0.76) \times 10^{-18} \text{ m}^2/\text{s}$ and $D_s(296\text{K}) = (6.06 \pm 0.55) \times 10^{-19} \text{ m}^2/\text{s}$.

The observation that surface diffusion is independent of bulk relaxation dynamics at each isothermal hold temperature is remarkable, given that the range of fictive temperatures spans over 35 K for the glasses surveyed. As discussed, this range of change in T_f translates into 13 to 20 orders of magnitude variations in τ_α between different glasses, with glasses deposited at $0.85T_g$ having the slowest and liquid-quenched glasses having the fastest relaxation times. However, as shown in Figure 3.4, even with such huge differences in bulk relaxation dynamics, the measured surface diffusion coefficients on different glasses remain constant within experimental error.

Theoretical models based on smooth gradients of dynamics from the free surface predict temperature-dependent relaxation dynamics at the free surface with lower activation en-

ergy compared to bulk [134, 19, 17, 66, 61]. For example, models developed for equilibrium super-cooled liquids such as random first order transition (RFOT)[134] and coupling model (CM)[19] predict that for glasses with short range interactions, such as TPD, the surface relaxation time, τ_{surface} , has a power-law dependence on τ_{α} . In both models, τ_{surface} is predicted to be highly correlated with τ_{α} . To the best of our knowledge there are no predictions for out of equilibrium systems, and whether the surface dynamics would be coupled to the equilibrium state through the energy landscape, or would be coupled to out of equilibrium state due to dynamic coupling of molecules that are going through relaxation. The data presented here does not show any correlation between the bulk and surface dynamics, suggesting that as the system falls out of equilibrium there is a decoupling between the surface and bulk either due to the decoupling of the surface and bulk relaxation dynamics or the decoupling of the surface diffusion from surface relaxation dynamics (hopping). Since the Mullins model[95] that is developed for continuum fluid fits the data well, the latter is less likely. We also note that the data presented here does not rule out the coupling of the surface and the corresponding supercooled liquid, which is the same at each temperature despite fictive temperature variations.

Elastically cooperative activated barrier hopping model developed by Mirigian and Schweizer[91, 93] predicts surface diffusion as $D_s = d^2/(6\langle\tau_{\alpha}\rangle)$, where d is the molecular size and $\langle\tau_{\alpha}\rangle$ is the average dynamics of the near-surface layer at different penetration depths, either half or one molecular size[93]. Thus in this model D_s is only associated with the near-surface relaxation dynamics as opposed to bulk τ_{α} that strongly vary between stable, aged, and liquid-quenched glasses. Since one would not expect $\langle\tau_{\alpha}\rangle$ to change strongly within the depth of 1 nm or so from the free surface (approximately one molecular size), we can simply assume $D_s \simeq d^2/(6\tau_{\text{surface}})$. As such, from the invariance of D_s one could conclude that τ_{surface} is also invariant and is of the orders of $10^{-2} - 10^{-1}$ s assuming $d = 1$ nm. Such short time scales imply that the surface could be at equilibrium regardless of the bulk state. If this assumption is correct, then the surface relaxation times are not only orders of magnitude faster than bulk dynamics similar to what has been measured on polymer glasses[47],

but they are also dynamically decoupled from the bulk dynamics such that a change of 20 orders of magnitude in the bulk relaxation times do not affect the surface relaxation times. Alternatively, the nature of the gradients in the dynamics in the layers immediately below the free surface could be different at various fictive temperatures, while the free surface dynamics are determined by the nature of the interface and not the properties of the bulk. In either scenario, the origins of the temperature-dependence of τ_{surface} , measured through temperature-dependent D_s are not very clear and merit further exploration. Figure 3.4 clearly shows that while D_s does not depend on T_f , it slows with decreasing temperature, consistent with previous measurements. It would be important to design experiments to independently observe the rotational dynamics of the free surface in order to directly measure τ_{surface} to verify this hypothesis.

Although less likely, it is still worthing discussing the possibility that surface diffusion is due to a hopping mechanism of loosely bound surface molecules on an energy landscape produced by the out of equilibrium glassy solid[40, 3]. In this case fast diffusion can proceed even when the surface dynamics are also arrested and out of equilibrium. As glass densities have only changed by 1.5% between the most and least stable glasses (Figure 3.8), the surface energy has not been significantly varied (detailed in SI). As such, it is plausible that the surface diffusion would also be independent of the fictive temperature. The activation energy for hopping in this scenario would only depend on the surface energy and molecular size.

The independence of D_s from the bulk relaxation dynamics is consistent with the proposed Surface-Mediated Equilibration (SME) process. The fact that D_s remains the same on glasses of various stabilities ensures that SME can proceed efficiently on the top surface layer regardless of the bulk dynamics. If the motion of molecules at the free surface slowed down significantly with the relaxation dynamics of previously formed layers, SME process would have been self-limiting and depends on film thickness, which is not the case[137, 30, 83]. However, the measurements presented here do not provide a full picture. Molecules

of various sizes can be made into stable glasses when deposited at $0.85T_g$ [137, 30, 83]. This implies that τ_{surface} at $0.85T_g$ must be roughly the same for these molecules. Other studies have shown that D_s slows with increasing molecular size[157, 125, 23]. These two observations can only be simultaneously correct if D_s scales with molecular size as d^2 as predicted by Mirigian and Schweizer[91, 93], to keep τ_{surface} size invariant or if τ_{surface} and D_s are decoupled. One can verify the former hypothesis by performing surface diffusion measurements on a homologous series of molecules with various sizes. The latter can only be verified by directly measuring τ_{surface} .

3.4. Summary

In summary, we report the first measurement of surface diffusion on ultra-stable glasses, and compare with physically-aged and ordinary glasses. We find no change in the surface diffusion coefficients when the bulk fictive temperature is varied over a range of 35 K, equivalent to 13-20 orders of magnitude in bulk structural relaxation times. Our results suggest that fast surface diffusion is decoupled from the bulk dynamics and is probably only associated with the near-surface dynamics that involve at most a few mono-layers of top surface molecules where they can always equilibrate at short time scales regardless of the bulk relaxations. However, the exact mechanism of this decoupling merits further investigation. Since surface diffusion can potentially contribute to fast crystallization and stable glass formation, a deeper understanding of the nature of fast diffusion and relaxation dynamics at the free surface are imperative for both glass theories and applications.

3.5. Acknowledgments

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3.6. Supplementary Material

Material and film preparation

N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) was purchased from Sigma-Aldrich and used without further purification. The glass transition temperature T_g was determined by differential scanning calorimetry (DSC) to be 330 K[161, 162] at a cooling rate of 10 K/min. 4400 nm thick stable glass films were prepared on silicon substrates (one side polished, 100 plates, Virginia Semiconductor) with 1-2 nm native oxide layer held at substrate temperatures of $T_{\text{dep}}=279\text{ K}=0.85\ T_g$, $T_{\text{dep}}=296\text{ K}=0.9\ T_g$, and $T_{\text{dep}}=312\text{ K}=0.95\ T_g$ with an average deposition rate of 0.2 nm/s. Ordinary TPD glasses were obtained by transforming stable glasses upon heating at $348\text{ K}=T_g + 18\text{ K}$ either on a Linkam heating stage while performing ellipsometry measurements or in a vacuum oven overnight. Ordinary glasses were then aged at $T_{\text{age}}=296\text{ K}=0.9\ T_g$ in a vacuum desiccator for a week for aging studies.

AFM images of the flat initial morphology of various samples surveyed are shown in Figure 3.5. Surface roughnesses on all films was measured to be less than 1 nm.

Tobacco mosaic viruses were purified from infected leaves and suspended in miliQ water as described in our earlier publication[162]. Dilute TMV was introduced onto the surfaces of TPD glasses by spin-coating and thoroughly dried with nitrogen for further imaging measurements. Isothermal measurements were performed with a custom thermoelectric heating-stage calibrated with melting point standards[162]. Non-contact atomic force microscopy (AFM) imaging was performed to track the evolution of the surface response at two isothermal temperatures $296\text{ K}=T_g - 27\text{ K}$ and $303\text{ K}=T_g - 34\text{ K}$. After the isothermal measurements of surface diffusion, the stability of stable and aged glasses were measured with spectroscopic ellipsometry (M-2000 V J. A. Woollam), by placing the samples on a Linkam heating stage (THMS 350 V) and measuring the thickness and birefringent index of refraction as a function of temperature.

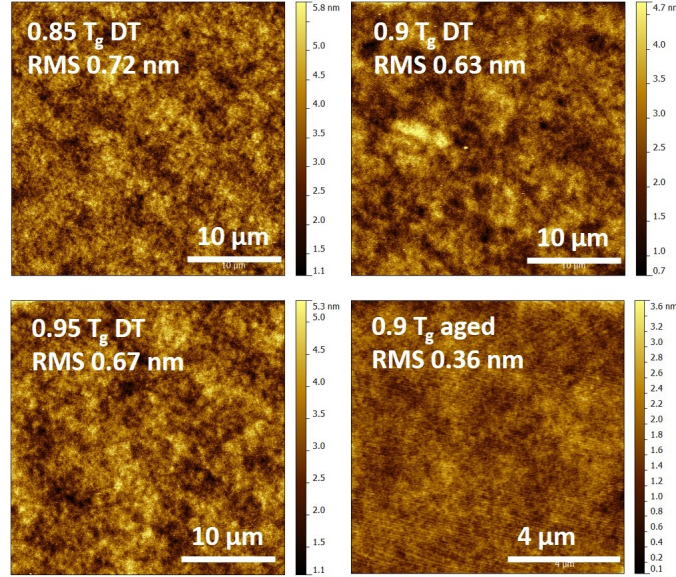


Figure 3.5: Initial flat morphologies of as-deposited stable glasses and as-aged glasses.

Ellipsometry measurements

Spectroscopic ellipsometry (M-2000 V J. A. Woollam) was used to measure the stability of films used in this study. An anisotropic Cauchy model was used to fit raw ellipsometry data of stable glasses from PVD. In this model ellipsometry angles $\Psi(\lambda)$ and $\Delta(\lambda)$ were fit to a model consisting of a temperature-dependent substrate, a native oxide layer, and an uniaxial anisotropic Cauchy layer to model the transparent TPD film. The anisotropic Cauchy model is described as $n_{xy}(\lambda) = A + \frac{B}{\lambda^2}$, and $n_z(\lambda) = n_{xy}(\lambda) + dA_z$, where $n_{xy}(\lambda)$ is the index of refraction in the xy-plane and $n_z(\lambda)$ is the index of refraction normal to the plane of the substrate. A , B , dA_z and the film thickness h were free fit parameters. A spectroscopic range of 600 nm-1600 nm was used for modeling. Figure 3.6 shows an example of the fit to an as-deposited PVD sample.

Temperature ramping experiments were applied to all films studied to evaluate their stabilities. An example of the ramping experiment on a 400 nm TPD film deposited at 0.95 T_g is shown in Figure 3.7. Panel A shows the temperature as a function of time. All films were heated at a rate of 10 K/min to a set temperature of 348 K ($T_g + 18$ K) and were held

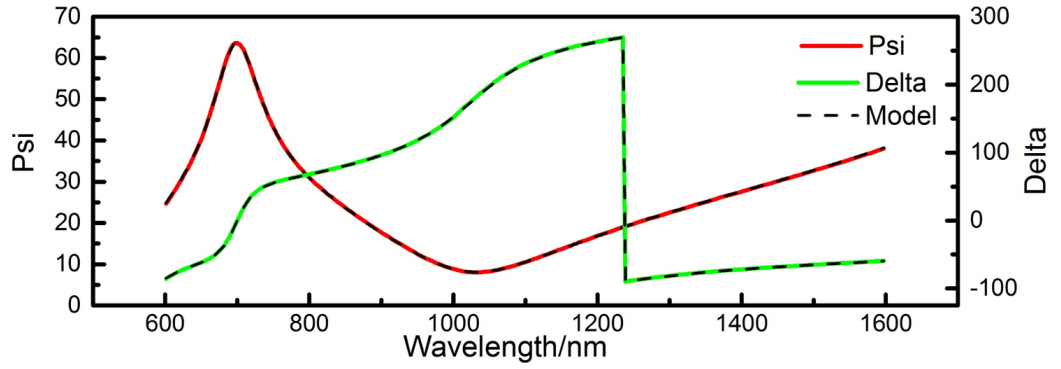


Figure 3.6: Ellipsometry angles Psi (Ψ , red) and Delta (Δ , green) vs. wavelength data for a thick TPD film. Anisotropic model fit of raw ellipsometry data is shown as dashed black lines.

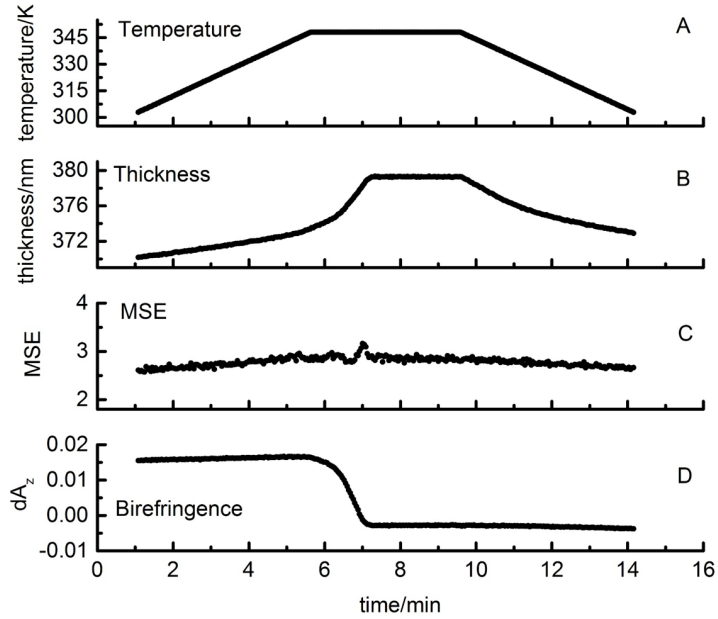


Figure 3.7: Experimental details of a typical temperature ramping experiment for transforming a stable glass film (400 nm TPD deposited at $0.95T_g$). From top to bottom: A: Temperature profile vs. time. B: Thickness vs. time. C: MSE vs. time obtained from anisotropic Cauchy fit. D: Birefringence (dA_z) vs. time.

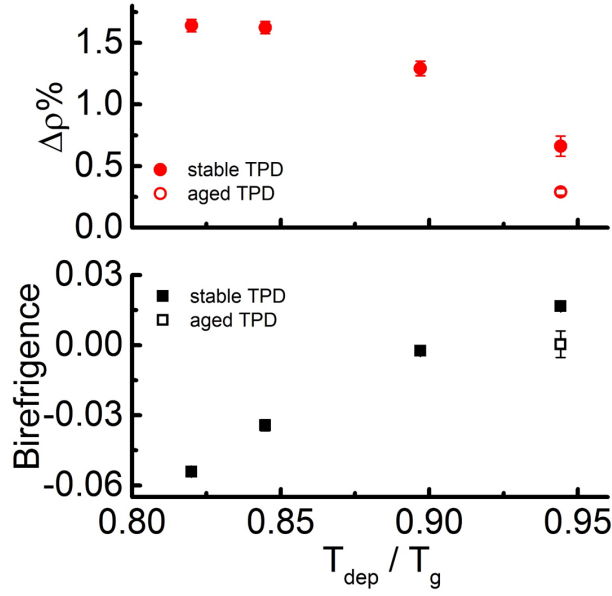


Figure 3.8: Change in density, $\Delta\rho$ (top) and birefringence ($n_z - n_{x,y}$, bottom) of TPD stable and aged glasses versus deposition temperatures.

isothermally until they were fully transformed into ordinary glass, indicated by a plateau in film thickness at the set temperature as shown in panel B (thickness vs. time). Then the films were cooled at 10 K/min to 303 K. Panel C shows the mean square error (MSE) throughout the ramping process for the model described above, representing a reliable fit to the data at all times. Panel D shows the birefringence during the ramp. The initially birefringent films become isotropic upon transformation to ordinary glass. In Figure 3.8, the density change and birefringence of TPD stable and aged glasses are plotted versus deposition temperatures.

Effect of TMV deposition and isothermal holding on the stability of stable glasses

To make sure that the processes of TMV deposition on the surface and the isothermal holding to measure diffusion do not affect the stability of PVD glasses, we performed the following control experiments on four samples of 400 nm films of TPD vapor-deposited at $T_{\text{dep}} = 0.9 T_g$ and compared the results in Figure 3.9. (1) We measured the stability of an as-deposited sample (black) by heating the sample to 348 K ($T_g + 18$ K), waiting for the

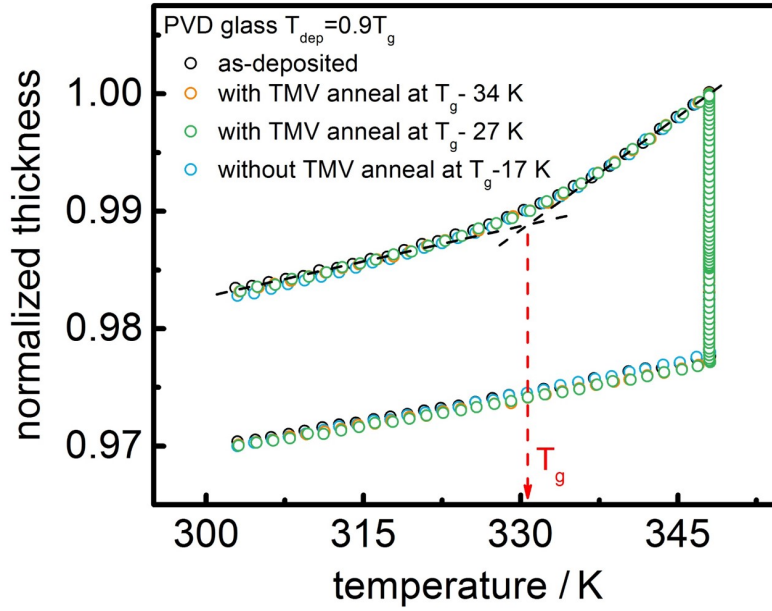


Figure 3.9: Stability tests on $T_{\text{dep}} = 0.9 T_g$ PVD glasses under different control experiments as detailed in the paragraph.

sample to transform into ordinary glass, and then cooling it back to room temperature. (2) The sample was isothermally held at $T = 313 \text{ K} = T_g - 17 \text{ K}$ for 22 hours prior to stability test (blue). (3) TMV was introduced on the surface, the sample was then isothermally held at $T = 303 \text{ K} = T_g - 27 \text{ K}$ for 24 hours prior to stability test (green). (4) TMV was introduced on the surface, the sample was then isothermally held at $T = 296 \text{ K} = T_g - 34 \text{ K}$ for 55 hours prior to stability test (orange). The results in Figure 3.9 show that there is no difference in the stability of these samples and all curves overlap each other almost perfectly. These control experiments show that the addition of TMV on the surface and isothermal holding below T_g do not affect the properties of the PVD stable glasses.

Estimation of bulk relaxation time of stable and aged glasses

In Figure 3.10 and Figure 3.11, we provide an estimation of the bulk relaxation of stable and aged glasses based on their fictive temperatures using both AGV and Arrhenius extrapolation near T_g as detailed in the main text.

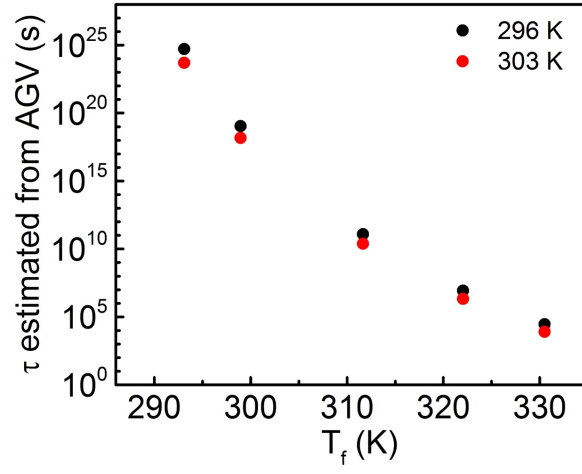


Figure 3.10: Estimation of τ_α of stable and aged glasses based on AGV equation as detailed in the main text.

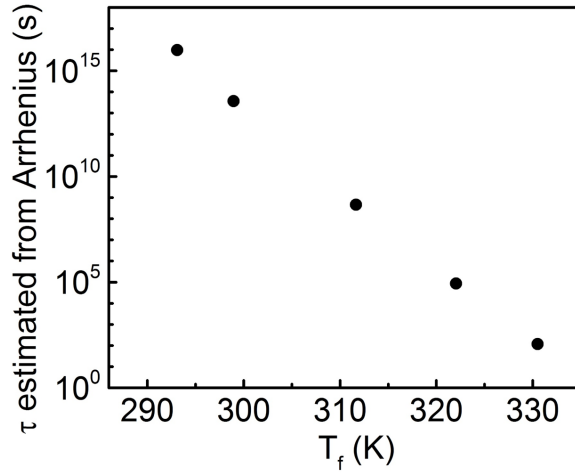


Figure 3.11: Estimation of τ_α of stable and aged glasses based on Arrhenius extrapolation near T_g .

Estimation of change in surface tension of stable and aged glasses

Using the Eötvös rule[44], we can roughly estimate the change of surface tension of TPD stable glasses compared to ordinary glasses by $\gamma V^{2/3} = k(T_c - T)$, where k is the Eötvös constant and has a value of $2.1 \times 10^{-7} \text{ J}/(\text{K} \cdot \text{mol}^{2/3})$, V is the molecular volume for TPD, which is estimated based on the molecular weight and relative density as $V = MW/\rho$. The largest density change in stable and aged glasses studied in this report is about 1.5% increase for the most stable glass deposited at $T_{\text{dep}} = 0.85 T_g$. The change in γ between this glass and ordinary glass is thus estimated to be less than 1%. All other glasses have even smaller changes in their surface tension. From this simple estimation, it is clear that the changes in γ are negligible in our study. However, we note that this is estimated from the overall density change in stable glasses, it is still unknown whether the surface density of the stable glass would be different from ordinary glass, but we don't expect those changes to be as large as or larger than 1.5% in density.

Error bars

The error bars in Figure 3.4 are from the error of 2-3 repeating trials or the error from the fit. Instrumental errors such as temperature variations were not included. For the two isothermal temperatures 296 K and 303 K studied, the temperature did not vary more than 0.5 K throughout the measurements.

CHAPTER 4 : Decoupling of Surface Diffusion and Bulk Dynamics in Molecular Glasses

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4.1. Abstract

Tobacco mosaic virus is used as a probe to measure surface diffusion of ultrathin films of N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD, $12\text{ nm} < h < 53\text{ nm}$) at various temperatures below the glass transition temperature, T_g , of all films. As the film thickness is decreased, T_g decreases rapidly and the average film dynamics are enhanced by 6 to 14 orders of magnitude. We show that the surface diffusion is invariant of the film thickness decrease and the resulting enhanced overall mobility. The values of surface diffusion coefficient and its temperature-dependence are invariant of film thickness and are the same as the corresponding bulk values ($h = 400\text{ nm}$). For the thinnest films ($h < 20\text{ nm}$), the effective activation energy for rearrangement (temperature-dependence of relaxation times) becomes smaller than the activation energy for surface diffusion. These results suggest that the fast surface diffusion is decoupled from film relaxation dynamics and is a solely free surface property.

4.2. Introduction

The diffusion coefficients on the surfaces of molecular glasses are reported to be orders of magnitude faster than the bulk diffusion[163, 34, 13, 162, 157, 125], with weaker temperature dependences and stronger dependences on the molecular size or intermolecular interactions[157, 125, 23]. The measured fast surface diffusion on molecular glasses has been hypothesized to affect the frequently observed fast surface crystallization[136, 96] and the formation of ultrastable glasses by physical vapor deposition[137].

We have recently investigated the surface diffusion of liquid-quenched bulk TPD glasses[162] as well as aged and vapor-deposited ultrastable TPD glasses[159], spanning a range of 35 K in fictive temperatures and 13 to 20 orders of magnitude variations in structural relaxation times of the glass. We found that when held below bulk glass transition temperature, T_g , the surface diffusion coefficient remains fast (about 6 orders of magnitude faster than the corresponding bulk diffusion coefficient of the ordinary glass at T_g), has a lower activation energy than bulk, and is invariant of the bulk dynamics on aged and ultrastable glass films. The lack of correlation between the surface diffusion and bulk dynamics of aged or ultrastable glasses motivates further exploration of the nature of the observed fast surface diffusion on glassy surfaces.

Nano-sized polymer films have been shown to have properties that deviate strongly from the corresponding bulk properties. In particular, their glass transition temperatures are reduced compared to bulk polymer glasses[76, 42, 116, 55, 39, 4]. The reduced T_g has been linked to enhanced relaxation dynamics near the free surface for both supported[76, 47, 21] and freestanding[51, 104] films, and the resulting enhancement of the overall relaxation dynamics[46, 55, 56] of ultrathin films. We have recently demonstrated that the viscosity and relaxation dynamics in ultrathin films of molecular glass TPD are similarly enhanced by 6 to 14 orders of magnitude depending on the measuring temperature[161], but a direct comparison with fast surface diffusion to our knowledge has not been made in molecular glass systems.

By investigating surface diffusion coefficients on ultrathin TPD films, surface diffusion can be measured in films with overall dynamics that are more similar to that of the free surface. These studies can help investigate whether the decoupling between surface diffusion and bulk relaxation dynamics in aged and ultrastable molecular glass films are due to large differences between the values (at least 6 orders of magnitude at T_g for ordinary glass and growing with lowering fictive temperature[159]), or whether it has a more fundamental origin. In addition, the typical thicknesses of molecular glasses used in applications such

as coatings and organic electronics are less than 100 nm, and as such it is imperative to directly characterize the surface mobility on these nano-sized glasses and to understand its role and effect in enhancing the dynamics in ultrathin films used in these applications.

Here we apply our recently developed TMV-probe method[162, 159] to measure surface diffusion of ultrathin TPD glass films supported on silicon substrates. The important advantage of the TMV-probe method is that it generates a mild perturbation on the free surface and requires no additional modification of the sample’s surface. As such, this is a robust method that can be easily extended to study the surface of ultrathin molecular glass films. In this method, the surface mobility can be evaluated by monitoring the temporal evolution of the surface response to TMV’s perturbation. In this study, the TMV-probe method is applied on the surfaces of ultrathin molecular glass films, ranging from 12 nm to 53 nm, to measure their surface diffusion. The surface diffusion coefficients on these ultrathin films are found to be constant within the experimental error at four measuring temperatures below the bulk or thin film T_g s. The results show that the surface diffusion has no dependence on the film thickness, while the T_g is reduced by as much as 20 K in 12 nm films and the average dynamics in these films are enhanced by 6 to 14 orders of magnitude. Furthermore, the activation energy of the thinnest films ($h < 20$ nm) are lower than that of the surface diffusion on the same films. These results suggest that the fast surface diffusion is fully decoupled from the overall film relaxation dynamics, down to film thicknesses where the film dynamics become comparable with the surface diffusion enhancement. Once the film is no longer glassy, the virus embeds into the film and surface diffusion can no longer be measured.

4.3. Results and Discussion

4.3.1. T_g reduction and enhanced overall dynamics in ultrathin films

The model system studied here is organic molecular glass N,N’-Bis(3-methylphenyl)-N,N’-diphenylbenzidine (TPD, $T_g = 330$ K, molecular structure shown in Figure 4.1B). Figure

4.1A shows the measured T_g values as a function of film thickness. The inset shows representative normalized thickness profiles for four different films during the cooling ramps. The glass transition temperature is defined as the intercept of the super-cooled liquid line with the glassy line. As the temperature is decreased, ultrathin films maintain equilibrium at lower temperatures compared to the 120 nm film and show broader T_g transitions. As a result, the T_g is reduced as the film thickness is decreased, with an onset of deviation from bulk T_g around 50 nm. This observation is consistent with previous measurements of T_g reductions in ultrathin films of molecular[70, 156, 161] and polymeric glasses[76, 42, 46, 55, 57] and shows similar range of thickness over which the T_g of the ultrathin films are affected by the enhanced surface dynamics.

We have recently measured the effective viscosity and average relaxation times of ultrathin TPD films at various temperatures below bulk T_g [161]. Using cooling-rate dependent T_g (CR- T_g) measurements, the film's average relaxation time at T_g can be estimated based on the inverse of cooling rates. Isothermal dewetting measurements were also performed in these studies to characterize the effective viscosity within films of various thicknesses and were related to relaxation times. Within the error of the experiments, both measures of dynamics (isothermal and temperature ramps) produced similar average relaxation times in ultrathin films. Using this data from Ref.[161], the average relaxation time at each temperature of interest (ranging from 296 K to 313 K) for each film thickness can be calculated. Figure 4.1B shows that depending on the temperature, the dynamics in ultrathin films can be 6 to 14 orders of magnitude faster than the corresponding bulk dynamics at the same temperature, with the differences increasing in magnitude with decreasing temperature, mostly due to stronger temperature dependence of bulk films compared to ultrathin films.

4.3.2. Surface diffusion measurements on ultrathin films

TMV-probe technique[162, 159] was applied to measure the surface diffusion of ultrathin TPD films. Dilute TMV particles were introduced onto the surfaces of ultrathin films by

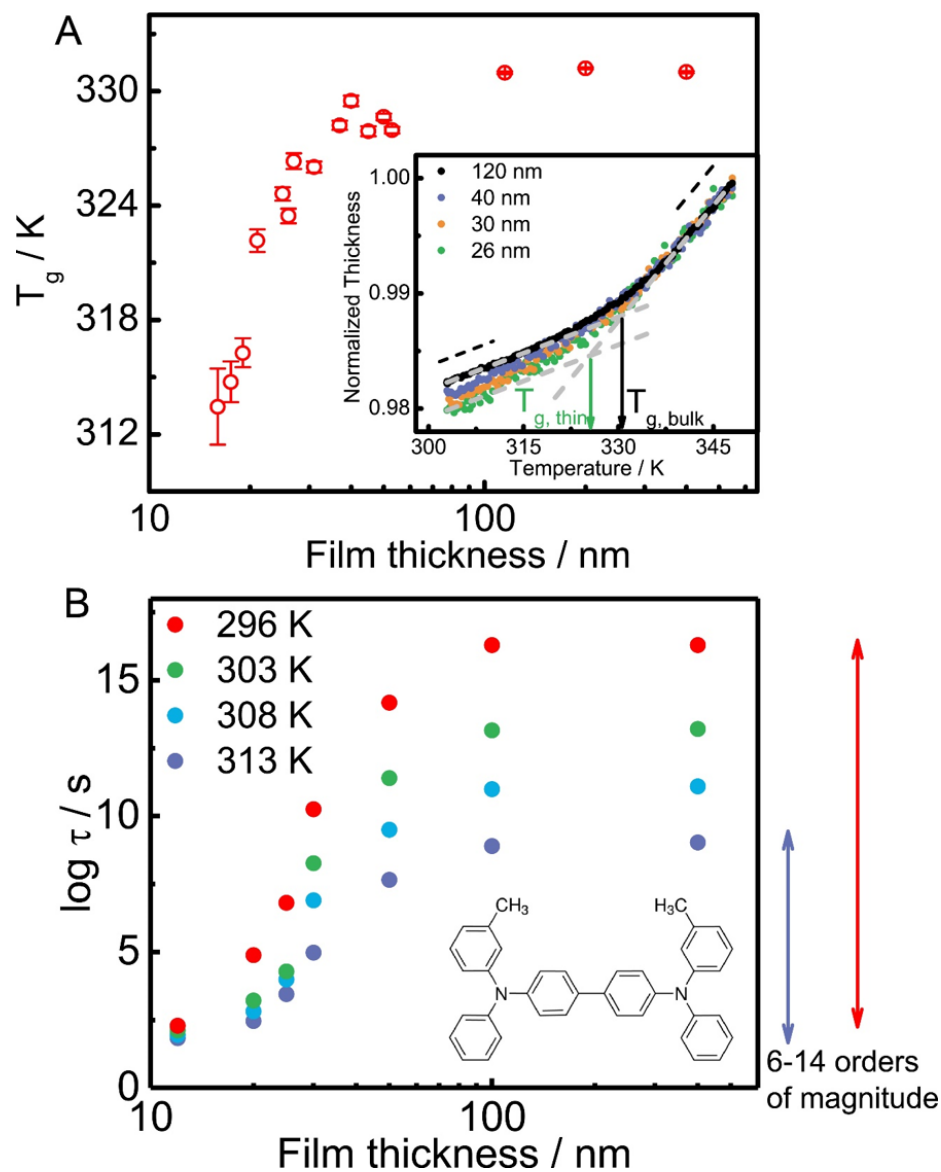


Figure 4.1: A: Glass transition temperatures, T_g , versus film thickness for TPD films supported on Si substrates measured using ellipsometry at a cooling rate of 10 K/min. Inset: Representative normalized thickness versus temperature plots for various film thicknesses. The black dashed lines show the slopes for thermal expansion coefficients of a bulk film in the super-cooled liquid and glassy regimes. The black and green arrows show the values of T_g for the 120 nm and 26 nm films respectively. B: Estimated average relaxation times at four temperatures versus film thickness, data taken from Ref[161]. Inset shows the molecular structure of TPD.

spin-coating and the response of the surface to the perturbation induced by TMV was monitored using non-contact AFM (Agilent 5420) equipped with an in-situ heating stage (Custom Thermoelectric TEC) to control the temperatures to within 2 K. Details of the setup can be found in our previous publications[161, 162]. Briefly, once a virus is placed on a glassy film surface, due to the surface energy differences, molecules on the free surface would flow towards TMV and form a meniscus around it that grows with time. Given the large aspect ratio of the virus (~ 18), the probe can be simply viewed as a semi-infinite 1D nanorod. The reduced dimension of the probe simplifies the flow towards the center of the TMV as semi-two dimensional flow, that is self-similar with time. We note that the technique only works on glassy surfaces, where the embedding due to viscous flow is much slower than the time to form self-similar profiles due to surface diffusion.

Figure 4.2 shows a typical example of the TMV-probe experiment. Figure 4.2A shows representative AFM images of the meniscus formation process on a 25 nm TPD film held isothermally at 296 K. The bright halos around TMV are indicative of the material accumulation resulting from the meniscus formation and growth with isothermal holding time. Figure 4.2B plots the temporal evolution of the line profiles across the center of the TMV probe, extracted from line profiles perpendicular to the center of the TMV. All measurements in this study were performed below the bulk T_g , as well as each film's corresponding T_g or the lower onset of the transition temperature T_- (details in SI Figure 4.8), to ensure that the profile evolution is due to surface diffusion as opposed to embedding due to viscous flow[162]. During the time and temperature windows of these measurements, no obvious embedding was observed. As such it is safe to assume that the surface flow is solely due to surface diffusion. Mullins[95] model describes the surface diffusion-mediated flow in two dimensions as:

$$\frac{\partial h(x, t)}{\partial t} = -\frac{D_s \gamma \Omega^2 \nu}{kT} \frac{\partial^4 h(x, t)}{\partial x^4} \quad (4.1)$$

with D_s representing surface diffusion coefficient, γ the surface tension, Ω the molecular volume, ν the number of atoms per unit area, and k the Boltzmann constant. Various earlier experiments and simulations have demonstrated the self-similar nature of the profiles that follow Equation 1[95, 162, 159, 127]. Figure 4.2C confirms the self-similarity of the surface diffusion-mediated diffusion process, where after scaling x with $t^{1/4}$ all profiles collapse onto a universal profile whose shape only depends on the pre-factor $\frac{D_s \gamma \Omega^2 \nu}{kT}$.

To better quantify the pre-factor, the half-widths of the profiles at a constant height are plotted versus isothermal holding time. The representative plot for films of various thicknesses at a temperature of 296 K are shown in Figure 4.2D. Measurements at other isothermal holding temperatures (303 K-313 K) are shown in Figure 4.9. The evolution of the profile widths for all films measured at 296 K as shown in Figure 4.2D, as well as data at all other temperatures in this study follow the 1/4 power law, with no indication of embedding, as measured by constant TMV height. These observations further confirm that the profiles are self-similar and that the evolution of the profiles in the time window of these experiments are solely due to surface diffusion[162]. By comparing the intercepts of ultrathin films with the intercept of the bulk 400 nm film, reported in our earlier publication[162], the absolute value of the pre-factor and thus the surface diffusion coefficients can be determined.

The good overlap of all the data on various film thicknesses in Figure 4.2D indicates that at 296 K the surface diffusion does not vary significantly with film thickness down to 12 nm. Similar effect is observed at other measuring temperatures (Figure 4.9). Figure 4.3 plots the measured surface diffusion coefficients versus film thickness at four isothermal temperatures. Indeed, the value of D_s remains constant within the experimental error for films of various thicknesses at four measuring temperatures. This is despite the fact that the films' average relaxation dynamics are enhanced by 6 to 14 orders of magnitude as the film thickness is decreased in this temperature range as shown in Figure 4.1B.

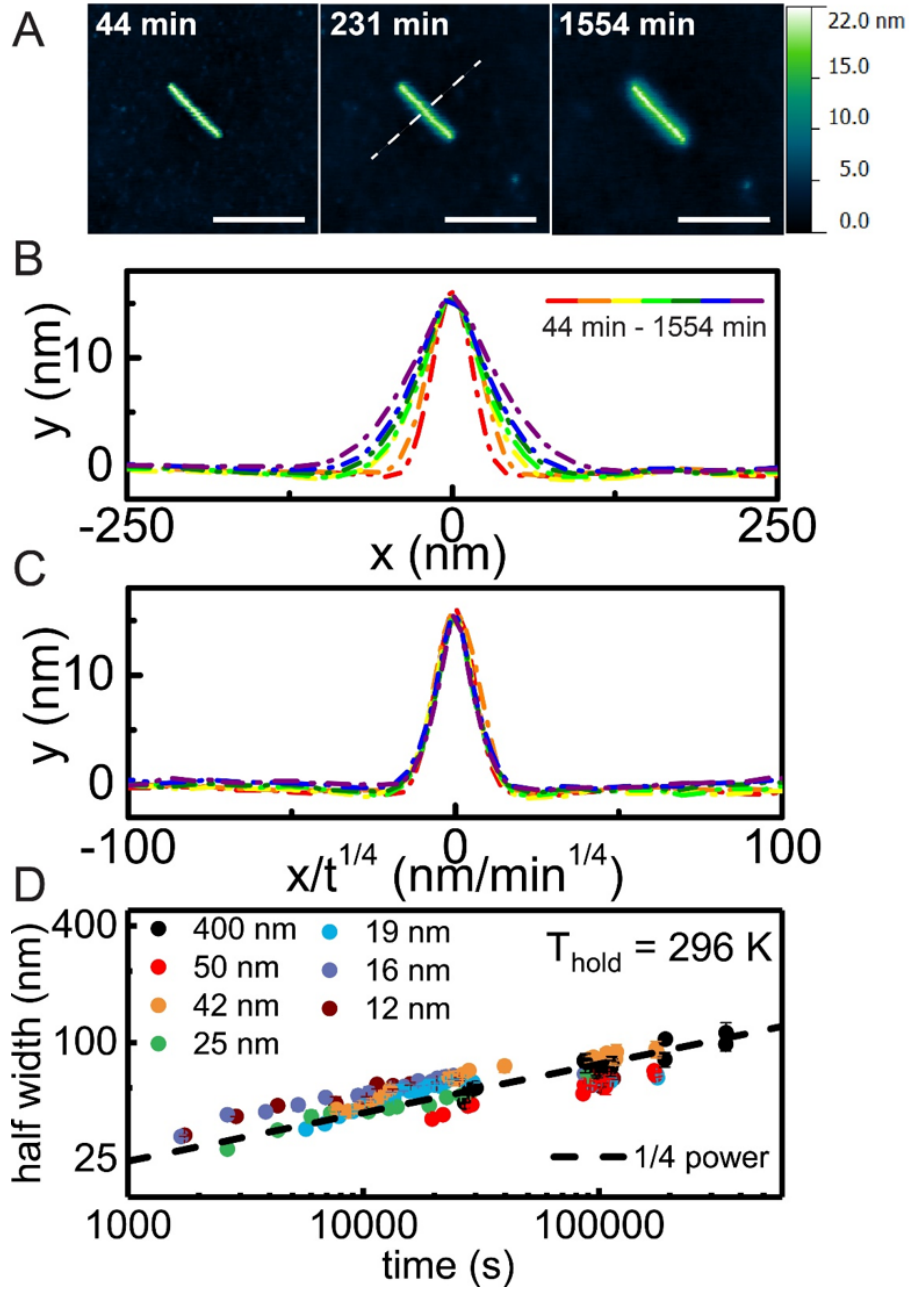


Figure 4.2: A: Typical AFM images of the meniscus formation on the surface of a 25 nm TPD film upon introduction of TMV while held isothermally at 296 K. Scale bars are 400 nm. B: Temporal profile evolution of the meniscus along the lines normal to the long axis of the virus in AFM images as shown in A. Each profile plotted is the average of five line profiles near the center of the virus. C: Demonstration of self-similarity of the profiles shown as the collapse of all profiles after scaling x with $t^{1/4}$. D: Half profile width at a constant height from the bottom of the TMV ($y = 2$ nm) versus isothermal holding time for films of various thicknesses held at 296 K. The black dashed line indicates the 1/4 power law.

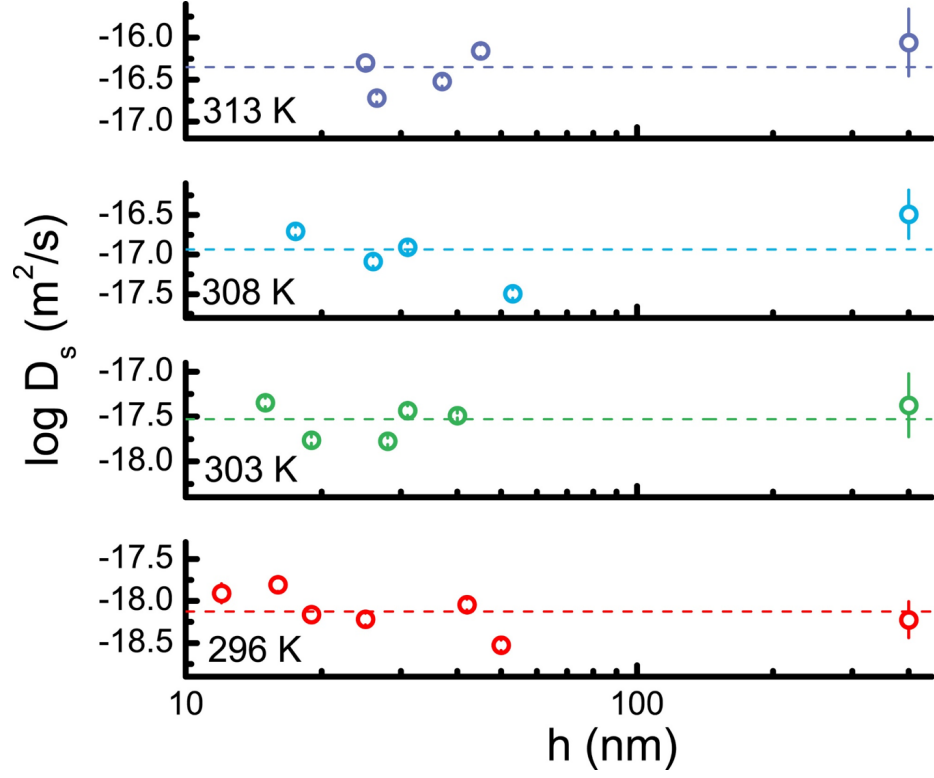


Figure 4.3: Surface diffusion coefficients measured at four isothermal temperatures plotted versus film thickness. Measurement temperatures from top to bottom: 313 K, 308 K, 303 K, and 296 K, respectively. The dashed line in each panel represents the average value of D_s at each temperature.

4.3.3. Decoupling of surface diffusion and relaxation times

The surface diffusion coefficients of films with various thicknesses are plotted in Figure 4.4A along with the average relaxation times τ_α of ultrathin films from Ref.[161] and bulk relaxation times from Ref.[161, 147]. This comparison is based on the empirical relation that at bulk T_g , the bulk diffusion coefficients of most organic glasses are about $D_{\text{bulk}} \approx 10^{-20} \text{ m}^2/\text{s}$ and the bulk relaxation times are about $\tau_\alpha \approx 100 \text{ s}$ (an alternative comparison method is shown in Figure 4.10). It is evident from Figure 4.4A that regardless of the film thickness, the apparent activation barrier for surface diffusion remains constant in the range of temperatures and film thicknesses studied here, and is measured to be $169.1 \pm 15.3 \text{ KJ/mol}$ for films ranging in thickness from 12 nm to 400 nm. Surface diffusion is enhanced at all temperatures by the same orders of magnitude compared to the bulk for films of all thicknesses, despite the fact that the average film relaxation times and the effective activation barriers for relaxation both decrease significantly with decreasing film thickness.

When the film thickness is reduced to 12 nm, the effective activation energy for relaxation decreases from 679.7 KJ/mol at 50 nm to 58.5 KJ/mol, a value smaller than that of the activation energy for the surface diffusion (plot of activation energies vs. film thickness shown in Figure 4.11 of SI). At this film thickness, the time scales of the average film relaxation dynamics are so fast that, as shown in Figure 4.4B, holes nucleate and grow in the film at a time scale that is required to measure the growth of the meniscus around the TMV virus. However, despite lower activation energy for rearrangement, and significantly low viscosity in this film, surface diffusion coefficient remain invariant and the same as the bulk value.

The complete independence of D_s from τ_α , while τ_α is **enhanced** by 6 to 14 orders of magnitude via decreasing film thickness, is consistent with previous observations where D_s was also found to be independent of τ_α , when τ_α was **suppressed** by 13 to 20 orders of magnitude via physical aging or stable glass formation[159]. Overall, we have varied the average bulk relaxation time τ_α over as large as 34 orders of magnitude either by

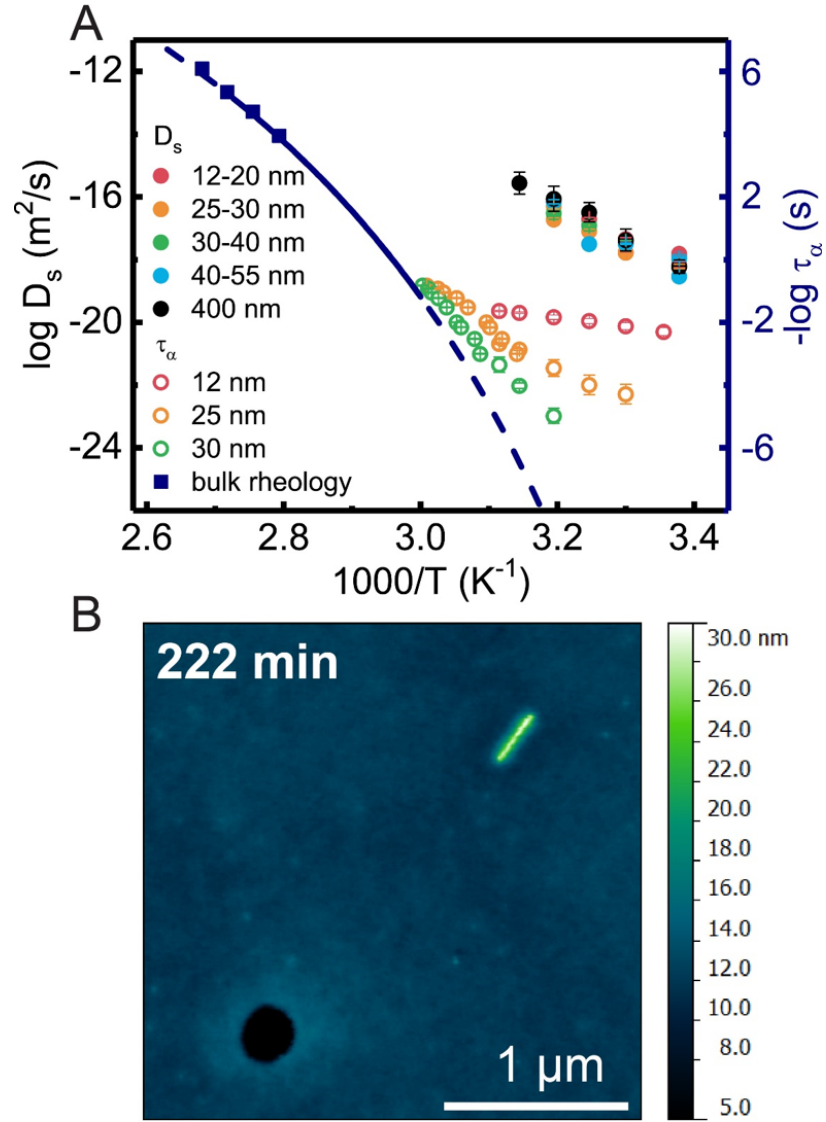


Figure 4.4: A: Surface diffusion coefficients measured on TPD films with thicknesses ranging from 12 nm to 400 nm (colored solid circles) are plotted along with average bulk relaxation times, τ_α , measured by bulk viscosity (navy squares)[161] and dielectric relaxation measurements (solid navy line)[147] as function of $1/T$. The average relaxation times in ultrathin films of 12 nm - 30 nm from Ref.[161] are also plotted for comparison (colored open circles). B: An AFM image of TMV on a 12 nm film after 222 minutes of isothermal hold at 296 K. The overall dynamics in these films are fast, such that the nucleation and growth of holes due to viscous flow occur at the same time scale as the meniscus formation due to surface diffusion-controlled flow. No embedding of the virus is observed in the time scale of these experiments and the meniscus formation follows the self-similar flow.

enhancing the dynamics upon confinement or by suppressing the dynamics upon vapor deposition/aging. Over this huge window of variations in average relaxation dynamics, no change of the fast surface diffusion D_s is observed.

The surprising aspect of the data presented in this study, compared to our previous study on aged and ultrastable glasses, is that the decoupling of surface diffusion and relaxation dynamics in ultrathin films is observed despite the fact that as the film thickness is decreased, the average relaxation times of ultrathin films becomes comparable to the fast surface diffusion (to within 1-2 orders of magnitude). As such, wide range of dynamical differences between the glass dynamics and its surface dynamics cannot be the reason behind the decoupling of the dynamics. It is also notable that as shown in Figure 4.4 and Figure 4.11, the activation energy for rearrangement (or fragility) of ultrathin films ($h < 20$ nm) decreases below that of the surface diffusion of the film of the same thickness. The observation that the activation barrier for surface diffusion does not correlate with the activation barrier for rearrangement in the thinnest film is another evidence of the decoupling of surface diffusion from bulk relaxation dynamics, suggesting that the surface diffusion process is possibly a distinct process and is uncorrelated to the viscosity or relaxation dynamics within the film or at the film surface. Direct measurements of free surface relaxation dynamics become important to directly verify this hypothesis. This observation, however, does not necessarily dispute the picture that enhanced dynamics at the free surface and its propagation into the film is the reason behind the overall enhanced film dynamics. It is instead an indication that surface diffusion alone, measured at temperatures below T_g where the system is out of equilibrium, is not a complete reporter of free surface dynamics and other experiments may be required.

Our observation of the decoupling of D_s from τ_α is also consistent with grating decay measurements on various molecular glasses where the surface diffusion varies strongly from molecule to molecule while the bulk diffusion or relaxation dynamics show little difference between those molecules[163, 157, 125]. In another extreme, polymer surfaces have been

shown to have enhanced segmental relaxation dynamics[47, 140, 104, 21], but their long chain can suppress their free surface diffusion[157], potentially due to the fact that part of the chain (or molecule in large molecular glass systems) at the free surface are anchored in layers underneath with significantly slower dynamics.

The decoupling of D_s and τ_α could be rationalized in two possible ways. One possibility is that D_s is not a direct measure of relaxation dynamics of the free surface and is instead a property that is only due to the potential energy that a molecule with a particular size located at the free surface feels, which is provided by the out-of-equilibrium molecules underneath. This is consistent with the fact that D_s is only measured when the rest of the system is either out of equilibrium or has dynamics that are slower than the time scale of measurements of D_s [157, 125, 23]. Alternatively, it is possible that D_s is correlated with the surface relaxation time τ_{surface} , while τ_{surface} itself for the layer immediately close to the free surface is insensitive to changes in the bulk. In this case, τ_{surface} can be estimated to be $\tau_{\text{surface}} = d^2/(6D_s)$, where d is the molecular size[91, 93]. The predicted surface relaxation times estimated from D_s based on this model are shown in Figure 4.10. While these values are larger than the average dynamics for the 12 nm film, as one would expect, the activation energy at the free surface is estimated to be larger than that of the 12 nm film, which is not expected, as the motion at the free surface is always expected to have lower activation energy than the average film dynamics. As such, the only way to rationalize the data in Figure 4.4, Figure 4.10 and Figure 4.11 is to assume that D_s and τ_{surface} are completely decoupled and measure two distinct properties. For example, it is possible that D_s primarily samples in-plane motions, while τ_{surface} measures an average between in-plan and out-of-plane relaxations, with out-of-plane relaxations having a lower energy barrier due to modified elasticity and anisotropy in interaction energies[91, 93]. Direct measurements of surface relaxation times are required to elucidate these differences and test these hypothesis.

Regardless of which hypothesis correctly describes the decoupling between the dynamics, surface diffusion measurements alone cannot provide a full picture of the extent of the

observed nanoconfinement effect in molecular glasses, or the length scale of enhanced dynamics from the free surfaces. Here we have assumed that only the top mono-layer of molecules participate in the surface diffusion process. However, the analysis used here does not provide the thickness of the mobile layer from the free surface. The invariance of fast surface diffusion suggests that the process can only involve at most a few layers of top surface molecules where they can always equilibrate themselves at very short time scales regardless of the bulk relaxation dynamics. However, if more than a mono-layer is assumed, the dynamics of these few layers must remain the same in films of all thicknesses, which is unlikely, given the large variations of the gradient estimated in our previous study[161]. As such, this process most likely only involves the top mono-layer of molecules.

4.4. Concluding Remarks

In summary, we report the first measure of fast surface diffusion on ultrathin molecular glass films that have thicknesses below 53 nm. Surface diffusion coefficients on films with a wide range of thicknesses were compared at four temperatures below bulk or thin film glass transition temperatures. We show that the surface diffusion coefficient remains constant within an order of magnitude at each measuring temperature. Furthermore, for films with thicknesses below 20 nm, the activation energy for rearrangement for the film becomes lower than that of the free surface diffusion. These results indicate that surface diffusion process is decoupled from relaxation dynamics at the free surface and that of the average film dynamics in ultrathin molecular glass systems.

4.5. Acknowledgments

This work was funded by NSF CAREER award, grant number DMR-1350044.

4.6. Experimental Details and Additional Discussions

Material and film preparation

N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) was purchased from Sigma-Aldrich and used without further purification. The bulk glass transition temperature T_g was determined by differential scanning calorimetry (DSC, Q2000 from TA Instruments) to be 330 K[161] at a cooling rate of 10 K/min. Ultra-thin TPD films with various thicknesses were spin-coated from different concentrations of TPD toluene solutions onto silicon substrates with 1~2 nm native oxide layer (Virginia Semiconductor). The thickness was confirmed with ellipsometry (M-2000 V J. A. Wollam) as detailed below. The as-spun thin films were carefully annealed at 343 K to remove any residual solvent or stress induced by spin-coating as detailed in the following paragraph.

Thin film annealing and ellipsometry measurements

Ultra-thin TPD films were carefully annealed with a Linkam heating stage (THMS 350 V) under ellipsometry to remove residual solvent or stress from the spin-coating, the thickness was monitored during annealing.

An isotropic Cauchy model was used to fit raw ellipsometry data as detailed in our previous publications[55, 82]. In this model, ellipsometry angles $\Psi(\lambda)$ and $\Delta(\lambda)$ were fit to a model consisting of a temperature-dependent substrate, a native oxide layer, and a Cauchy layer to model the transparent TPD film. The Cauchy model is described as $n(\lambda) = A + \frac{B}{\lambda^2}$, and $k(\lambda) = 0$, where n and k are the real and imaginary parts of the index of refraction. For all films studied here, A , B , and the film thickness h were free fit parameters. A spectroscopic range of 500 nm-1600 nm was used for modeling. Figure 4.5 shows the an example of the fit.

Figure 4.6 shows a typical annealing process for as spun-cast ultrathin TPD films. The as spun-cast ultrathin films were first heated at 10 K/min to 343 K ($T_g + 13$ K) and held

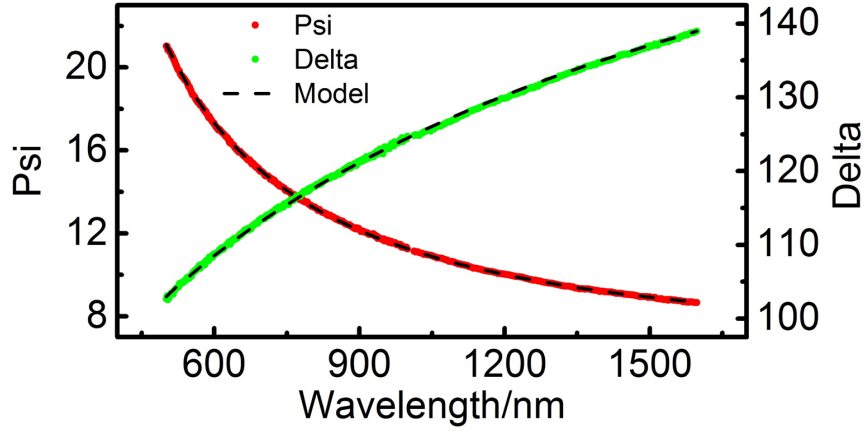


Figure 4.5: Example of Cauchy fit (black dashed line) to raw Ellipsometry data Ψ (red) and Δ (green). The film thickness was determined to be 26 nm.

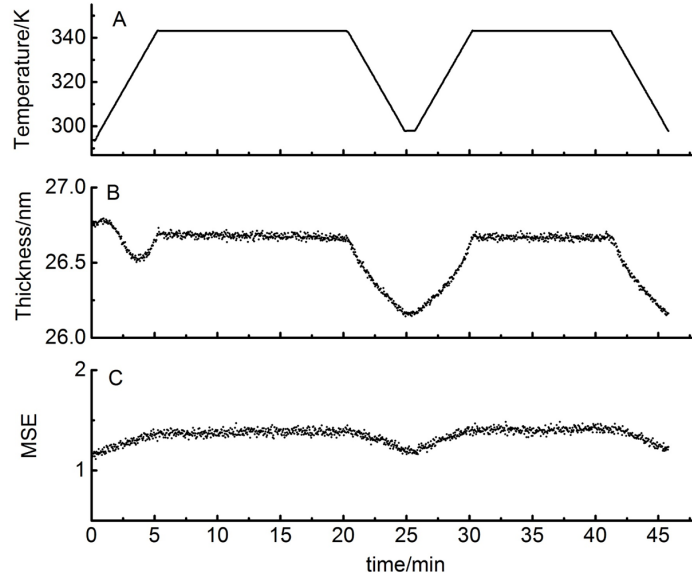


Figure 4.6: Example of the annealing details for spin-coated TPD film. Panel A: Temperature ramp cycle applied on the sample. Panel B: Thickness change of a 26 nm film during the temperature ramp. Panel C: Mean square error (MSE) of the fit during the temperature ramp.

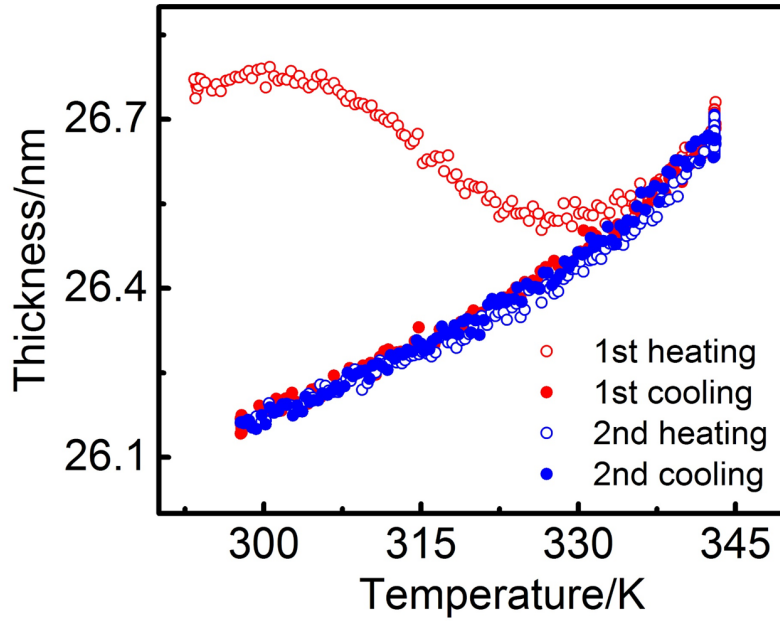


Figure 4.7: Thickness change as a function of temperature for the sample shown in Figure 4.6 for the two heating and cooling cycles applied.

isothermally until the thickness plateaued before cooling the film back to room temperature at 10 K/min. Another ramp of heating, holding and cooling was applied to make sure the film was fully annealed (free of solvent or stress induced from spin-coating process) and the two cooling curves overlapped. Panel A shows the typical temperature ramps applied for annealing on a 26 nm TPD film. Panel B shows the thickness change during the applied temperature ramps. During the first heating ramp, the drop in thickness is indicative of the removal of residual solvent or stress. Panel C shows the mean square error (MSE) of the Cauchy fit described above during the annealing, which indicates that the fit is reliable at all times during the temperature ramp cycles. To better show the thickness change during the annealing, in Figure 4.7, the thickness of the same film is plotted versus temperature. The thickness drop in first heating ramp is indicative of residual solvent evaporation. The good overlap between 1st and 2nd cooling cycles indicates that the film is fully annealed.

Glass transition temperatures of ultrathin TPD films

The average glass transition temperature and the transition width of each TPD film were obtained by fitting the normalized thickness versus temperature profile using the following equation.

$$h(T) = w\left(\frac{M - G}{2}\right)\ln\left(\cosh\left(\frac{T - T_g}{w}\right)\right) + (T - T_g)\left(\frac{M + G}{2}\right) + c \quad (4.2)$$

Here M and G are the thermal expansion coefficients of the super-cooled and glassy regimes, w is the width of the glass transition, and c is the thickness of the film at T_g . The values of the thermal expansion coefficients of the super-cooled liquid and glass regions were kept constant and equal to the corresponding bulk values for thick films measured to be $M = 6.6 \times 10^{-4}$ and $G = 2.1 \times 10^{-4}$. w , T_g , and c were free fit parameters.

The high and low onset of transition T_+ and T_- were obtained assuming $T_{\pm} = T_g \pm \frac{w}{2}$. Figure 4.8 shows the change of T_g , T_+ and T_- as a function of film thickness. While all three values decrease with film thickness, T_- decreases more rapidly than T_+ , resulting in the broadening of the transition as film thickness is reduced.

Surface evolution at other isothermal holding temperatures

Figure 4.9 shows the profile evolutions on various film thicknesses at three other isothermal holding temperatures studied.

Contact area of the TMV probe with film surface

Here we estimate the possible penetration depth of TMV probe onto the film surface upon contact with the surface as follows. Since all the measurements were performed below T_g , and no embedding was observed in the time scale of experiment, it is safe to assume that the response of the under-layer is elastic. If we consider the normal elastic response of a cylindrical object in line contact with an elastic surface, the quasistatic Hertz theory[141, 81]

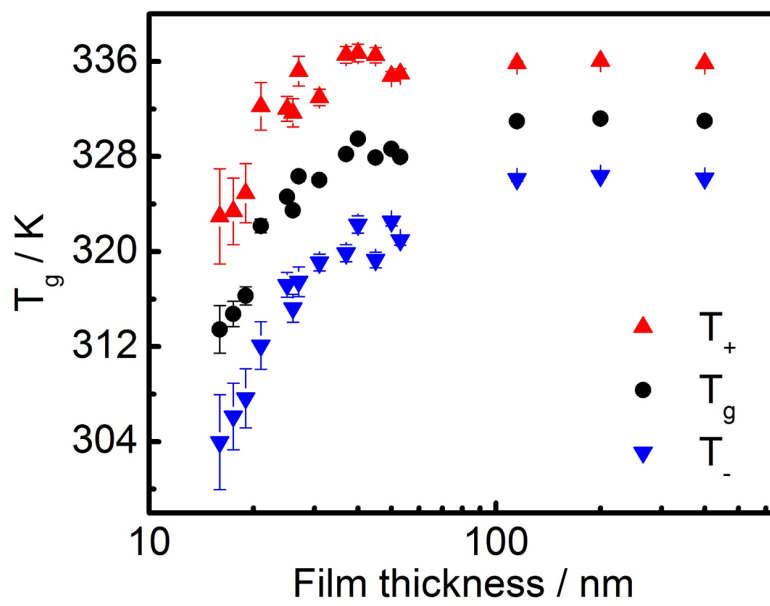


Figure 4.8: T_g , T_+ and T_- for various ultrathin TPD films. For each film thickness studied with TMV method, the isothermal holding temperatures used are chosen below its T_- value.

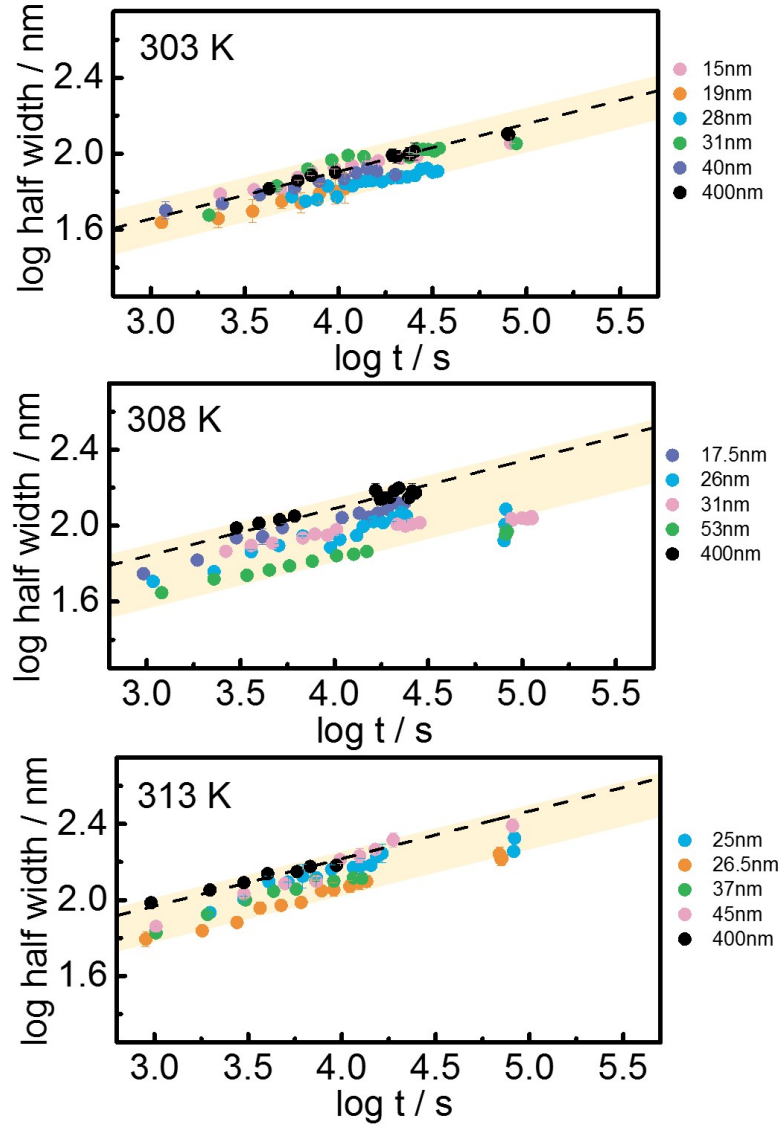


Figure 4.9: Log half width versus log time for the three other isothermal holding temperatures surveyed in this study for various thickness films.

provides the radius of the contact circle a in terms of the normal contact force F as: $a = \sqrt{4RF(1 - \nu^2)/\pi E}$, where E is the Young's modulus, ν is the Poisson's ratio, F is the normal load, R is radius of the cylinder. In this case, $R \simeq 9$ nm for the TMV probe, for Young's modulus and Poisson's ratio, we use the reported values from a similar organic molecule tris naphthyl benzene (TNB) to be $E = 3.9$ GPa and $\nu = 0.37$ [74], the deformation radius a necessary to cancel the surface tension force $F = 0.07$ N/m is at most equal to $a = 4.2$ Å, the deformation depth, h can be further estimated from $h = R - \sqrt{R^2 - a^2} = 0.1$ Å, which is a negligible effect. We note that based on the AFM height measurements, during the time window for surface diffusion measurements we didn't observe a height decrease of the TMV beyond the instrument error of our AFM, thus we don't consider the penetration of TMV as an issue for surface diffusion measurement.

Comparison between estimated surface and average film relaxation dynamics

In Figure 4.10, instead of using the shift factor to relate the diffusion coefficients and relaxation times as shown in Figure 4.4, we estimate the surface relaxation time τ_{surface} based on equation[91, 93]:

$$\tau_{\text{surface}} = d^2/(6D_s) \quad (4.3)$$

Here d is the diameter of the particle, which we estimate to be 1 nm. The estimated τ_{surface} based on this equation can be directly compared with thin film average relaxation times τ as reported in Reference [161] shown as open symbols in Figure 4.10.

Figure 4.11 shows a plot of the activation barrier for fast surface diffusion measured from both ultrathin and bulk films compared with the apparent activation barriers of relaxation in ultrathin films measured from effective viscosity and cooling-rate dependent T_g measurements[161].

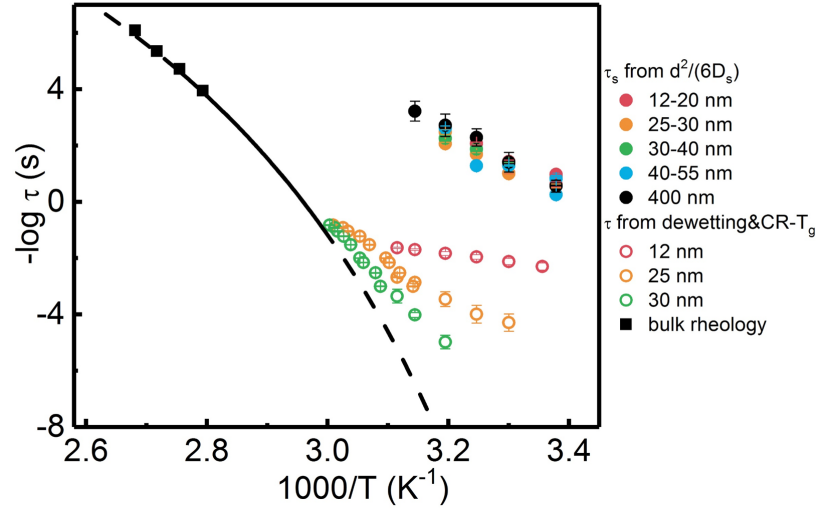


Figure 4.10: Comparison between estimated surface relaxation time from $\tau_{\text{surface}} = d^2/(6D_s)$ (solid circles) with the thin film average relaxation time from Ref[161] (open circles).

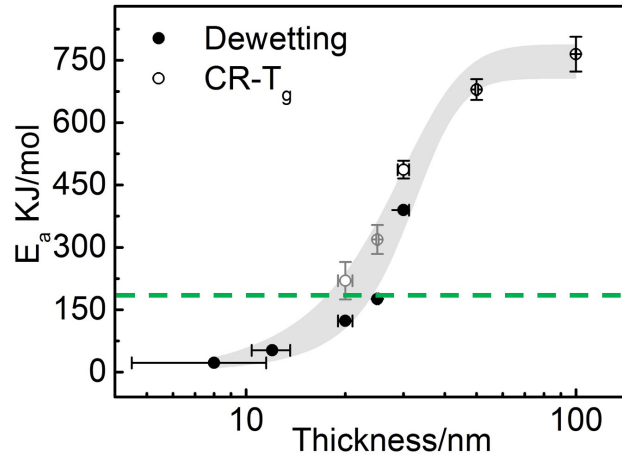


Figure 4.11: Comparison between activation barrier for surface diffusion (green dashed-line) with the activation barriers of ultrathin films of TPD [161].

CHAPTER 5 : Long-range Correlated Dynamics in Ultrathin Molecular Glasses

Reprinted with Permission from Yue Zhang, Ethan C. Glor, Mu Li, Tianyi Liu, Kareem Wahid, William Zhang, Robert A. Riggleman and Zahra Fakhraai Long-Range Correlated Dynamics in Ultra-thin Molecular Glass Films. *The Journal of Chemical Physics*, 145: 114502, 2016. Copyright 2016 American Institute of Physics.

5.1. Abstract

It has been previously shown that the free surface of molecular glasses have enhanced surface diffusion compared to the bulk. However, the degree by which the glass dynamics are affected by the free surface remains unexplored. Here, we measure enhanced dynamics in ultra-thin molecular glass films as a function of film thickness. We demonstrate that these films exhibit a sharp transition from glassy solid to liquid-like behavior when the thickness is reduced below 30 nm. This liquid-like behavior persists even at temperatures well below the glass transition temperature, T_g . The enhanced dynamics in these films can produce large scale morphological features during physical vapor deposition (PVD) and lead to a dewetting instability in films held at temperatures as low as $T_g - 35$ K. The effective viscosity of these films are measured by monitoring the dewetting kinetics. These measurements combined with cooling-rate dependent T_g measurements show that the apparent activation barrier for rearrangement decreases sharply in films thinner than 30 nm. This sharp transition in the dynamics suggests long-range correlated dynamics exists in these films such that the enhancement induced by the free surface can strongly affect the dynamics of the film over a length scale that is ten times larger than the size of the molecules.

5.2. Introduction

Nanometer-sized thin films of small organic molecules are widely used in applications ranging from organic photovoltaics[131] and light emitting diodes[146, 139], to protective coatings[85] and high resolution nano-imprint lithography[112]. It is advantageous to use

amorphous films because, compared to crystals, they do not have grain boundaries to hinder charge transport, generate cracks and defects, or disrupt the writing processes. Physical vapor deposition (PVD), the common method used to manufacture these films, is usually performed at substrate temperatures below T_g to produce films in the glassy state. However, if the properties at nanoscale deviate significantly from bulk properties, the resulting films can have reduced kinetic and thermal stability. Recent experiments suggest that diffusion at the free surface of organic glasses can be several orders of magnitude faster[163, 34], with weaker temperature dependence compared to bulk diffusion.

The free surface has been shown to result in enhanced and weakly temperature-dependent dynamics on the surface of polymeric glasses[47, 104] and significantly affect the properties of ultra-thin polymer films[76, 39, 42, 129, 55, 152, 104, 118, 115]. In polymeric systems, the molecular weight of the polymer[55], and the temperature range of the measurement[47, 104, 55] seem to also affect the observed properties, resulting in ambiguity in the relationship between enhanced dynamics at the free surface and properties of ultra-thin glass films. As such, these results can not be easily extrapolated to molecular and atomic glass systems. Direct measurements of dynamics in ultra-thin films of molecular glasses can help resolve some of the outstanding questions about enhanced dynamics in polymeric glass systems.

Thick PVD films have been shown to form exceptionally stable glasses upon deposition at temperatures just below T_g [137, 79, 48, 83]. While the detailed mechanisms of the formation of stable PVD glasses are still under investigation, most studies[137, 79, 25, 132] indicate that surface-mediated equilibration (SME) is critical to their production. As such, understanding the length scales of mobility gradients can help elucidate the mechanisms of stable glass formation. Such studies may also help predict the performance of thin films devices, which can in turn help design better thin glassy layers for applications.

A systematic study of the dynamics of ultra-thin organic glasses over a wide thickness and temperature can also help estimate length scales of mobility gradients which can be compared with fundamental length scales of glass transitions as proposed by various

theories[109, 91, 65, 16]. There are very few studies that measure the dynamics of ultra-thin films of organic glasses with thicknesses less than 100 nm[120, 20]. There is some evidence suggesting that the properties of these films may be strongly thickness-dependent[128]. Many other experimental efforts have focused on direct characterization of the dynamical heterogeneity and the length scales of the cooperative motions in glassy systems, most of which were performed near or above T_g . In these studies the sizes of the correlated domains were reported to be a few nanometers [12, 38, 144, 27, 121, 126, 64]. In addition to the direct characterizations of the cooperative rearranging regions, these length scales have also been probed by investigating the interfacial effects on glass properties under confinement. Measurements of glass transition temperature of organic liquids in small pores suggest modified dynamics in pores that are a few nanometers in diameter [70, 6], while measurements in thin polymer films widely vary depending on experimental techniques as well as the temperature ranges performed and the measure dynamical variations in thicknesses that range from a few nanometers to several tens nanometers[70, 4, 6, 42, 115, 118, 104, 106]. One challenge in understanding these results of polymer thin film studies in the context of correlation lengths of glass transition, is the effect of molecular weight on the experimental results[122, 55].

In this article, we use dewetting kinetics, and cooling-rate dependent T_g (CR- T_g) experiments to measure the dynamics of ultra-thin films of the molecular organic glass, N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD). While a direct measure of absolute viscosity of thin films can not be obtained due to potential mobility gradients induced by the free interface, by relating the characteristic dewetting times with CR- T_g measurements[55, 56], we are able to measure the “effective viscosity” of ultra-thin films as function of film thickness and temperature. In the absence of gradients in the dynamics, the effective viscosity equals the film viscosity. We show that ultra-thin films remain mobile far below bulk T_g , and the apparent activation energy for rearrangements decreases sharply for film thicknesses below 30 nm. The sharp decrease in the activation energy indicates that the dynamics in films thinner than 30 nm are strongly correlated and enhanced due to the enhanced surface dynamics.

5.3. Experimental Methods

5.3.1. Material and film preparation

Small organic molecule N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) was purchased from Sigma-Aldrich and used without further purification. Bulk DSC and rheology characterization can be found in Figure 5.7 for DSC and Figure 5.8 for ellipsometry characterization. All films in this study were prepared using physical vapor deposition (PVD) in a custom built high vacuum (HV) chamber with a base pressure of $\sim 10^{-7}$ torr. The details of the chamber are described elsewhere[83]. Silicon (one side polished, 100 plates from Virginia Semiconductor) with 1~2 nm native oxide layer was used as substrates for all films. For films used for dewetting studies the substrate temperature during deposition was held at bulk T_g to ensure that the film was at equilibrium during deposition and it did not form a stable glass. A deposition rate of 0.02 nm/s was used for all films. An in-situ quartz crystal micro-balance (QCM) was used to monitor film thickness during deposition. After deposition of a desired average film thickness, the substrate temperature was brought back to room temperature before the sample was removed from the chamber. The total time between the end of deposition to the first atomic force microscopy (AFM) measurement was typically 10-15 minutes. The thickness of films were also verified by measuring the depth of holes formed during dewetting using atomic force microscopy (Agilent 5420).

5.3.2. Imaging and characterization

For ultra-thin films ($h = 8 - 30$ nm), dewetting experiments were performed under isothermal conditions using a custom thermoelectric heating-stage, equipped with a thermoelectric module (Custom Thermoelectric TEC) and a thermistor (Oven industries TR91-170) to measure the value of the temperature, along with a DC power supply to control the temperature (Mastech HY3010E). The morphology of the films were simultaneously imaged using AFM. The temperature of the heating-stage was calibrated with melting-point standards (Sigma-Aldrich), the temperature fluctuations were within ± 2 K throughout

the experiments for the temperature range used. Non-contact AFM tips (Budget Sensors, Tap-300G, resonance frequency 300 kHz, tip radius of curvature <10 nm, force constant 40 N/m) were used for these measurements. To ensure the isothermal conditions, the stage was preheated and equilibrated. As-deposited films were transferred onto the preheated AFM stage immediately after removal from the chamber and were scanned continuously. Dewetting experiments for thick films ($h \geq 100$ nm) were performed using optical microscopy (OM) (Olympus BV51) with an in-situ Linkam heating stage (THMS 350 V). Image analysis softwares Gwyddion[99] and ImageJ[1] were used to calculate the surface coverage of each sample at various points of time for further analysis. For AFM images, a height threshold was set to evaluate the surface coverage, while for OM images, an intensity threshold was set for surface coverage evaluations. Optical microscopy measurements were performed with and without nitrogen purge as a control and no significant difference in the dewetting dynamics were observed. All the AFM measurements were performed at atmospheric conditions in an isolation box. No evidence of the atmosphere effect, moisture adsorption or any sign of oxidation of the material was observed at the temperature ranges applied. All measurements were performed above room temperature to avoid water condensation on the surface. Water condensation are typically observed in AFM imaging as increased noise, and no evidence of this was found during imaging above room temperature.

5.3.3. Cooling-rate dependent T_g measurement

Cooling-rate dependent T_g (CR- T_g) measurements were performed using spectroscopic ellipsometry (M-2000 V J. A. Woollam). Details of the technique can be found in our earlier publications[55, 82]. For CR- T_g measurements, films were deposited at a substrate temperature of $0.85T_g$ (279 K) to ensure that the substrate was fully covered with no holes. These as-deposited films were then heated above T_g to transform into ordinary glass for CR- T_g measurements as shown in Figure 5.15. The samples were then cooled at various cooling rates between 1 K/min-150 K/min and heated at 150 K/min to a set temperature of 348 K as shown in Figure 5.16. An isotropic Cauchy model was used to fit raw ellipsometry data

as detailed in SI and previous publications[55, 82]. AFM imaging was performed before and after measurements (Figure 5.17) to ensure that the films did not dewet during the process. All ellipsometry measurements were carried out under dry nitrogen purge conditions and at temperatures above room temperature to prevent water condensation on the surface.

5.4. Results

5.4.1. Initial morphology of as-deposited films

Thin films of TPD were prepared by PVD under high vacuum (HV) conditions, HV conditions ensure that the silicon substrates have uniform interfacial energies, so that dewetting is caused only by homogeneous nucleation and hole growth induced by thermal capillary and density fluctuations (Figure 5.9). Figure 5.1 shows the root mean square (RMS) roughness of as-deposited PVD films produced at a deposition rate of 0.02 nm/s, while the substrate temperature was held at bulk T_g . The insets show representative AFM images of the observed as-deposited morphologies at various film thicknesses. Measurements were typically performed within 15 minutes after deposition.

Figure 5.1 shows that during vapor deposition at T_g , ultra-thin films become rough and have morphology of the same height scale as the film thickness. The film morphologies at thicknesses below 12 nm resemble semi-continuous morphologies typically observed in spinodal dewetting experiments[150], with similar spectral distribution functions. A uniform layer starts forming at thicknesses above 20 nm, and the film gradually becomes smoother. For films thicker than 30 nm, the morphology flattens with both time and film thickness. This evolution in the morphology implies that during the deposition there is significant reconfiguration and motion of the molecules due to interfacial interactions, which allow for the formation of spinodal-like features. As the film thickness is increased, surface diffusion becomes more prominent and interfacial tension acts to smoothen the film.

Because these films exhibit a spinodal morphology only minutes after deposition and before a complete film is ever formed, the deposition rate and the size of the spinodal features can

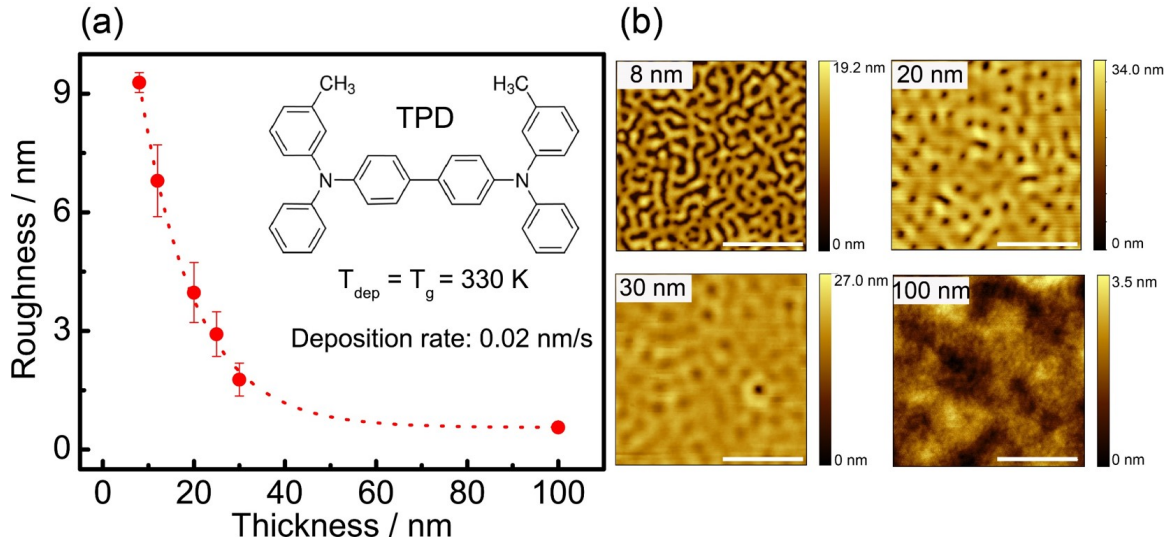


Figure 5.1: (a) The root-mean-square (RMS) roughness of as-deposited PVD films as a function of film thickness. All films were deposited at T_g with a deposition rate of 0.02 nm/s . The molecular structure of TPD is also shown as inset. (b) Representative AFM topography images of the as-deposited PVD films of various thicknesses, from which RMS values were calculated. The scale bar in each image is $2 \mu\text{m}$.

be used to provide an estimate of the average diffusion of the molecules during PVD. Based on the spectral distribution shown in Figure 5.10, the average lateral size of these features in an 8 nm film deposited at T_g is 350 nm . Given the deposition rate of 0.02 nm/s , it takes 600 seconds to deposit this film. Thus, the average diffusion coefficient of the 8 nm film is in the order of $3 \times 10^{-16} \text{ m}^2/\text{s}$. As a point of comparison, the bulk diffusion coefficient for most organic molecules at T_g is about $10^{-20} \text{ m}^2/\text{s}$ [158]. This simple estimation implies that the average dynamics in 8 nm films, measured at T_g , are several orders of magnitude faster than the bulk dynamics, even at a temperature where the bulk material is still at equilibrium. Similar morphological features have been observed in PVD films even when the substrate temperature during deposition was below T_g [49]. Since organic films used in applications are usually less than 100 nm thick, the morphologies caused by dewetting in thin films must be accounted for, as they may have a strong influence on the performance and stability of the device.

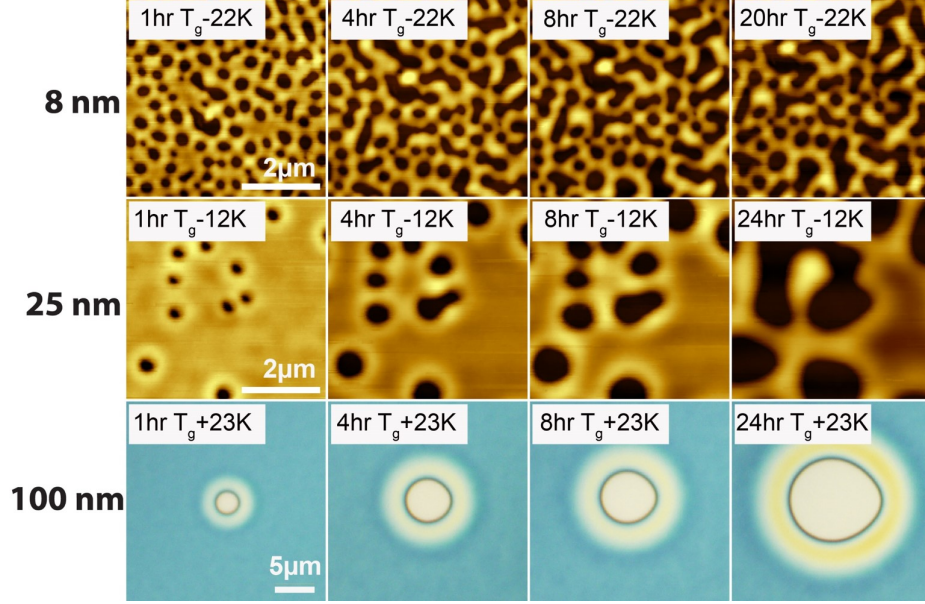


Figure 5.2: Time evolution of the morphology of TPD films during isothermal dewetting. All films were deposited at T_g with a deposition rate of 0.02 nm/s. Top row: 8 nm film held at T_g-22 K. Middle row: 25 nm film held at T_g-12 K; Bottom row: 100 nm film held at T_g+23 K. Dewetting of 8 nm and 25 nm films were monitored by AFM, while 100 nm films were monitored by optical microscopy.

5.4.2. Isothermal dewetting measurements

The rough structures of as-deposited ultra-thin films were used as templates for further isothermal dewetting experiments. AFM or optical microscopy (OM), showed that the film morphology continued to evolve with time (examples shown in Figure 5.2 and Figure 5.11). Dewetting of ultra-thin films ($h < 30$ nm) progressed both through the growth of existing holes and bi-continuous features, as well as the nucleation and growth of new holes due to thermal capillary fluctuations. Isothermal dewetting was observed at temperatures as low as $T_g - 32$ K, where the bulk viscosity is not measurable and any reasonable extrapolation of the values of viscosity would predict a dewetting time longer than the age of the universe for a bulk film. As the holes continued to grow, material from the holes accumulated in rims, resulting in an increase in the local film thickness outside the holes, which slowed down and eventually stopped the process. In contrast, 100 nm films only dewetted well above T_g ($T > T_g + 18$ K), where the bulk viscosity is orders of magnitude lower.

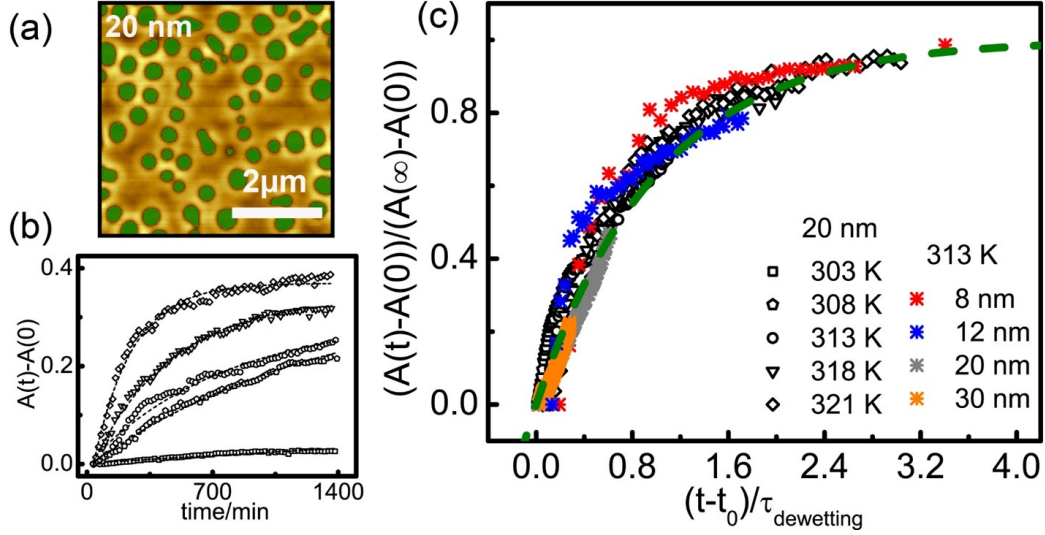


Figure 5.3: (a) An appropriate height threshold is set to obtain the total dewetted area, marked as green. (b) Dewetted area, $A(t)$, as a function of time for 20 nm films at five annealing temperatures. (c) Relative dewetted area as a function of reduced time $t/\tau_{\text{dewetting}}$. Open symbols are data from 20 nm films, shown in (b). Colored asterisks show dewetting of 8 nm, 12 nm, 20 nm, and 30 nm films at 313 K. Dashed green line is the universal fit function $y = 1 - \exp(-t/\tau)$. Each data point in (b) and (c) is obtained from a single AFM image.

Characteristic dewetting time

Due to the strong apparent film thickness-dependence of the dynamics, and non-uniform initial film morphologies, it is not possible to use models based on uniform viscosity and uniform film thickness[103] to model the kinetics of dewetting in these films. Furthermore, the preexisting morphology can make the dewetting process appear faster, as the growth of existing holes in thin films is typically faster than the spontaneous nucleation of new holes in thick films. Besides, the substrate interaction potentials in these models[150, 103] are poorly understood and slip condition at substrate interface is not explicitly included.

Despite these difficulties the effective viscosity can be indirectly measured by investigating the temperature dependence of the characteristic dewetting time, $\tau_{\text{dewetting}}$ [88]. This is because substrate interactions, surface tension, and the film's initial morphology are all weak functions of temperature, leaving the film's effective viscosity as the only temperature-

dependent parameter driving dewetting (more details in SI). As such, $\tau_{\text{dewetting}}$ should be proportional to the effective viscosity of the film. Since the viscosity in molecular glasses has been shown to follow the structural relaxation time (τ_{α}), $\tau_{\text{dewetting}}$ should also be proportional to τ_{α} [26, 59].

Samples prepared under the same condition have the same initial dewetted area, $A(0)$, which is dictated by the initial morphology of the as-deposited films. $\tau_{\text{dewetting}}$ was measured by tracking the time evolution of the total dewetted area, $A(t)$, indicated by green color in Figure 5.3(a). Figure 5.3(b) shows the change of $A(t)$ as a function of time for a 20 nm film at five different isothermal annealing temperatures. More examples are provided in Fig. S6. A single exponential function can be used to evaluate the characteristic time scale of dewetting [88, 101], $A(t) = A(\infty) + (A(0) - A(\infty))\exp(-t/\tau_{\text{dewetting}})$, where $\tau_{\text{dewetting}}$ is the time scale of dewetting. As seen in Figure 5.3(b), $A(t)$ increases with time in a manner that depends both on the thickness of the film and the annealing temperature. At high enough temperatures dewetting stops when the equilibrium contact angle has been reached. At lower annealing temperatures the dewetting process can take longer than the experimental time. Furthermore, dewetting may slow down due to the fact that as the film continues to dewet, it thickens and its viscosity may increase dramatically. To ensure the accuracy of the fit for films held at low temperatures, $A(\infty)$ was defined as the free fit value from the data at the highest temperature for the same thickness. It is observed that for films of all thicknesses, within the experimental errors, a single exponential function fits the evolution of the dewetted area, shown as the green dashed line in Figure 5.3(c). In Figure 5.3(c), the data of various thicknesses and annealing temperatures collapsed nicely onto the universal curve $y = 1 - \exp(-t/\tau)$ after scaling with $\tau_{\text{dewetting}}$, indicating the validity of exponential description. We note that variations in choosing $A(\infty)$, which can have a large error due to variability of AFM images does not significantly affect $\tau_{\text{dewetting}}$, or the final calculated activation energies, as these values change more strongly with temperature than small errors in the fit values. It is also important to note that to the best of our ability to fit the data, all data follows a single exponential decay, and a stretched exponential fit to the data, results

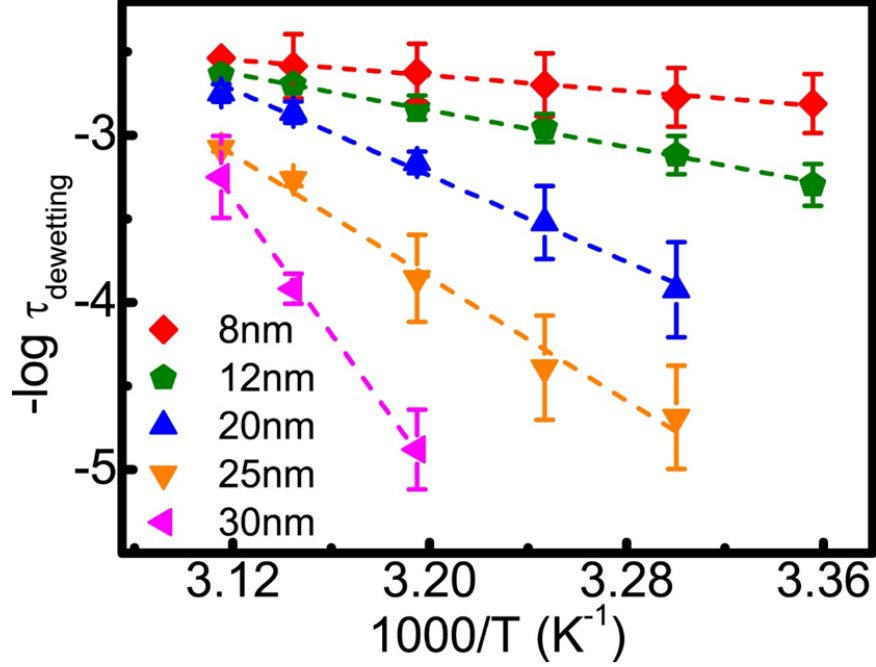


Figure 5.4: $-\log(\tau_{\text{dewetting}})$ vs. $1/T$ for various thicknesses. Dashed lines are Arrhenius fits.

in stretched exponents between 0.9 to 1, but does not improve fitting accuracy. More details can be found in SI and Figure 5.12.

Thickness-dependent activation barrier for dewetting

If dynamics of thin films were identical to those of bulk, one would expect the temperature dependence of $\tau_{\text{dewetting}}$ to be the same regardless of film thickness, even if absolute dewetting times depend on the film thickness due to different initial morphologies, and non-trivial thickness-dependence of the driving forces of dewetting. Figure 5.4 shows an Arrhenius plot of $-\log(\tau_{\text{dewetting}})$ versus inverse temperature, $1/T$. It is evident that in this temperature range, the slopes of the curves, which represent the apparent thermal activation barriers for rearrangement, E_a , have strong thickness dependence. For an 8 nm film $\tau_{\text{dewetting}}$, and therefore the effective viscosity, changes less than half a decade over the temperature range of 298 K - 321 K. $\tau_{\text{dewetting}}$ for 30 nm films show a much stronger temperature dependence, changing more than two decades over the same temperature range. It is important to note

that all of these temperatures are well below bulk T_g . The low apparent activation energy of ultra-thin films is consistent with previous studies of dynamics on polymeric thin films[152, 55, 56].

5.4.3. Cooling-rate dependent T_g measurement

To extend the range of available viscosities of bulk films to lower temperatures and to determine the vertical shift factors for thin film dewetting data, cooling-rate dependent T_g (CR- T_g) measurements were also performed using ellipsometry. For most bulk organic glasses when the system is cooled at 10 K/min, the supercooled liquid falls out of equilibrium when the average structural relaxation time of the system is equal to $\tau_\alpha \simeq 100$ s, or the viscosity reaches $\eta \simeq 10^{10}$ Pa.s. If the system is cooled more slowly, it falls out of equilibrium at a larger value of viscosity. As such cooling-rate CR is inversely proportional to both η and τ_α with measurements at 10 K/min used as a point of reference.

Figure 5.5(a) shows a typical graph of normalized thickness vs. temperature for a 100 nm (bulk) film for various cooling rates. T_g values for films of all thicknesses and at all cooling rates were evaluated as the intersection of two lines, fit in the temperature range of 303 K to 314 K for the glassy region and 339 K to 348 K for the super-cooled liquid region. To ensure accuracy in thin film data fitting, common values of the apparent expansion coefficient were used for the glassy and supercooled liquid regions, obtained from fits to the data for the thickest film (more details described in our earlier publications[55, 82]). These values were $\alpha_G = (2.10 \pm 0.02) \times 10^{-4} K^{-1}$ and $\alpha_{SC L} = (6.57 \pm 0.03) \times 10^{-4} K^{-1}$, respectively.

We note that for films with a thickness thinner than $h < 25$ nm, T_g assignments are subject to some error at low cooling rates that may result in overestimating the value of T_g . As shown in Figure 5.18 ultrathin films at low cooling rates show very broad transition, which has also been previously observed in polymeric thin films[55]. As such, the measurements need to be extended to lower temperatures to observe complete transition into glassy state. Unfortunately, in our current setup, we cannot monitor the full transition at lower temper-

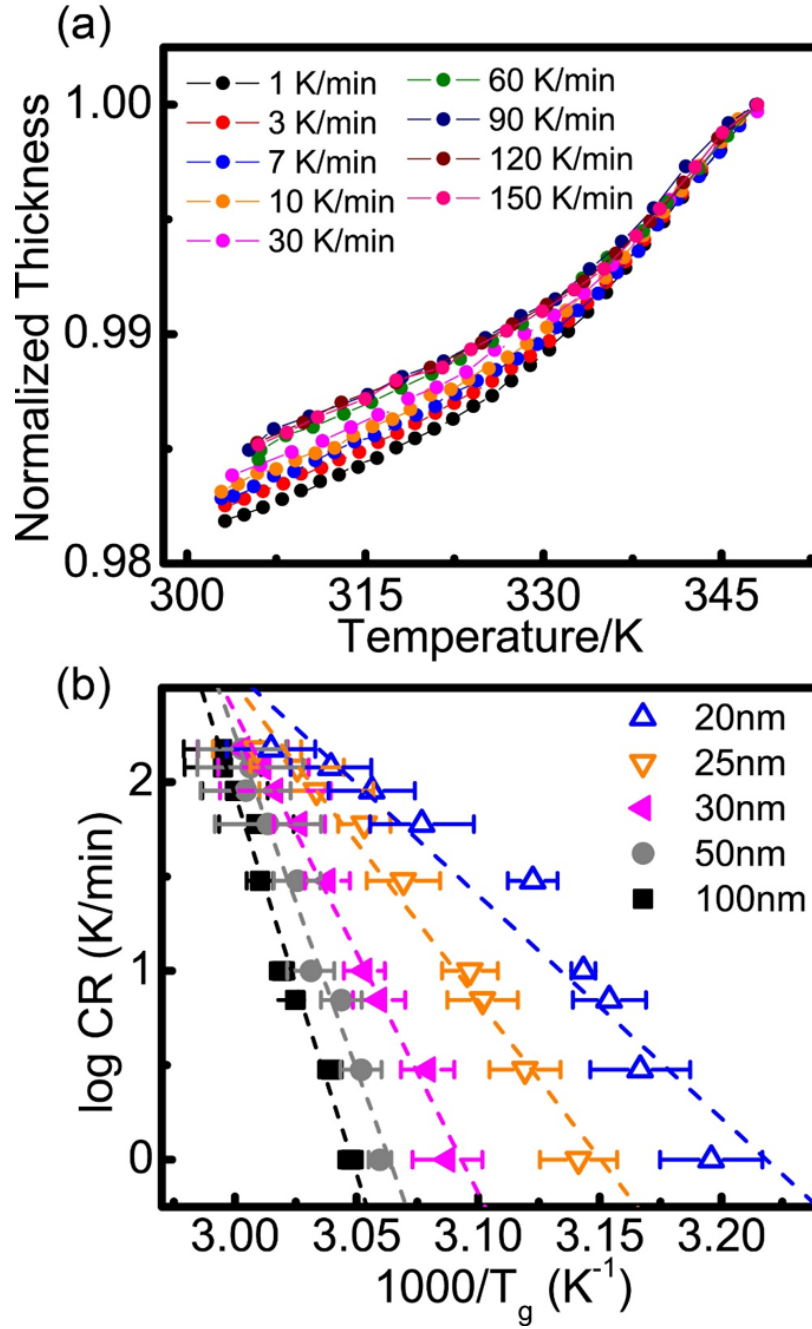


Figure 5.5: (a) Normalized film thickness as a function of temperature obtained upon cooling a 100 nm film at various cooling rates. Different T_g values can be assigned from thickness profiles with different cooling-rates. (b) Log (cooling rate) as a function of $1/T_g$ for films of various thicknesses. Open symbols for 20 nm and 25 nm T_g values indicate potential uncertainties due to onset of dewetting and broadening of T_g as discussed.

atures due to possible water adsorption, despite nitrogen purge used to dry the samples. Thus large experimental error in the values of T_g are expected at these cooling rates. However, the measured T_g can be considered as an upper bound to the real value of the average T_g in these films, with discrepancy increasing with decreasing cooling rates. As a result, the values of the apparent activation energy from CR- T_g (the slope of lines in Figure 5.5(b)) are also measured to be larger than the actual values and these measurements provide an upper bound for the value of activation energy. These data points with large uncertainties are indicated by open symbols in Figure 5.5(b) and affect activation energies for films with thicknesses less than 25 nm.

Once the T_g is evaluated at all cooling rates, the data can be plotted as Arrhenius plots of $\log(\text{cooling rate (CR)})$ vs. $1/T_g$ for various film thickness surveyed as shown in Figure 5.5(b). The CR- T_g for the bulk film 100 nm can be directly compared with rheology experiments by the assumption that at the temperature where the system falls out of equilibrium (T_g) at a cooling rate of 10 K/min, the relaxation time for most organic glasses are measured to be $\tau_\alpha = 100$ s. As shown in Figure 5.19, this corresponds to a viscosity of $\eta = 10^{10}$ Pa.s. for TPD, where the rheology data matches dielectric relaxation measurements.

5.5. Discussion

5.5.1. Evaluating the effective thin film viscosity

In order to relate $\tau_{\text{dewetting}}$ to viscosity, the vertical shift factors were obtained by comparing the data for bulk films (100 nm) with rheology measurements of bulk TPD as shown in Figure 5.6(a). CR- T_g measurements were used to extend the dynamical range of the bulk measurements (100 nm film) to temperatures close to bulk T_g . More details about the shift factors used can be found in Figures 5.19 5.20 5.21.

Figure 5.6(a) shows the combined data of dewetting and CR- T_g measurements, and provides a direct comparison between the bulk and the effective thin film viscosities. In the temperature range of these experiments, there is excellent agreement between the data

obtained for 100 nm films and the viscosity and structural relaxation time measurements of bulk TPD[147]. This strongly indicates that firstly, 100 nm films behave bulk-like and their effective viscosity matches that of bulk viscosity in the entire dynamical range of these measurements for both types of experiments, and secondly, other related parameters for the dewetting process, such as substrate interaction energy and surface tension, did not have strong temperature dependences.

As detailed above, the initial morphology of films of various thicknesses are different. As such, the shift factor used to match the 100 nm dewetting data to bulk viscosity is not applicable to other films. Instead, for films of 25-30 nm, the CR- T_g experiments were used to calculate the appropriate shift factors (Figure 5.21). It is important to note that CR- T_g could not be reliably used for ultra-thin films ($h \leq 20$ nm) due to early onset of dewetting. As such, the exact shift factors for these data sets are unknown and the data presented here for these films only reflect the temperature dependence of the effective viscosity and not their exact values. However, based on the simple analysis of diffusion presented above, the effective viscosity is at least about a factor of four faster than that of bulk at T_g , which is consistent with data presented in Figure 5.6(a).

Figure 5.6(a) provides a clear picture of the extent by which the dynamics are enhanced in ultra-thin films. While at bulk T_g the dynamics are enhanced by only two to four orders of magnitude, the difference between thin film and bulk dynamics continues to diverge as the temperature is decreased below T_g . For example, at a temperature of T_g-35 K, the bulk viscosity becomes unmeasurable, while the effective thin film viscosity only changes by less than two orders of magnitude from the value at T_g .

5.5.2. Length scale of interfacial effects

Figure 5.6b) shows the apparent activation energy, E_a (slope of log viscosity vs. $1/T$) as a function of film thickness as determined via both dewetting and CR- T_g experiments. We note that E_a may vary outside the range of temperatures presented here, for example closer

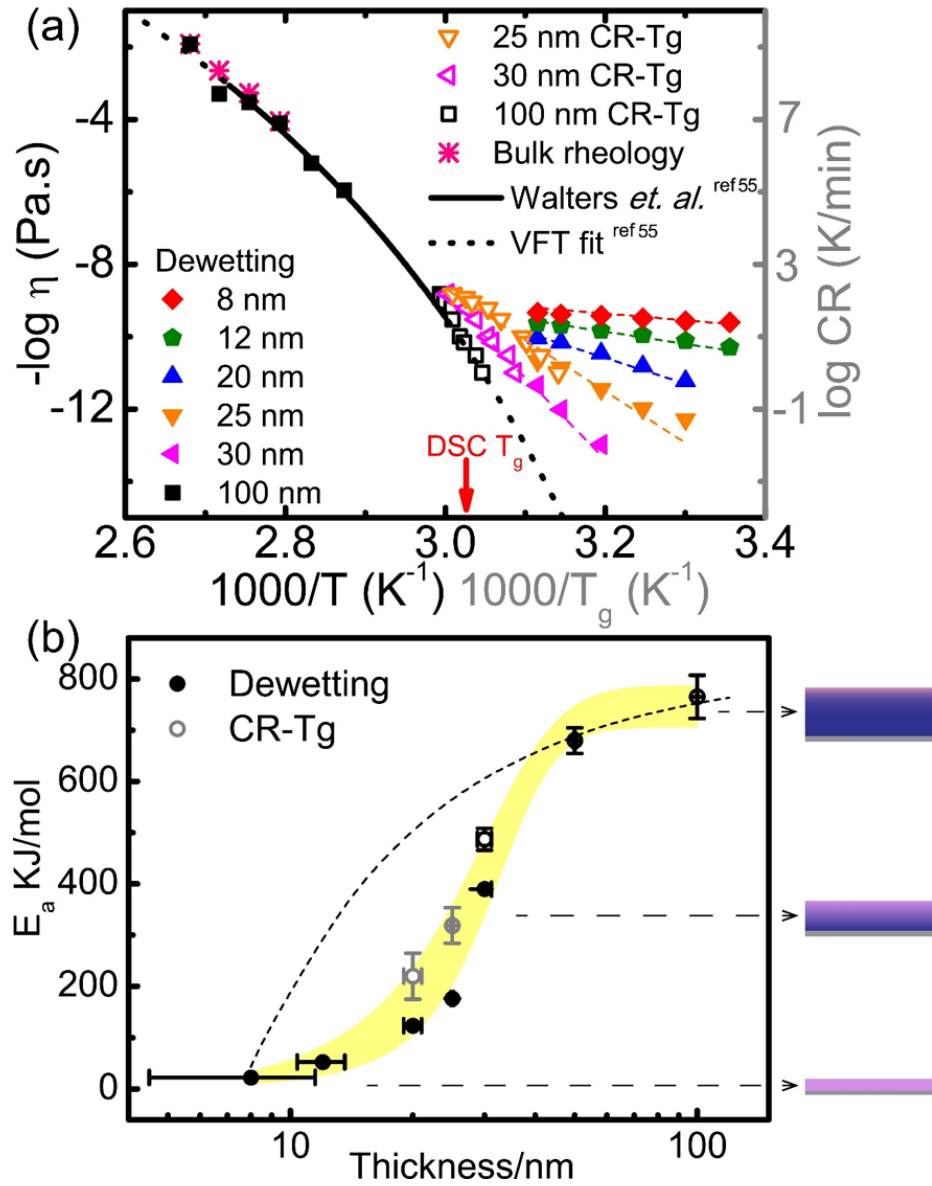


Figure 5.6: (a) Viscosity (left axis) vs. $1/T$ obtained by rheology (pink asterisk) compared with dewetting data, and CR- T_g (right axis). Solid line represents dielectric relaxation data by Walter *et al.*[147]. Dotted black line is VFT fit to bulk viscosity. (b) Apparent activation energy, E_a obtained from Arrhenius fits of Figure 5.4 (filled) and Figure 5.5(b) (open) as a function of film thickness. Shaded area is a guide to the eyes for potential values of activation energy as measured by various methods. The dashed black line is the activation energy prediction of a two-layer model with a mobile surface layer thickness of 8 nm for all films, meaning that there are surface and bulk dynamics are not correlated (details in SI and Figure 5.23.)

to or above T_g . As shown in Figure 5.6(b), in films with $h < 20$ nm, the E_a is much lower than that of the bulk and has a weak thickness-dependence. The low activation barrier for dewetting confirms that the rough morphologies observed in ultra-thin PVD films are due to fast dewetting during the deposition. E_a increases sharply in films with thicknesses between $20 \text{ nm} < h < 30 \text{ nm}$, and becomes very similar to bulk at $h > 40 \text{ nm}$. In this regime, the dynamics of the film are bulk-like during PVD, and surface diffusion acts to smoothen the film. Interestingly, in ultra-thin films, once the local film thickness around the rims reaches 40 nm the dewetting process also slows down significantly and appears to stop in films with thicknesses ranging between 8 nm to 25 nm as shown in Figure 5.14.

This remarkably sharp transition in the dynamics suggests that the gradient of dynamics induced by the interfacial effects is not the same in films of different thicknesses, as schematically shown on right of Figure 5.6(b). In ultra-thin films, the dynamics are enhanced in the entire film, showing little thickness dependence, while in films with thicknesses of 40 nm or more, the dynamics in the entire film is bulk-like except for perhaps a few liquid-like mono-layers near the free surface. If the interfacial effects propagated over the same length scale and with the same strength in films of all thicknesses, then the overall dynamics can be simply described by a weighted average function of faster interfacial dynamics due to the existence of a mobile surface layer with a constant thickness and slower bulk dynamics. One would then expect a gradual decrease in E_a with decreasing film thickness. This behavior is shown in Figure 5.6(b) as black dashed-line by assuming a mobile layer with a thickness of 8 nm, with identical dynamics as that of the 8 nm film measured in this study. Details of this prediction can be found in SI and Figures 5.23 and 5.22. While assuming a different thickness for the mobile layer, or different dynamics may change the onset of the changes in E_a or its final value, the shape of the curve would qualitatively remain the same, showing a gradually decreasing E_a with film thickness. Instead, in experiments a sharp transition is observed around 30 nm (Figure 5.6(b)) suggesting strongly correlated dynamics in thin films that result in enhancement in the overall dynamics of the film, not just the top 8 nm.

It is important to note that the temperature dependence of diffusion coefficients measured on the surface of bulk films[163, 34, 125] is stronger than the temperature dependence for dewetting measured in ultra-thin films in this study, further confirming that the dynamics at the surface of a bulk film are also slower than those measured in ultra-thin films. These observations suggest that the dynamics of the glassy material are correlated over a length scale of $\sim 10\text{-}30$ nm and the dynamics of thin films are influenced both by the interfacial dynamics and the glassy dynamics in the layers closer to the center of the film. As such, surface diffusion measurements on the surface of bulk-like films alone are inadequate in predicting the activation barrier for the dynamics in ultra-thin films and the length scale of the interfacial effects. Direct measurements of properties as a function of film thickness are required for determining the correlation length for the dynamics.

While few studies probe dynamics of ultra-thin molecular glass films, observations in polymeric glasses[56] show a similar non-linear transition in E_a as a function of film thickness, with the midpoint of transition in the 20-30 nm film thickness region. Earlier studies by Ellison and Torkelson also suggest correlated dynamics in the top and bottom layers of a polymeric film as the film thickness is reduced below 20 nm[42]. However, the transition appears to be much sharper in organic thin films with much lower activation barriers in ultra-thin film regime. This may imply that chain effects are also important in facilitating the dynamics in polymeric thin films. Regardless, the general similar trend and length scale of enhanced dynamics in both small organic molecular and polymeric glasses suggest that long range facilitation of the dynamics may be a characteristic feature of glassy systems. Future studies on more glassy systems are needed to confirm whether these observations are ubiquitous in organic glassy systems.

Our results are difficult to rationalize with existing theories and simulations of the glass transition. Models based on a constant length scale of interfacial effects[134] are unlikely to capture the strong, almost sigmoidal transition in apparent activation barriers observed here. Instead, models based on long range elastic response[91, 93], or which use growing

cooperative length scales[65, 16] may be able to predict such strong correlated dynamics.

Simulations have observed a growing mobile surface layer that correlates strongly with the size of cooperative rearrangements[130, 62], but these simulations have not observed the sharp transition in apparent activation energy for films thicknesses of 20-30 nm. The sharp transition in dynamical behavior with increasing film thickness is reminiscent of the non-equilibrium phase transitions to *immobile* phases that have been observed in simulations that were biased to sample low-mobility trajectories [22, 18, 54]. However, it is not obvious at all how to map film thickness, enhances the mobility of the glass, to the biasing potential or pinning procedures used to observe the non-equilibrium transitions.

The long length scales that we observe would be difficult to rationalize with the typical sizes of dynamic heterogeneity that have been measured either experimentally or computationally, which are commonly cited to be on the order of 2-3 nm near T_g . Certainly it is known that surface effects can propagate over large length scales in polymer glasses, where the mobile surface layer associated with T_g confinement effects has been found to approach 10 nm, so it is possible that the same mechanism could be responsible in these molecular glass films. Simulations of polymer glasses have connected the size of the mobile surface layer to the size of cooperatively rearranging regions in the glass[130, 62], so it is possible that an Adam-Gibbs picture could explain the large length scale component of our results. An alternative possibility is the theory of Mirrigian and Schweizer, which captures long-range elastic effects on monomer rearrangements and predicts changes in properties over long length scales away from free surfaces[91, 93].

5.6. Concluding Remarks

In summary, we have presented that the temperature dependence of the effective viscosity, and thus the structural relaxation time, of thick and ultra-thin films of molecular glasses can be measured via a combination of isothermal dewetting and CR- T_g measurements. We have demonstrated that the rough initial morphology of vapor-deposited thin films are

closely related to the enhanced dynamics in ultra-thin films. Films as thick as 30 nm dewet spontaneously well below bulk T_g , indicative of greatly enhanced dynamics in these films. An examination of the thickness dependence of the apparent activation barrier in these films reveals a sharp, sigmoidal transition in the dynamics as the thickness varies between 20 to 40 nm indicating a strong correlation between the dynamics of the free surface and the bulk of the film. This implies an interplay between the facilitation of the dynamics by the interface and the bulk glass, with a considerably large length scale of about 30 nm.

5.7. Acknowledgments

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5.8. Supplementary Material

Material characterization

The glass transition temperature of bulk TPD was determined using ellipsometry (M-2000 V J. A. Woollam) and DSC (Q2000 DSC, TA Instruments) to be 328 ± 1 K, and 330 ± 1 K at cooling rates of 1 K/min, and 10 K/min, respectively (Figure 5.7). $T_g = 330$ K from DSC is used as the reference temperature throughout this manuscript. Measurements of viscosity were performed on bulk TPD between 358 K and 373 K using rheometer (Bohlin CVO, Malvern Instruments). The data is shown in Figure 5.8.

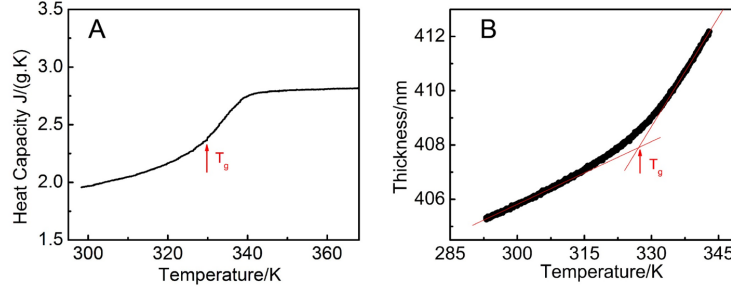


Figure 5.7: A) Heat capacity vs. temperature as measured by DSC on bulk TPD. T_g is determined upon cooling at 10 K/min and is determined to be 330 ± 1 K. B) Thickness as a function of temperature of a 400 nm film of TPD produced by PVD with a deposition temperature of 298 K and rate of 0.2 nm/s, the sample was held at 348 K in vacuum oven overnight to transform into ordinary glass. The heating and cooling rates were 1 K/min. T_g was determined to be 328 ± 1 K. Here, we refer to 330 K as bulk value of T_g for TPD.

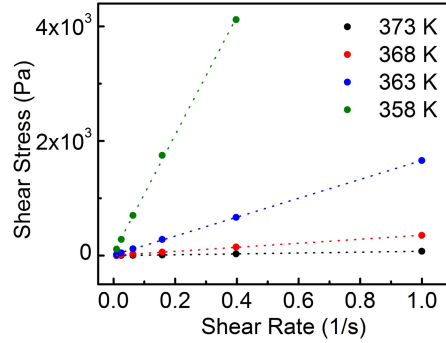


Figure 5.8: Shear stress versus shear rate applied to bulk TPD at various temperatures ranging from 358 K to 373 K. Bulk viscosity was evaluated based on the slope of these curves.

Influence of substrate cleanness and sample preparation on dewetting dynamics

As shown in Figure 5.9, the sample preparation and the cleanness of the substrate can strongly affect the kinetics of dewetting. The top panel in Figure 5.9 shows the overnight morphology evolution of a spin-coated TPD film ($h \sim 7$ nm thick) spontaneously dewetting at 298 K. The fractal growth of initial nucleated holes may result from the heterogeneity of the substrate in air and/or residual stress or density fluctuations induced by spin-coating. Similar patterns are observed when the substrate is cleaned using various methods. For thicker films heterogeneous nucleation results in holes that grow with different rates. In comparison, the bottom panel shows an example of a film prepared under high vacuum (HV) conditions as described above, where the substrate is free of physical adsorbed water and has uniform surface energy. In this film homogeneous hole nucleation is observed and holes grow symmetrically without bifurcation into fractal patterns.

As-deposited morphology of 8 nm PVD films

The as-deposited morphology of an 8 nm PVD film is shown in Figure 5.10A along with the Fast Fourier Transform (FFT) pattern of the morphology in Figure 5.10B. The ring pattern in the FFT image indicates that there is well-defined preferred length scale within this morphology, representative of a spinodal pattern. The average radial distribution of the FFT pattern is also shown in Figure 5.10C, with a peak indicating a characteristic wavelength that corresponds to 350 nm lateral features.

Additional AFM images

Figure 5.11 shows additional AFM images of the isothermal dewetting of various thickness films below bulk T_g .

Thin film equation

During the dewetting process, the evolution of local height profile within a film is mainly determined by three terms as shown in Equation 5.1[103],

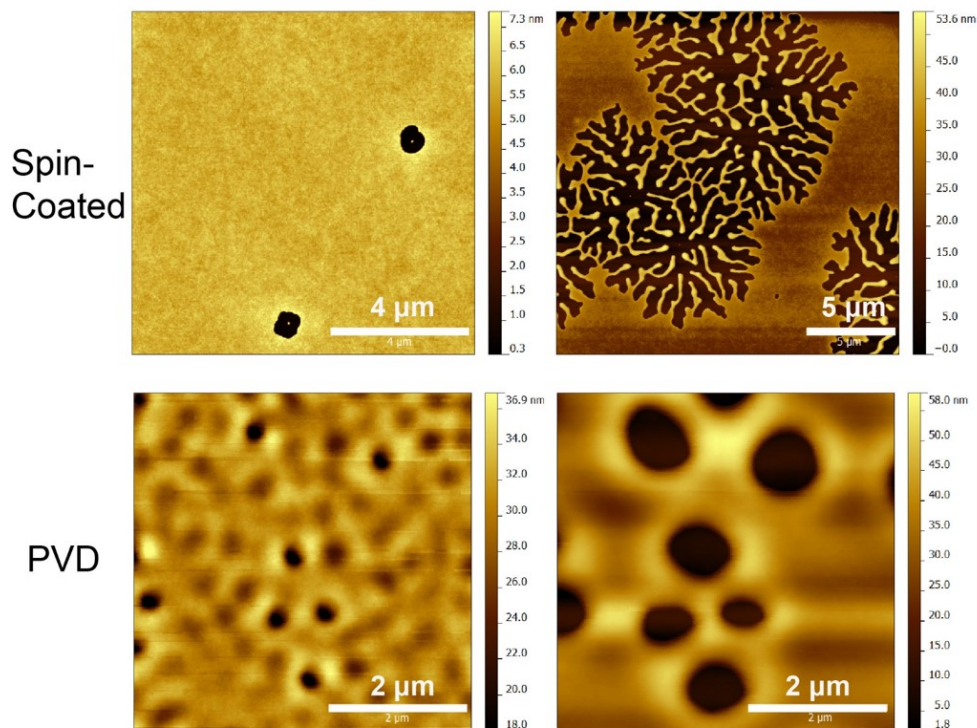


Figure 5.9: Top row: A 7 nm film of TPD Spin-coated on Silicon (left) and its dewetting morphology after overnight annealing at 298 K (right). Bottom row: A 20 nm PVD film deposited under HV conditions as detailed in the text (left) and its dewetting morphology after overnight annealing at 298 K (right).

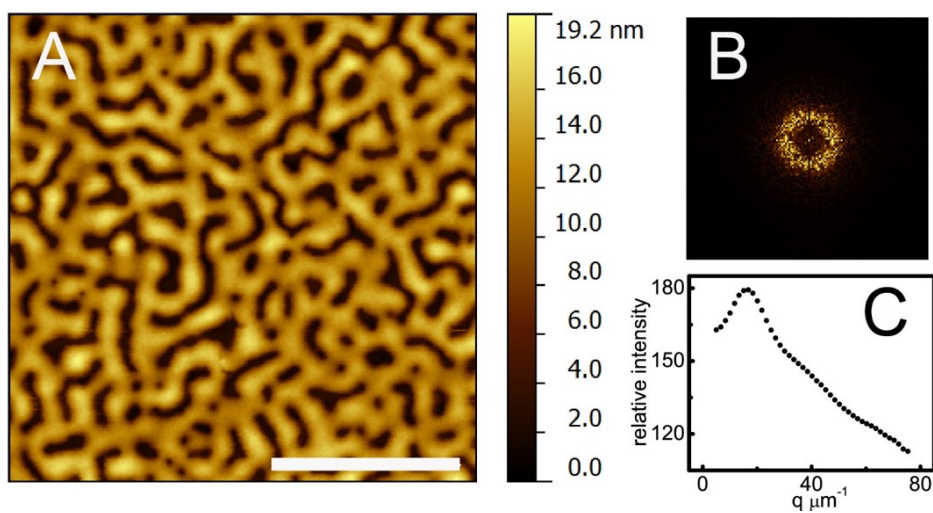


Figure 5.10: A) AFM image of the morphology of an as-deposited 8 nm film deposited at T_g , scale bar corresponds to 2 μm . B) Fast Fourier Transform of the image in A). C) Average radial distribution of FFT pattern in B).

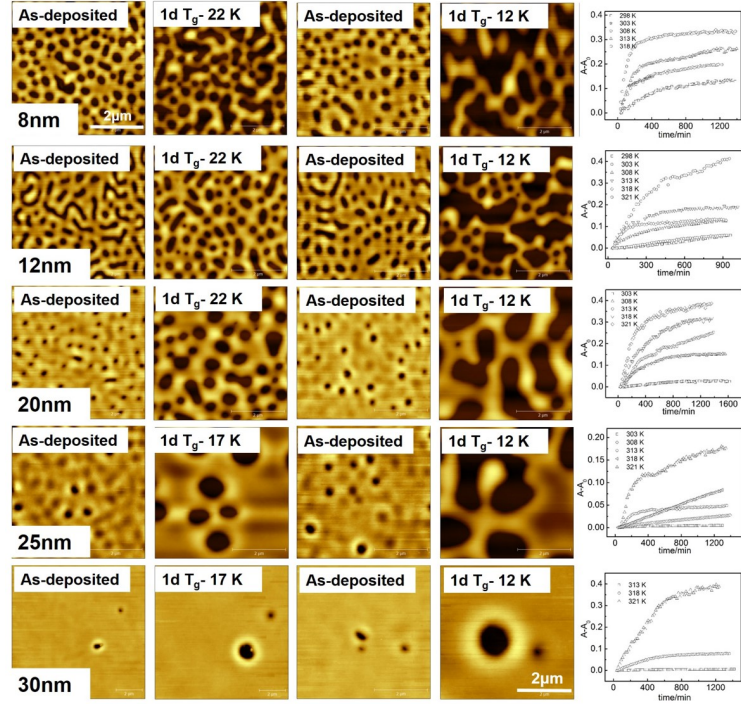


Figure 5.11: As-deposited morphology (first and third columns) of thin films are compared with the morphology after 1 or 2 days of annealing (second and fourth columns) for films of 8 nm (first row), 12 nm (second row), 20 nm (third row), 25 nm (fourth row) and 30 nm (fifth row). The last column shows dewetted area ($A(t)-A(0)$) as a function of time at various isothermal annealing temperatures for these five thicknesses.

$$3\eta \frac{\partial h(x,t)}{\partial t} + \frac{\partial}{\partial x} [\gamma h^3(x,t) \frac{\partial^3 h(x,t)}{\partial x^3}] - \frac{\partial}{\partial x} [h^3(x,t) (\frac{\partial^2 \Delta G}{\partial h^2}) \frac{\partial h(x,t)}{\partial x}] = 0 \quad (5.1)$$

where η is the viscosity, γ is the surface tension and ΔG is intermolecular potential. The first term is viscous term which usually retards the process of dewetting, the second term is the surface tension term which tends to control the film morphology in the direction to minimize the surface area, the last term is related to the intermolecular forces which are determined by the interaction between the two interfaces of a film. This equation can be simplified and solved if the fluctuations in height can be assumed to be much smaller than the film thickness h . In a more general case where the height fluctuations are of the same order of the film thickness, the form of ΔG becomes increasingly important and ΔG can not be assumed to be constant. However, ΔG is not well defined on a molecular level and does not capture potential substrate heterogeneities. Furthermore, this equation does not capture potential slip at the substrate, which needs to be included as a boundary condition.

In addition to the complex form of the thin film equation and the poorly defined intermolecular force (ΔG), it is also possible that in the deeply super-cooled regime, which is of interest in the studies presented in this manuscript, the viscosity itself also depends on the distance from the interfaces. This gradient in viscosity ($\eta(h)$) is not captured in the thin film equation and is not a priori known. As such, it is mathematically difficult to solve the thin film equation analytically to predict the kinetics of dewetting. Current work can only use numerical approaches or utilize a linear thin film approximation to understand this complex problem.

Temperature dependence of TFE variables

Using the Eötvös rule[44], we can roughly estimate the temperature dependence of surface tension of TPD by $\frac{\partial \gamma}{\partial T} = \frac{-k}{V^{2/3}}$, where k is the Eötvös constant and has a value of 2.1×10^{-7} J/(K· mol^{2/3}), V is molecular volume for TPD, which is calculated based on the molecular weight and relative density, to be 4.34×10^{-4} m³/mol. Thus $\frac{\partial \gamma}{\partial T}$ is calculated

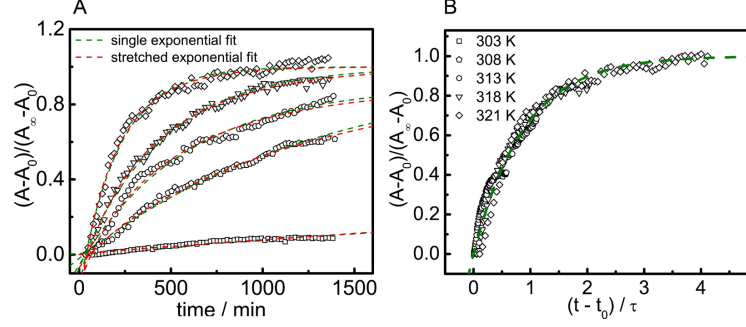


Figure 5.12: A: Single and stretched exponential functions were fit to the dewetted area at various temperatures of 20nm films, where no obvious effect on $\tau_{\text{dewetting}}$ was found. B: After scaling time with $\tau_{\text{dewetting}}$, dewetted area at various temperatures collapse onto the universal function $y = 1 - \exp(-t/\tau)$.

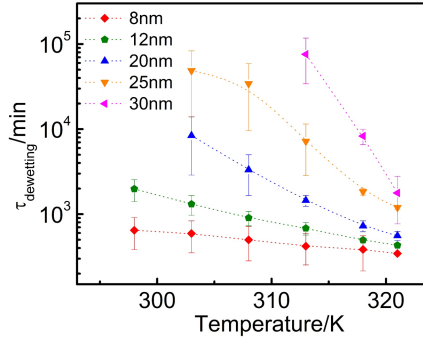


Figure 5.13: $\tau_{\text{dewetting}}$ is plotted versus annealing temperature for five thicknesses.

to be $-3.66 \times 10^{-5} \text{ N}/(\text{m} \cdot \text{K})$. Compared to the surface tension of TPD at 295 K, which is equal to $\gamma = 7.23 \times 10^{-2} \text{ N}/\text{m}$, the changes in γ are negligible in the temperature range of the experiments reported here. Intermolecular potential ΔG , is determined by the distance between two interfaces and interfacial interactions, which are both weakly temperature dependent variables. As such, the viscosity η is the only strong temperature-dependent term driving the dewetting kinetics at different temperatures.

Characteristic dewetting time

In Figure 5.12, we also tried to fit the data with a stretched exponential function, and the resulting stretch factor is only slightly below 1, with an average around 0.9 indicated

by the red dashed line. In Figure 5.12B, the data collapsed onto the universal curve $y = 1 - \exp(-t/\tau)$ after scaling with $\tau_{\text{dewetting}}$.

Average and local film thickness change

Here we provide an estimate of the average and local film thickness change of films dewetted at the highest annealing temperatures (321 K) from AFM volume and height data. The first column in Figure 5.14(b) shows the actual film thickness determined by QCM. The second column is the initial average film thickness calculated from the volume over AFM image size, which is consistent with the thickness by QCM, within errors of ± 1.5 nm. The third column is the initial average thickness of unexposed area, which is slightly larger than the desired film thickness because of preexisting holes within these films. This value is calculated based on the volume of the film divided by the projected area. The fourth column shows the final average thickness of unexposed area after dewetting at 321 K for 24 hours, calculated by dividing the volume of the film by the final covered area, which shows a modest increase. In the last column, the local film thickness is reported based on the height of the profiles just outside the holes as measured by AFM. This value is measured after 24 hours of dewetting at 321 K, when the dewetting process usually stops. It is interesting to note that the maximum local thicknesses is about 40 nm, which is the same thickness, where properties of the film become bulk-like according to Figure 5.6.

Cooling-rate dependent T_g measurements

To extend the range of available viscosities of bulk films to lower temperatures and to determine the vertical shift factors for thin film dewetting data, cooling-rate dependent T_g (CR- T_g) measurements were performed using spectroscopic ellipsometry (M-2000 V J. A. Woollam). The details of the technique can be found in these publications[55, 82].

For CR- T_g measurements, films were deposited at a substrate temperature of $0.85T_g$ (279 K) to ensure that the substrate was fully covered with no holes. These as-deposited films were then heated above T_g to transform into ordinary glass for CR- T_g measurements as shown

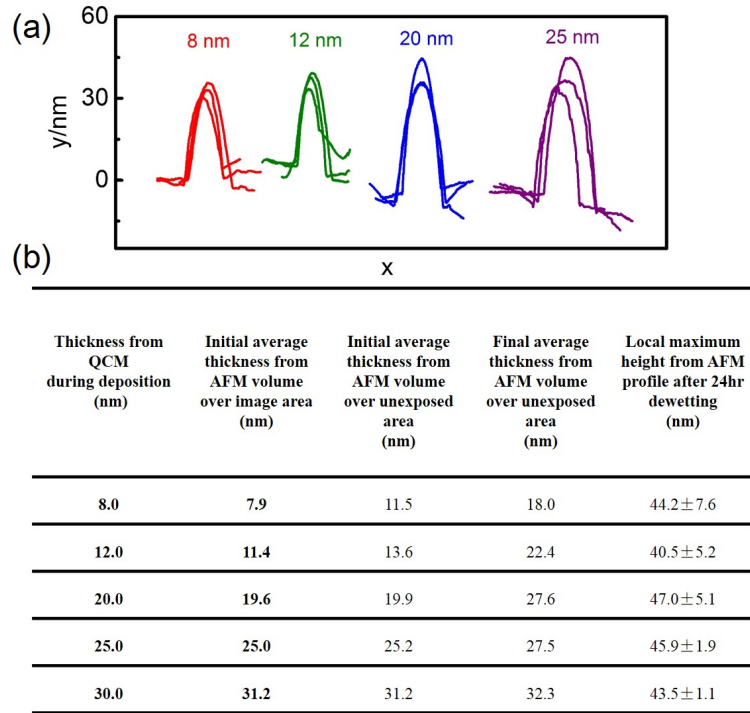


Figure 5.14: (a) Representative profile heights of films of various thicknesses after dewetting at 321 K after 24 hours, where dewetting has stopped or significantly slowed. (b) Evaluation of average and local film thickness change for films dewetted at 321 K for roughly 24 hours.

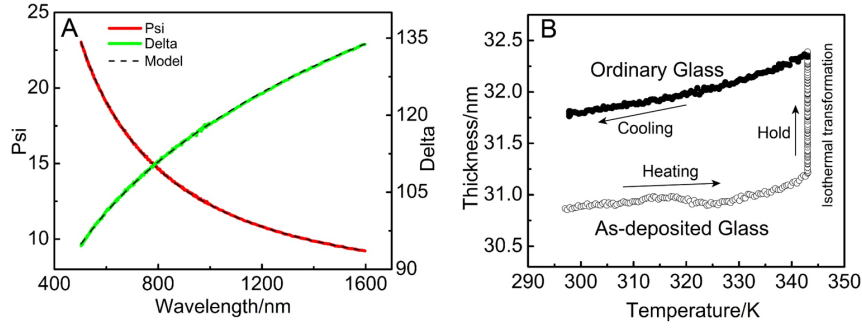


Figure 5.15: A) Raw ellipsometry data for 30 nm film at room temperature. Ellipsometry angles Psi ($\Psi(\lambda)$) and Delta ($\Delta(\lambda)$) are plotted as a function of wavelength (λ) in the range 500 nm-1600 nm. Dashed line represents the Cauchy model fit to the data. B) An example of the transformation of a 30 nm as-deposited film (deposited at $0.85T_g$) upon heating above T_g .

in Figure 5.15B. The samples were then cooled at various cooling rates between 1 K/min-150 K/min and heated at 150 K/min to a set temperature of T_g+18 K (348 K) as shown in Figure 5.16.

An isotropic Cauchy model was used to fit raw ellipsometry data, in this model ellipsometry angles $\Psi(\lambda)$ and $\Delta(\lambda)$ were fit to a model consisting of a temperature-dependent substrate, a native oxide layer, and a Cauchy layer to model the transparent TPD film. The Cauchy model is described as $n(\lambda) = A + \frac{B}{\lambda^2}$, and $k(\lambda) = 0$, where n and k are the real and imaginary parts of the index of refraction. For all films studied here, A , B and the film thickness h were free fit parameters. A spectroscopic range of 500 nm-1600 nm was used for modeling. Figure 5.15A shows the an example of the fit to a single data point and Figure 5.16C shows the mean square error (MSE) as a function of time for this model that represents a reliable fit to the data at all times. AFM imaging was performed before and after measurements (Figure 5.17A and B) to ensure that the films did not dewet during the process.

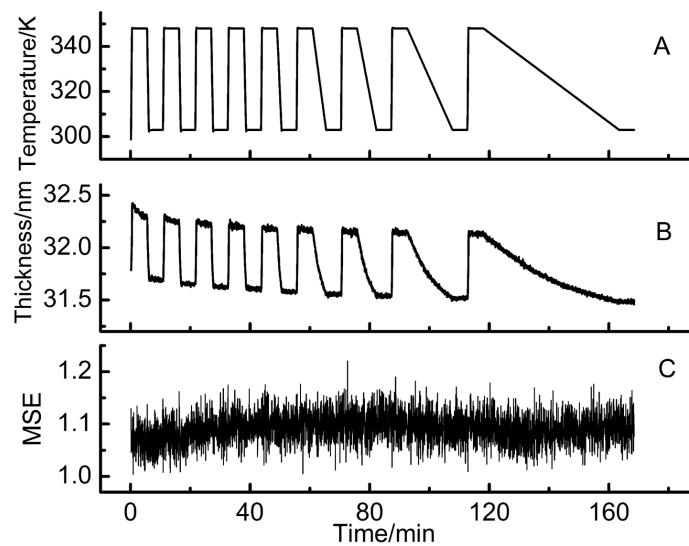


Figure 5.16: An example of typical CR- T_g measurement on a 30 nm film. Panel A): Temperature profile of CR- T_g experiment. Transformed films were heated to 348 K, held for 5 min and then cooled with various cooling rates: 150 K/min, 120 K/min, 90 K/min, 60 K/min, 30 K/min, 10 K/min, 7 K/min, 3 K/min, and 1 K/min. Samples were kept at 303 K for 5 min after each cooling cycle. Panel B): Corresponding thickness from Cauchy model as described in Figure 5.15 as a function of time. C): Mean square error of the Cauchy fit as a function of time.

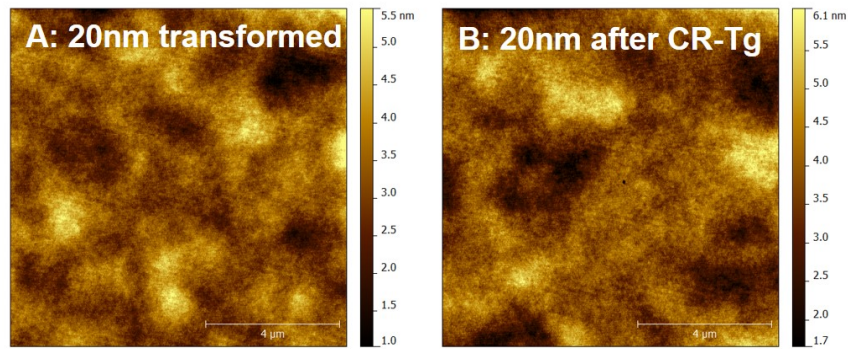


Figure 5.17: A) and B) Morphology of the thinnest film (20 nm) before and after CR- T_g measurements. No obvious morphological failure is observed at the spot where ellipsometry measurement were performed. Scale bars correspond to 4 μm . However, evidence of the dewetting were observed near the edges of the substrate for this film.

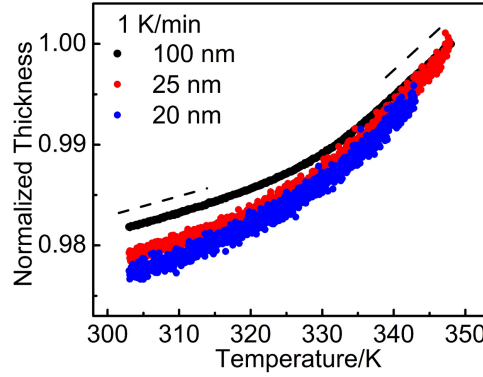


Figure 5.18: Normalized film thickness as a function of temperature for 100 nm, 25 nm, and 20 nm films upon a cooling rate of 1 K/min. It's clear from the thickness profile of 20 nm that the thermal expansion coefficient at glassy region is slightly larger than 100 nm film, indicating incomplete transition and need to extend measurements to lower temperatures.

Possible range of apparent activation energy E_a measured by dewetting and CR- T_g measurement

Due to possible onset of dewetting and the broadened T_g in films with thickness of $h \leq 20$ nm, T_g is potentially overestimated at lower cooling rates, and thus, E_a obtained by CR- T_g can serve as an upper bound value for E_a . Conversely, in dewetting experiments it is possible that enhanced surface diffusion speeds up the dewetting rate beyond the rate expected for a viscous flow process. This effect would be stronger at lower temperatures, resulting in an apparently lower viscosity. Furthermore, slip at the substrate can also serve to enhance the dewetting rate. Therefore, the slope of the line for dewetting experiments can serve as a lower bound to the value of E_a at a given film thickness. The yellow highlighted region in Figure 5.6(b) shows the range of possible values for apparent activation barriers for rearrangement near bulk T_g for various thicknesses.

VFT fit of bulk data and vertical shift factors for CR- T_g and dewetting measurements

A fit to the Vogel-Fulcher-Tammann (VFT) with all bulk data described in Figure 5.6(a) is from the dielectric relaxation time measurements on bulk TPD reported by Walters *et*

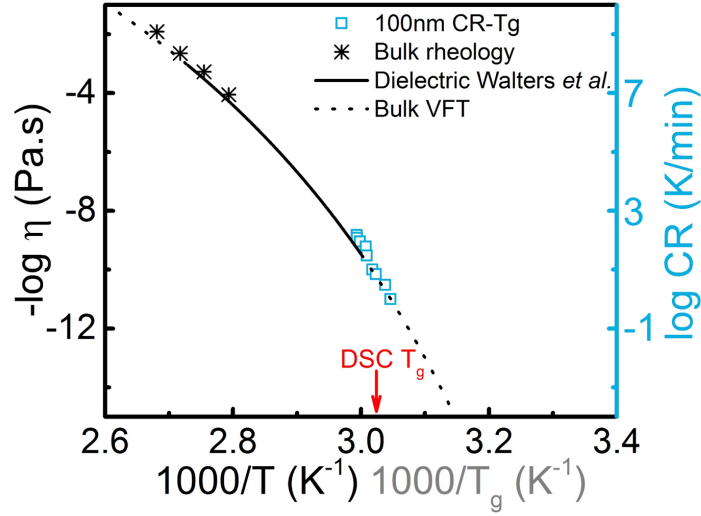


Figure 5.19: Bulk rheology, dielectric and 100 nm CR- T_g can be compared directly and described by bulk VFT.

al.[147] and described by $\tau = \tau_0 \exp(\frac{B}{T-T_0})$ with $B = 3493$ K and $T_0 = 258.9$ K[147]. In Figure 5.19 and Figure 5.20 we show how we shift 100 nm CR- T_g data and characteristic dewetting time with viscosity. The 100 nm data matches well with bulk dynamics from rheology and dielectric, and can be described by a single bulk VFT fit. Using similar shift approach, the vertical shift factors used to plot the CR- T_g and dewetting measurement in conjunction with bulk viscosity and dielectric relaxation measurements for all film thicknesses are shown in Figure 5.21.

Comparison between experimental data and two layer model

Here we present the comparison between the thickness-dependent activation curve observed in our experiments as presented in Figure 5.6(b) and the expected activation curve predicted by a simple two layer model with a constant liquid-like surface layer thickness. We assume that the overall dynamics in a film can be simply viewed as a weighted average of the enhanced dynamics induced by the free surface and the bulk dynamics. We assume a $h_{mob} = 8$ nm mobile layer induced by the free surface that has the relaxation dynamics described by an Arrhenius function, obtained by fitting the data for the 8 nm film shown in Figure

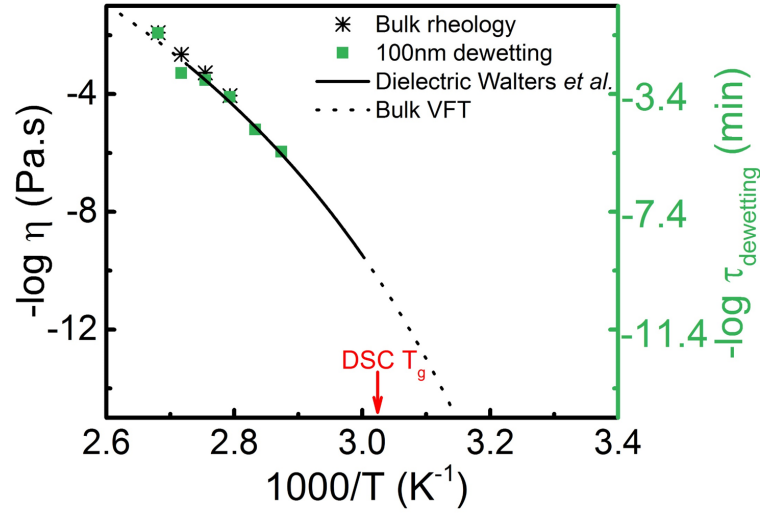


Figure 5.20: Bulk rheology, dielectric and 100 nm dewetting data can be compared directly and described by bulk VFT.

Vertical Shift Factors for CR-T _g	
-log η = log CR - 11	
Vertical Shift Factors for Dielectric	
-log η = -log τ _α - 8	
Vertical Shift Factors for Dewetting	
100nm	-log η = -log τ _{dewetting} - 0.6
30nm	-log η = -log τ _{dewetting} - 8.1
25nm	-log η = -log τ _{dewetting} - 7.6
20nm	-log η = -log τ _{dewetting} - 7.3
12nm	-log η = -log τ _{dewetting} - 7.0
8nm	-log η = -log τ _{dewetting} - 6.7

Figure 5.21: Vertical shift factors for CR-T_g, dielectric relaxation measurement[147] and dewetting measurements. CR-T_g data are shifted according to empirical relation: Cooling rate:10 K/min ~ relaxation time:100 s ~ viscosity:10¹⁰ Pa.s; 100 nm dewetting data are shifted vertically to match the bulk rheology data in the same temperature range; Thin film dewetting data are shifted vertically to match thin film CR-T_g data in the similar temperature range; With no CR-T_g data, 12 nm and 8 nm dewetting data are shifted accordingly with uncertainties marked with gray shades.

5.6(a).

$$\tau_{surface} = \tau_{surface,0} \exp\left(\frac{E_{surface}}{RT}\right) \quad (5.2)$$

with $\frac{E_{surface}}{R} = 2670$ K and $\tau_{surface,0} = 0.00006$ s according to experimental data.

The bulk dynamics can be described by a VFT function:

$$\tau_{bulk} = \tau_{bulk,0} \exp\left(\frac{B}{T - T_0}\right) \quad (5.3)$$

Based on data shown in Figure 5.6(a) $B = 3493$ K and $T_0 = 258.9$ K, $\tau_{bulk,0} = 10^{-19.2}$ s [147]. For a film with thickness h , if we assume no correlation between the surface and bulk dynamics, then the overall dynamics can be described by a weighted average of the two relaxation dynamics.

$$\tau(h, T) = \frac{h_{mob}}{h} \tau_{surface,0} \exp\left(\frac{E_{surface}}{RT}\right) + \left(1 - \frac{h_{mob}}{h}\right) \tau_{bulk,0} \exp\left(\frac{B}{T - T_0}\right) \quad (5.4)$$

It is also possible that the average relaxation can be described by the weighted average of the log relaxation of surface and bulk as

$$\log \tau(h, T) = \frac{h_{mob}}{h} \log[\tau_{surface,0} \exp\left(\frac{E_{surface}}{RT}\right)] + \left(1 - \frac{h_{mob}}{h}\right) \log[\tau_{bulk,0} \exp\left(\frac{B}{T - T_0}\right)] \quad (5.5)$$

The exact way of averaging surface and bulk relaxation time is nontrivial [93] and possibly depends on the type of measurements performed. One can imagine that if T_g is measured, then Equation 5.5 is the more appropriate option, while direct measurements of relaxation time, depending on their sensitivity and range of time scale may probe Equation 5.4 or something similar with a different weight for averaging surface and bulk. While these details are beyond the scope of this work, we can compare our experimental results with both equations. From this simple two-layer model with no strong dynamical correlation we can generate a series of relaxation dynamics for films of various thicknesses as shown in

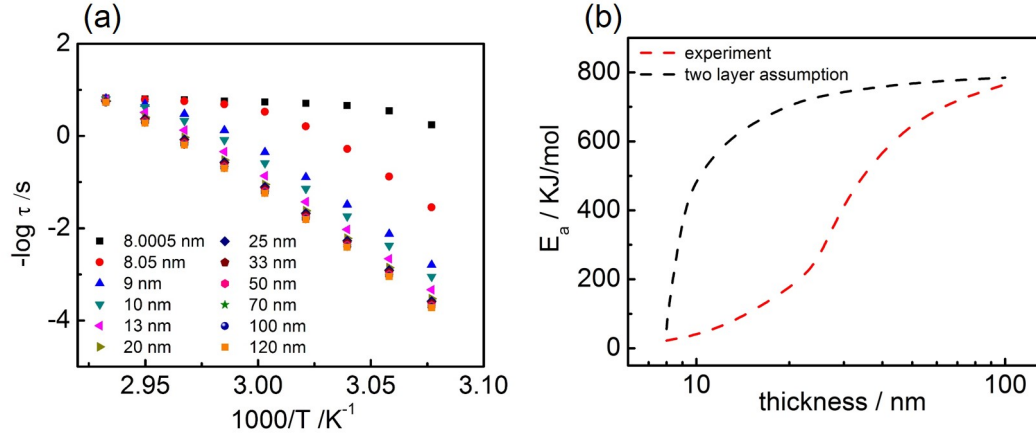


Figure 5.22: (a) Calculated relaxation time versus temperature assuming the overall dynamics can be described by a weighted averaged function of absolute relaxation time of surface layer and bulk layer. (b) Activation barrier versus film thickness obtained from (a) near T_g (black) and comparison with experimental data (red).

Figures 5.22a and 5.23a for Equations 5.4 and 5.5, respectively. We note that these curves do not necessarily look Arrhenius, as the bulk VFT changes strongly with temperature. However, in the limited temperature range here we can obtain an apparent activation barrier for rearrangement near T_g from the slopes of these curves and plot the predicted E_a versus film thickness as shown in black dashed-line in Figures 5.22b and 5.23b for Equations 5.4 and 5.5, respectively. Both curves show a monotonic trend with film thickness regardless of the details of averaging. The experimental data is plotted in red dashed-line for comparison. We note that changing the thickness of the mobile layer, for example by assuming there are two free surfaces, or assuming thicker mobile surface layer may affect the strength of the decrease in E_a but will not result in a sigmoidal transition.

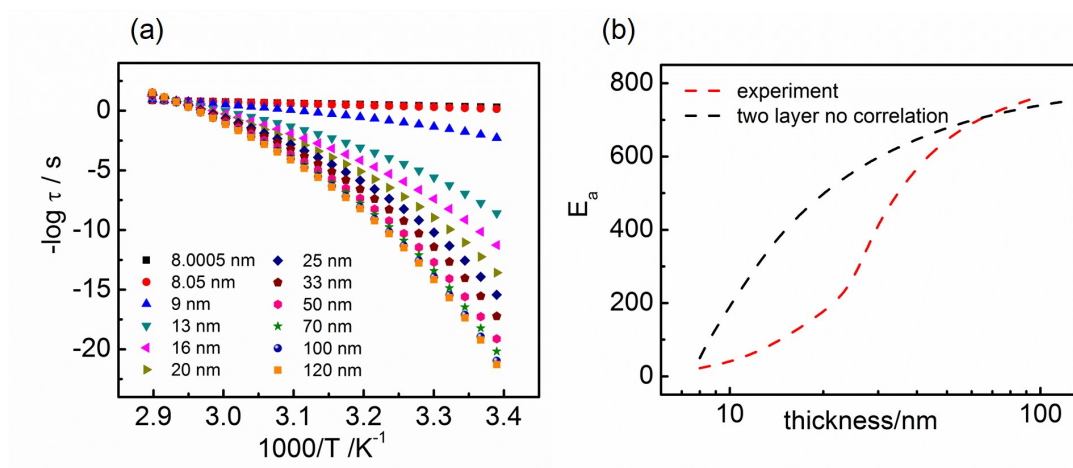


Figure 5.23: (a) Calculated relaxation time versus temperature assuming the overall dynamics can be described by a weighted averaged function of log relaxation time of surface layer and bulk layer. (b) Activation barrier versus film thickness obtained from (a) near T_g (black) and comparison with experimental data (red).

CHAPTER 6 : The Effect of Substrate Interactions on the Glass Transition and Correlated Length Scale of Dynamics in Ultrathin Molecular Glass Films

Yue Zhang and Zahra Fakhraai The Effect of Substrate Interactions on the Glass Transition and Correlated Length Scale of Dynamics in Ultrathin Molecular Glass Films.

6.1. Abstract

Interfaces play important roles in the glass transition temperatures in ultrathin polymer films as extensively investigated in the past few decades. We have recently shown that ultrathin molecular glasses have similar property deviations from bulk with long-range correlated dynamics induced by the free surface, but the effect of substrate interface is not known yet. In this study, we investigate the film/substrate interface effect on the glass transition temperatures (T_g), apparent activation barriers for rearrangement, and correlated length-scale of dynamics in thin supported molecular glass films. The model system studied here is molecular glass N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD). By coating the silicon substrates with an ultrathin (< 5 nm) polystyrene dead layer, we can modify the TPD/silicon interface from repulsive to neutral interaction. TPD ultrathin glass films that are below 30 nm supported on polystyrene dead layer coated silicon show T_g reduction to a lesser extent and stronger morphological stabilities than those supported on bare silicon substrates. Upon cooling-rate dependent T_g measurements on various thickness films, we observed a sharp transition from bulk-like to liquid-like behavior in the thickness dependent apparent activation barrier, indicating long-range propagation of interfacial effects. While the dynamics slow down, and T_g increases, the transition thickness range remains the same when substrate attraction is increased. The same bulk-limit (thick films) remains the same, while a higher ultrathin film activation energy is observed on polystyrene dead layer substrates.

6.2. Introduction

Thin glassy films have drawn great interest in research over the past few decades due to their striking property differences from bulk counterparts[76, 51, 52, 122, 42, 117, 55]. In thin glassy films, with the reduction in dimensions, the interfaces become more dominant in controlling the overall properties or dynamics within the films. In an effort to understand the effect of the free surface or air/film interface, various studies have focused on free-standing polymeric glassy films. Measurements of T_g [51, 123, 117] suggested that the free surface tend to enhance the overall film dynamics. Direct near-free surface measurements also confirmed the enhanced dynamics near the free surface of these films[140, 47, 69, 104, 119].

For supported thin glassy films, there are two interfaces playing roles in the overall film dynamics simultaneously, the free surface and the film/substrate interface. In ultrathin film regime, the substrate-film interface also comes into play and the overall properties of the film will be determined by the interplay between the two interfaces. The characteristics of the substrate interface such as the surface energy[143, 53, 151, 5], roughness[62], rigidity[62] and so on may all affect the local near substrate dynamics as well as overall film behaviors by extension, making it an interface with more possible variations compared to the air/film interface. It was found that depending on the nature of film-substrate interactions, the substrate interface can either suppress or enhance the thin film dynamics[53, 124].

For example, ultra-thin polystyrene films are widely shown to have reduced glass transition temperatures when supported on silicon substrates with native oxide layer while ultra-thin Poly(2-vinylpyridine) (P2VP) films show increased T_g on the same substrates due to strong hydrogen bonding interactions at the film/substrate interface[145, 108, 58]. Poly(methyl methacrylate) (PMMA) has a lesser degree of hydrogen bonding interactions with the silicon substrates and the resulting overall T_g shows neither reduction or increase trend with film thickness decrease, mostly due to the competition between enhanced near-surface dynamics and suppressed near-substrate dynamics[124]. Similar observations were also reported in simulations, where the confinement effect on glass transition temperatures can

be tuned by changing the film/substrate interactions[143, 62]. There have also been many efforts done to modify the substrate interface to control the degree of confinement effect, approaches includes but not limited to: the modification of surface energies by coating silicon substrates with self-assembly monolayers (SAM)[53, 151], promoting irreversibly adsorbed polymer layer on the substrate interface[111], tuning long-range van der Waals interactions on silicon substrates[155]. The film/substrate interaction can also be changed by promoting the growth of irreversible adsorbed polymer layer or polymer dead layer at the substrate interface[97, 15, 111]. When annealed well above bulk T_g , the polymer melt will adsorb onto the substrate interface and form a very thin irreversible layer which is found to affect the local[77, 15] and overall dynamics of thin polymer glasses[97, 111].

Despite many existing studies in polymeric glass systems, very few studies have focused on molecular glass systems. As nanometer-sized molecular glasses have wide applications in organic electronics[139, 131, 146], nano-imprint lithography techniques[112] and coatings[85], it is imperative to investigate the interfacial effects on the overall properties of these nanometer-sized molecular glasses. We have previously shown that for ultrathin N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) films supported on silicon substrates, the glass transition temperature is substantially decreased when the film thickness is decreased below around 50 nm, and the ultrathin TPD films dewet spontaneously from the substrates at temperatures well below their glass transition temperatures suggesting the repulsive nature of the silicon substrate for TPD glasses[161]. We have also measured the apparent activation barrier for various thickness ultrathin TPD films from both isothermal dewetting and cooling-rate dependent T_g measurements, the results showed a sharp transition from bulk-like to liquid-like dynamics at thickness around 30 nm, indicating a long-range correlated dynamics induced by the interfacial effects. Such long-range correlation were also observed in pure polystyrene (PS) thin films and PS/poly (phenylene oxide) (PPO) miscible blends films, with the transition happening at similar length-scales around 30 nm[55, 56]. Although such large length scales have been observed in several glassy systems, the origin of the long-range correlation is not yet very clear. It is not clear whether

the long-range correlated dynamics is originated from bulk glass or solely from interfaces. In order to gain a deeper understanding of the fundamentals of such long-range correlations, it is also important to investigate the potential effect from the interface natures. Such studies may help elucidate the question of whether the large length scale is set by the bulk or depends on the details of the interface.

In this study we investigate the substrate effect on the glass transition temperatures and long-range correlated dynamics in ultrathin small molecule organic glass former TPD. We develop a facile way of modifying the SiO_x -Si substrate interface by introducing a very thin layer (< 5 nm) of polystyrene dead layer on it. It was found that the wettability of TPD films on the modified PS dead layer coated SiO_x -Si substrates (PS- SiO_x -Si) was improved significantly. Similar T_g reduction was observed when the thickness of TPD film is decreased below 50 nm, but to a lesser extent than on the original SiO_x -Si substrates. Cooling-rate dependent T_g (CR- T_g) measurements were performed on various film thicknesses supported on PS- SiO_x -Si and the results were compared with previous dewetting and CR- T_g results on SiO_x -Si. The increased morphological stability of TPD films on PS- SiO_x -Si allows the possibility of successful application of CR- T_g measurements on very thin (≤ 20 nm) TPD films without any sign of dewetting. This easy and convenient way of including a PS dead layer coating on widely used silicon substrates helps improve the thermal and morphological stabilities of ultra-thin molecular glassy films for applications. Despite the increased attraction of PS- SiO_x -Si with the TPD films, from the CR- T_g measurements, we find similar long-range correlation happening around the same thickness range 30 nm. The results suggest that by increasing the substrate-film interface attraction, the extend of T_g reduction can be modified due to the competition between substrate/film interface and air/film interface. However the length scale of the correlated dynamics appears to remain unchanged, signifying the universal feature of this observation. The observation may suggest that the interfaces only act as perturbations and the long-range length scale of correlated dynamics is determined by the bulk glass.

6.3. Experimental Details

preparation of PS dead layer coated silicon substrates and TPD films

Polystyrene with a molecular weight of 342,000 g/mol was purchased from Polymer Source and used without further purification. Silicon substrates with 1~2 nm native oxide layer (one side polished, 100 plates) were purchased from Virginia Semiconductors. PS films were spin-coated onto silicon substrates from a 3 wt% PS toluene solution. The as-spun PS films were annealed in a vacuum oven (MTI Corporation DZF-6020-HT500P) at temperature of 423 K for 24 hours to promote the growth of the dead layer near the substrate interface. The annealed PS films were then soaked in a good solvent, toluene, for 30 min to dissolve away the loosed adsorbed PS layer and then rinsed several times with fresh toluene. The PS dead layer was then thoroughly dried by annealing at room temperature in the vacuum oven for 12 hours. The resulting PS-SiO_x-Si substrates were confirmed with atomic force microscopy (AFM, Aglient 5420) for smooth surface and with ellipsometry (M-2000 V J. A. Wollam) for thickness measure, the roughness and resulting thickness are shown in Figure 6.1. TPD was purchased from Sigma-Aldrich and used without further purification. TPD films were prepared by spin-coating various concentrations of TPD toluene solutions onto previously prepared PS-SiO_x-Si substrates. As-spun TPD films were annealed at 338 K in vacuum oven for 12 hours to remove any residual solvent or stress induced by spin-coating process.

Dilute TPD solutions (0.05-0.15 wt%) were spin-coated onto two types of substrates using same spinning rates of 8000 rpm. The as-spun morphologies were imaged with AFM as shown in Figure 6.2, the average film thicknesses of these films range from 3 - 6 nm. Under same concentration and spinning conditions, TPD forms fully covered smooth films on PS-SiO_x-Si that remains stable upon heating above T_g , while it forms partially covered or dewetted patterns on SiO_x-Si which further dewet with time and annealing. The morphology differences in Figure 6.2 indicate that TPD has a stronger attraction with PS dead layer than with bare silicon substrates.

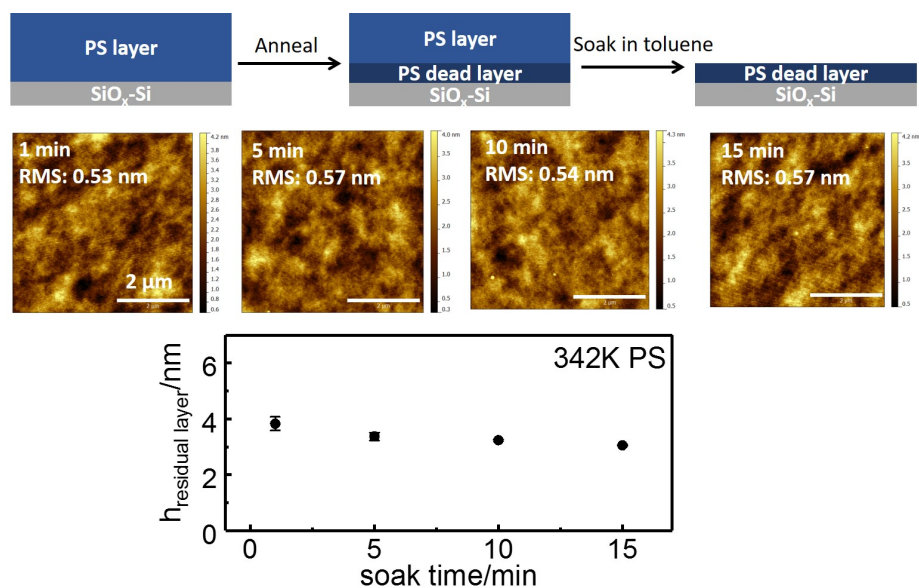


Figure 6.1: Top panel: Schematic of the preparation of polystyrene dead layer coated silicon substrates. Middle panel: AFM images and roughness of the resulting PS- $\text{SiO}_x\text{-Si}$ substrates with different toluene soaking time. Bottom panel: The thickness of the resulting PS dead layer versus toluene soaking time.

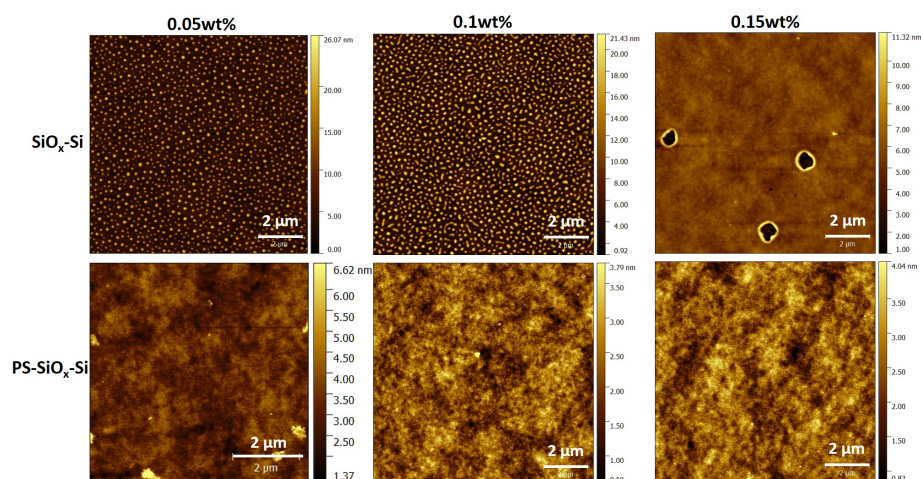


Figure 6.2: Top panel: As-spun TPD films on $\text{SiO}_x\text{-Si}$ from dilute solution show dewetted not fully covered morphologies. Bottom panel: As-spun TPD films on PS- $\text{SiO}_x\text{-Si}$ from the same solutions show fully covered morphologies.

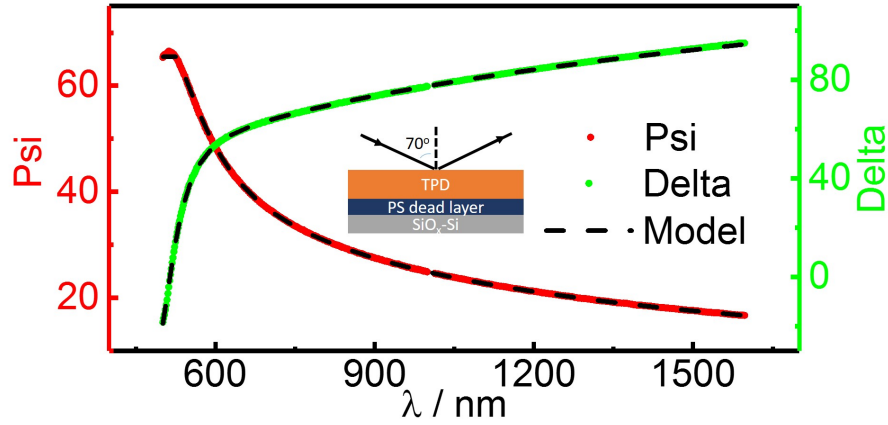


Figure 6.3: An example of the Cauchy fit to a 80 nm TPD supported on PS-SiO_x-Si. Colored symbols are raw Psi and Delta data and black dashed lines are Cauchy model.

Ellipsometry and CR-T_g Measurements

Ellipsometry was used for T_g and CR-T_g measurements. An isotropic Cauchy model was used to fit raw ellipsometry data as described in detail in previous publications[55, 82]. Ellipsometry angles $\Psi(\lambda)$ and $\Delta(\lambda)$ obtained at 70deg incidence angle were fit to a model consisting of a temperature-dependent substrate, a native oxide layer, a PS dead layer (if needed) and a Cauchy layer to model the transparent TPD film supported on PS-SiO_x-Si. The thickness of the PS dead layer was measured independently on SiO_x-Si prior to coating TPD film and was kept as a constant in later modeling. The Cauchy model is described as $n(\lambda) = A + \frac{B}{\lambda^2}$, and $k(\lambda) = 0$, where n and k are the real and imaginary parts of the index of refraction. A , B and the film thickness, h , were free fit parameters for the TPD layer. A spectroscopic wavelength range of $\lambda = 500$ nm-1600 nm was used to fit the data. Figure 6.3 shows the an example of the Cauchy fit to a TPD film supported on PS-SiO_x-Si and the thickness was determined as $h = 80$ nm.

CR-T_g measurements were performed using ellipsometry equipped with a temperature control stage (Linkam THMS 600). The details of the technique can be found in our previous publications[55, 56, 82, 161]. For CR-T_g measurements, films with various thicknesses were cooled at various cooling rates between 1 K/min-150 K/min and heated at 150 K/min to

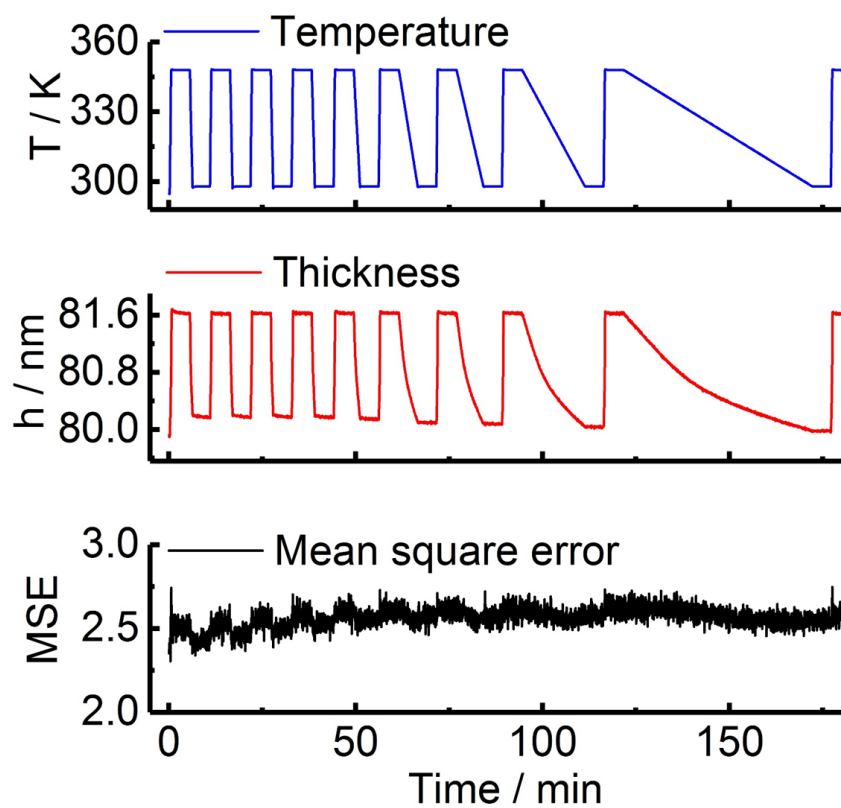


Figure 6.4: An example of the CR- T_g measurement on a 80 nm TPD film supported on PS-SiO_x-Si. Top panel: temperature profile of the measurement; Middle Panel: thickness change during the measurement; Bottom panel: mean square error (MSE) of the Cauchy fit during the measurement.

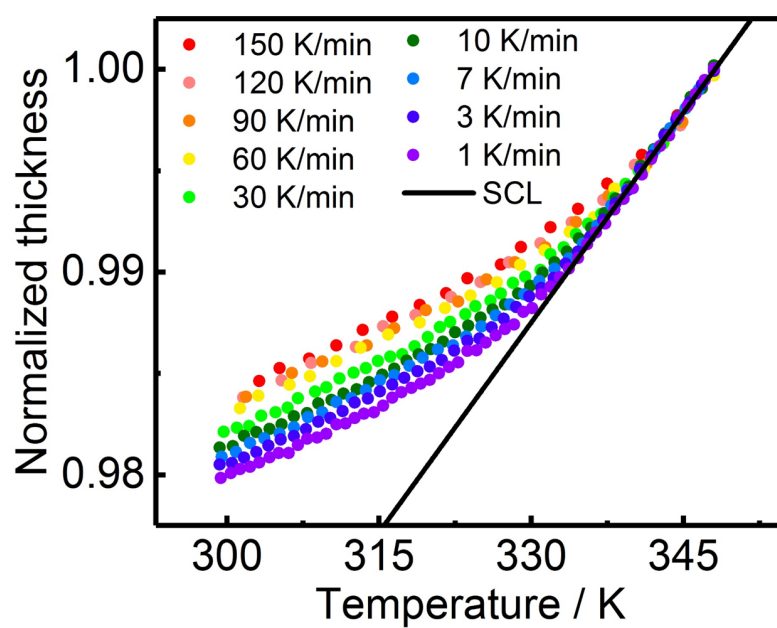


Figure 6.5: An example of the normalized thickness change versus temperature at different cooling rates for a 80 nm TPD film supported on PS-SiO_x-Si. The black line is the super-cooled expansion line.

a set temperature of $T_g + 18$ K (348 K) to equilibrate the film. The temporal temperature profile, representative calculated thickness change and error of the fit during CR- T_g are shown in Figure 6.4. Figure 6.5 shows a representative example of the normalized thickness of an 80 nm TPD film supported on PS-SiO_x-Si at various cooling rates.

6.4. Results and Discussion

6.4.1. Glass transition temperatures of ultrathin TPD films supported on different substrates

The glass transition temperatures of ultrathin TPD films supported on PS-SiO_x-Si were first compared with films supported on SiO_x-Si at a cooling rate of 10 K/min. The T_g was measured upon cooling a supercooled TPD liquid from 348 K into glassy state to 303 K, and the thickness change during the cooling were monitored by in-situ ellipsometry. Figure 6.6(a) shows the typical normalized thickness cooling curves for thick (115 nm) and ultrathin (18 nm) films supported on SiO_x-Si (solid symbols) and PS-SiO_x-Si (open symbols) respectively. The black dashed line is the supercooled liquid line for TPD and describes all film thicknesses supported on these two different types of substrates very well. The thickness curves for the 115 nm thick films on the two types of substrates overlap with each other, indicating that the change of substrate didn't effect the thick film overall properties of the supercooled liquid and bulk glass. However, the cooling curves for 18 nm TPD films show different behaviors beyond the instrumental noise when the silicon substrate is coated with a PS dead layer. The 18 nm TPD films supported on PS-SiO_x-Si falls out equilibrium at a higher temperatures than a film with the same thickness supported on SiO_x-Si, indicative of an overall slower dynamics in the ultrathin films supported on PS-SiO_x-Si. This is mostly due to a stronger attraction of TPD films with the PS dead layer resulting in a slower dynamics near the PS-SiO_x-Si substrate interface and thus a slower overall dynamics in the film.

The average glass transition temperature and the transition width of each TPD film were obtained by fitting the normalized thickness versus temperature profiles using the following

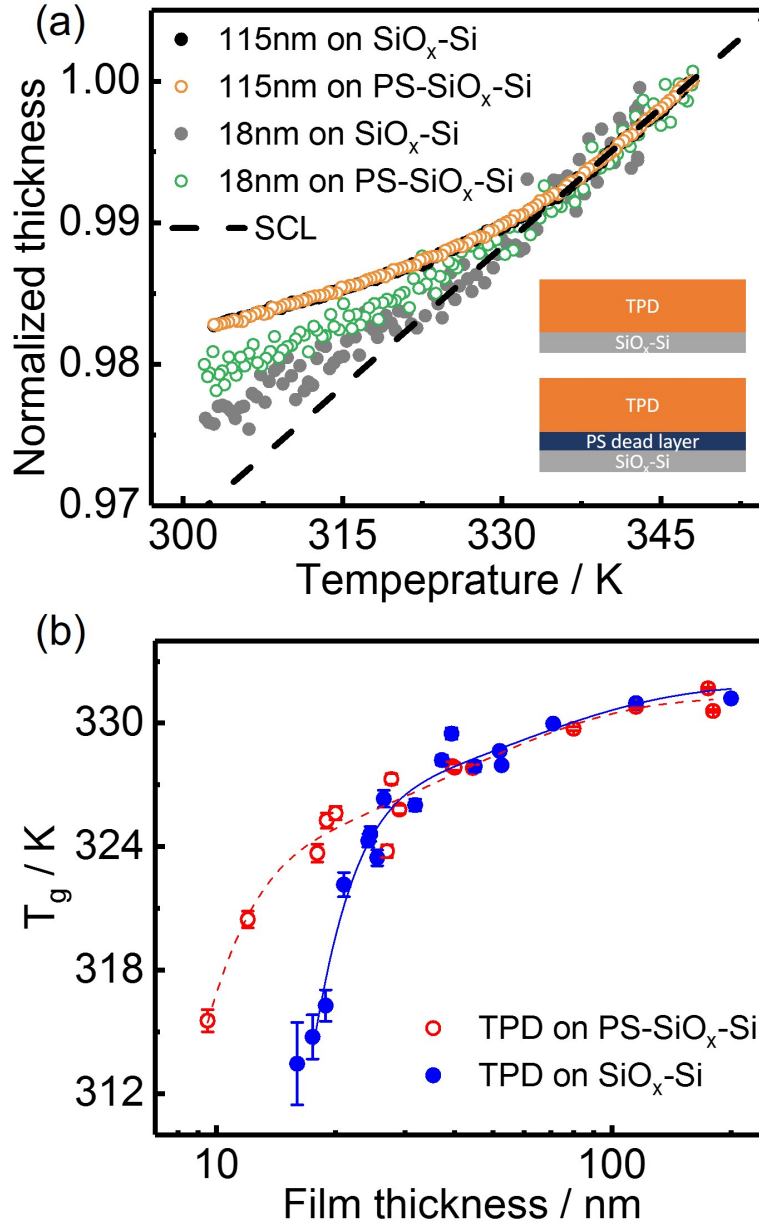


Figure 6.6: (a): The normalized thickness changes of a thick (115 nm) and an ultrathin (18 nm) TPD films supported on Si (closed symbols) and on polystyrene dead layer coated Si (open symbols) upon cooling at 10 K/min, thickness monitored by ellipsometry. Insets show the sample geometries. (b): The glass transition temperatures on two types of substrates versus film thickness.

equation.

$$h(T) = w \left(\frac{M - G}{2} \right) \ln \left(\cosh \left(\frac{T - T_g}{w} \right) \right) + (T - T_g) \left(\frac{M + G}{2} \right) + c$$

Here M and G are the thermal expansion coefficients of the supercooled and glassy regimes, w is the width of the glass transition, and c is the thickness of the film at T_g . The thermal expansion coefficients of the supercooled liquid and glass regimes were kept constant and equal to the corresponding values for the thick films (bulk values) measured to be $M = (6.6 \pm 0.3) \times 10^{-4} \text{ K}^{-1}$ and $G = (2.1 \pm 0.2) \times 10^{-4} \text{ K}^{-1}$. w , T_g , and c were free fit parameters.

Figure 6.6(b) plots the average T_g for various film thicknesses supported on two types of substrates. The general trend is the same and consistent with various previous studies in thin glassy films, where T_g decreases with decreasing film thickness. However, the extent of the T_g reduction is clearly different at lower film thicknesses on different substrates. At thicknesses below $\sim 30 \text{ nm}$, the T_g decreases more sharply on $\text{SiO}_x\text{-Si}$ than on $\text{PS-SiO}_x\text{-Si}$.

The high and low onset of transition temperatures T_+ and T_- were obtained assuming $T_{\pm} = T_g \pm \frac{w}{2}$. T_+ signifies the onset of transition from supercooled liquid to glassy state where the slower portion within the film starts to fall out equilibrium. While T_- signifies the completion of the T_g transition which is more representative of the fast portion within the film falling out equilibrium.

Figure 6.7 shows the change of T_g , T_+ and T_- as a function of film thickness. For bulk-like films with thicknesses larger than 60 nm , there are nearly no significant changes in T_g , T_+ or T_- , and the width of the transition comes mostly from the dynamic heterogeneity inherent to glassy systems. When the film thickness is decreased below 60 nm , there are immediate drops in T_- on both substrates, consistent with the increased contribution from free surface

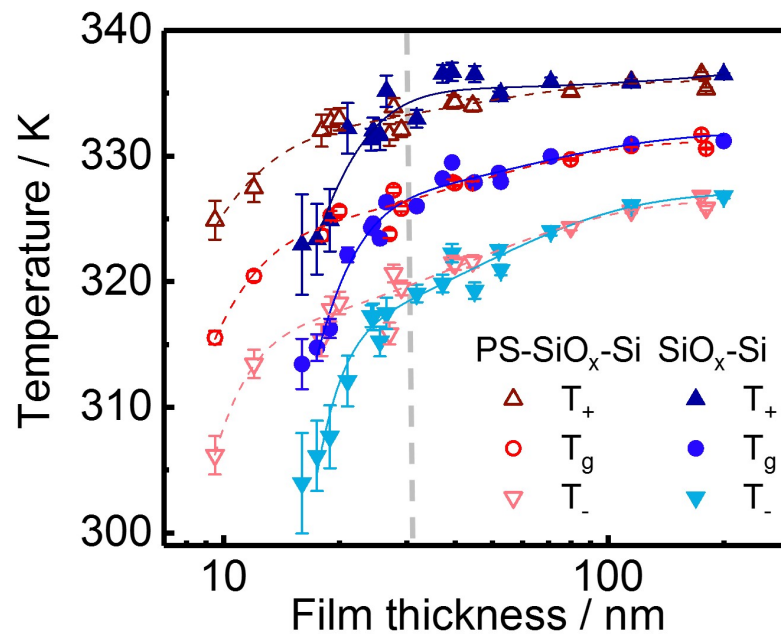


Figure 6.7: T_+ , T_g and T_- of TPD glasses on two types of substrates versus film thickness, measured at a cooling rate of 10 K/min.

enhancement with the reduction of film thickness. While the T_+ on both substrates remain more or less constant in the thickness range of 30 nm - 60 nm, indicating that some portions of these films still have bulk-like glassy dynamics. Thus the average T_g reduction in this thickness range is mostly coming from the increasing contribution from free surface induced enhancement in the dynamics, that prevents the near-free surface region from falling out of equilibrium.

When the film thickness is decreased below 30 nm, there are growing differences between T_g , T_+ and T_- on these two types of substrates. The first observation is that on two types of substrates, below 30 nm, both T_+ and T_- decrease sharply, resulting a sharper decrease in overall average T_g . The decrease in T_+ may suggest that there is no longer any part within the film that behave bulk-like and the overall dynamics is influenced by the free surface effect. The second interesting observation is the differences of T_g , T_+ and T_- changes on the two different substrates. It is clear that the T_+ decreases less sharply on PS-SiO_x-Si than on SiO_x-Si, this is mostly due to the difference in the strength of the attractions between the film and the substrate interfaces. From our previous studies[161] we observed spontaneous dewetting of ultrathin TPD films on SiO_x-Si substrates, indicating a repulsive nature of the film/substrate interaction. However, when supported on PS-SiO_x-Si, TPD ultrathin films show increased morphological stability and are much less prone to experience dewetting as shown in Figure 6.2. We attribute the interaction between TPD and PS dead layer as neutral interaction, possibly due to the similar surface energies between TPD and PS dead layer. Similar difference also shows in T_- versus film thickness, where on SiO_x-Si it shows a sharper decrease than on PS-SiO_x-Si below 30 nm. The similar trend in T_+ and T_- below 30 nm is interesting and may suggest that the dynamics in ultrathin films are becoming uniform and overall enhanced, and the degree of enhancement will be determined by the interplay between the near surface and near substrate dynamics. Thus a slightly stronger interaction with the substrate interface will decrease the enhancement than on a repulsive substrate. We note that the PS-SiO_x-Si substrate here doesn't represent a very strong attractive substrate for TPD films, otherwise an increase in T_+ may be observed, such as

the case of P2VP on silicon[145, 108, 58]. On the two types of substrates we compared here, the enhancement from the free surface still dominates below 30 nm resulting in overall enhanced dynamics with slightly less enhancement with a stronger substrate interaction. One may expect a further increase in the film/substrate interaction would alter the average T_g behavior from reduction trend to constant as the example of PMMA on silicon or increase trend as seen in P2VP on silicon[124].

6.4.2. Cooling-rate dependent T_g measurements of TPD films supported on PS-SiO_x-Si

In the previous part, we compared the glass transition behavior at a constant cooling rate of 10 K/min. From the different extent of T_g reduction in ultrathin film we confirmed that there is an increase in the interaction strength between TPD and PS dead layer than silicon. Here we have applied cooling-rate dependent T_g (CR- T_g) measurements to indirectly probe the relaxation dynamics in ultrathin TPD films supported on PS-SiO_x-Si and compare with our previous measurements on SiO_x-Si substrates. CR- T_g method is an efficient way to indirectly probe the relaxation times in glasses at temperatures near their T_g . For most bulk organic glasses when the system is cooled at 10 K/min, the super-cooled liquid falls out of equilibrium when the average structural relaxation time of the system is equal to $\tau_\alpha \simeq 100$ s, or the viscosity reaches $\eta \simeq 10^{10}$ Pa.s. If the system is cooled more slowly, it falls out of equilibrium at a larger value of viscosity. As such cooling rate CR is inversely proportional to both η and τ_α with measurements at 10 K/min used as a point of reference. The relaxation time can be estimated based on the empirical relationship that $\tau \times CR = 1000$. The details of CR- T_g measurements were described in the experimental details and in our earlier studies[161, 82, 55]. In Figure 6.8, we plot the log CR versus $1000/T_g$ for various thickness TPD films supported on PS-SiO_x-Si. In the limited temperature window near the glass transition temperature, we can use Arrhenius fit to each data set. The slope of each film thickness represents the apparent activation energy for relaxation near T_g . Similar to what has been observed in polymer[55, 56] and molecular glasses[161], it's apparent that with a decrease in film thickness the activation barrier and therefore the fragility decreases,

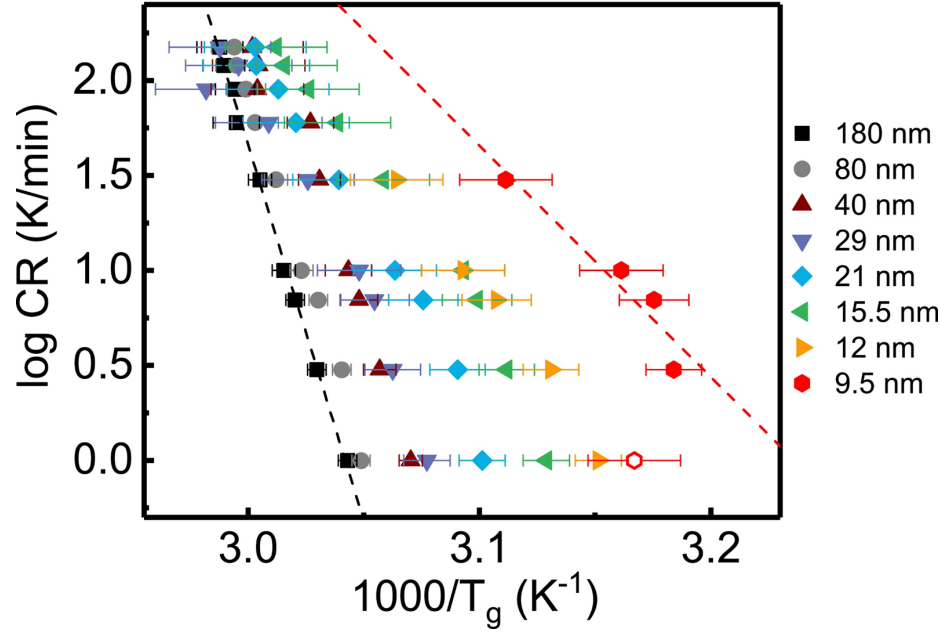


Figure 6.8: Log cooling-rate (CR) versus $1000/T_g$ for TPD films with various thicknesses supported on PS-SiO_x-Si substrate.

indicating overall enhanced dynamics in ultrathin films.

6.4.3. Length-scale of correlated dynamics on different substrates

In Figure 6.9, the apparent activation barrier for TPD films, evaluated from the slopes in Figure 6.8, is plotted versus film thickness for films supported on PS-SiO_x-Si together with previous results from dewetting and CR-T_g measurements supported on SiO_x-Si[161]. The apparent activation barrier or the fragility decreases as film thickness decreases, consistent with previous observations on polymer glasses and molecular glasses. It is interesting to note that the activation barrier does not show any difference on two types of substrate until the film thickness is decreased below 30 nm, consistent with the thickness range where we start to observe T_g variations on different substrate as shown in Figure 6.6(b). On both substrates we observe sharp non-linear transitions in the dynamics happening around 30 nm, above which the overall dynamics mostly behave bulk-like and show weak thickness dependence with similar activation barriers. Around the thickness range of 30 nm, the changes in overall dynamics are significant due to the perturbation of interfaces and this is where we

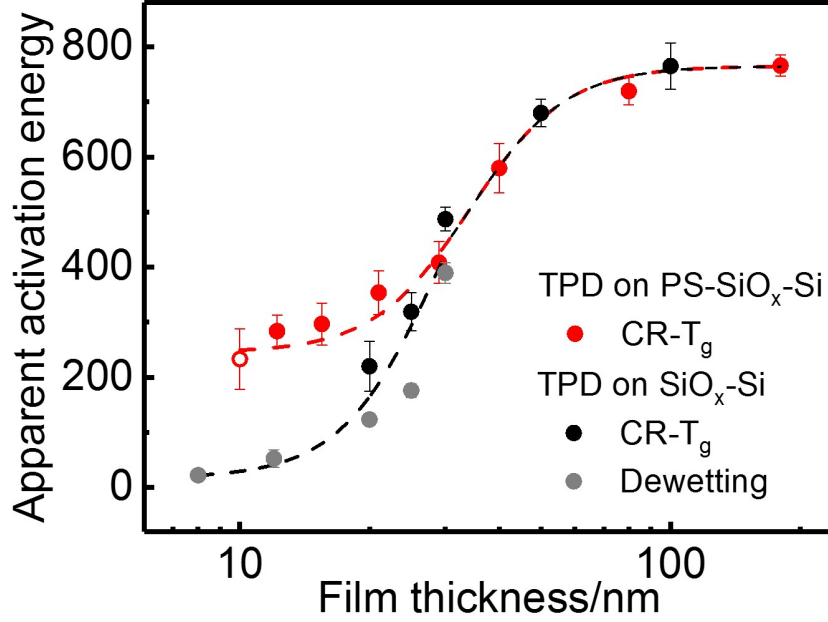


Figure 6.9: Apparent activation energy measured from CR-T_g measurements versus film thickness on two types of substrates. The dashed lines are guide to the eye.

propose the bulk and interfacial dynamics are most strongly correlated. Below 30 nm, the average dynamics become weakly thickness dependent again with low activation energies, where the interfacial dynamics dominate the overall dynamics and there is no bulk-like dynamics as observed in thick films. Such transitions in the thickness-dependent dynamics suggests that the interfacial effects can propagate and facilitate the overall dynamics in a non-linear fashion over a very large length scale. In addition to the similar general trend, it's interesting to notice that the lower activation energy plateau is higher for TPD ultrathin films on PS-SiO_x-Si than on SiO_x-Si substrate. If we consider the average activation barrier in the ultrathin film regime below the transition thickness is dominated and determined by the interplay of dynamics near the two interfaces, the slightly higher activation barrier on PS-SiO_x-Si is consistent with the observation that TPD has a stronger interaction with PS dead layer than bare silicon.

It's also worthy noting that the bulk activation limit would only depends on the molecule

studied and the value of the bulk activation can also be tuned by changing chemistry, as demonstrated in our previous studies on PS and PPO blends with varying compositions[56]. We can conclude that the lower end of the transition can be tailored by changing the nature of the interfacial interactions, in most cases we can change the nature of the film/substrate interactions, while the higher end of the transition can be changed by the chemistry.

The most interesting observation is that despite the fact we have modified the silicon substrate with a very thin dead PS layer which increases the attraction with the above TPD films, the midpoint of the transition remains the same around 30 nm. Very similar transition thickness was also observed in polymer glasses with varying compositions[55, 56]. Despite the seemingly universal behavior we observed in different systems, the physical nature of such sharp transition is not very clear yet. From current and previous studies, we find that the lower activation limit or interfacial limit can be tuned by the strength of the interactions at the interfaces and the upper activation limit or bulk limit can be tuned by changing chemistry of the studied system. Such tunability can be important for helping understand the nature of such transitions in the dynamics, as we can have access to tune the two end limits of the transition and watch the shape or position of the transition change in experiments. We hope to conduct more detailed and systematic studies in the effects of controllable chemistry or interfacial interactions in these organic glass systems to gain more insights into the fundamentals of such long-range correlated dynamics.

6.5. Summary

In this study, we have changed interactions at the substrate/film interface in ultrathin TPD glasses from repulsive to neutral by a simple approach of coating the silicon substrates with a very thin dead polystyrene layer. We have confirmed a stronger film/substrate interaction for TPD on PS-SiO_x-Si from the smaller extent of T_g reduction below around 30 nm. From CR- T_g measurements, we observed similar long-range propagation length and sharp transition in the overall dynamics of TPD thin glasses supported on PS dead layer modified silicon substrates. Compared with TPD thin glasses supported on bare silicon

substrates, the length-scale of the transition remains same but with a slightly increased activation barrier at the lower limit of the transition, and the change is mostly resulting from the modified strength in film/substrate interface.

CHAPTER 7 : Stability of Ultrathin Physical Vapor Deposited Molecular Glasses

Morphology Evolution and Stability of Ultrathin Molecular Glass Films Prepared by Physical Vapor Deposition

7.1. Introduction

As first discovered in 2007[137], physical vapor deposition (PVD) can produce small molecule organic glasses with exceptional properties that are not accessible by conventional liquid-quenching methods. Molecular glasses prepared by PVD at deposition temperatures below bulk glass transition temperature (T_g) have lower enthalpy[137, 79], higher kinetic stability[137, 138, 73, 25], increased density[83, 71, 32], higher mechanical moduli[74], and lower water uptake[35]. Such molecular glasses prepared by PVD are known as stable glasses, and the properties of stable glasses are shown to be highly dependent on deposition parameters such as the deposition temperature and the deposition rate[71, 83, 25, 75, 32]. Some properties of PVD stable glasses can also be achieved by physical aging such as lower enthalpy and higher density, although the time scale required for aging to achieve the same amount of enthalpy decrease or density increase can be many orders of magnitude longer than PVD[135]. In addition, PVD stable glasses also exhibit tunable optical properties or birefringence[29, 33, 30] that are not observed in aged glasses.

Various experimental studies have successfully characterized the unique properties of PVD stable glasses, yet the exact forming mechanism of stable glass production is not very clear yet. Many studies have attributed stable glass formation as contributions from enhanced surface mobility in molecular glasses. The main hypothesis is that during vapor deposition, the surface molecules have enough mobility to rearrange themselves into a better configuration or lower energy state before the next layer arrives. As this process continues in a layer-by-layer manner, every molecule from the vapor phase has the opportunity to explore for a lower energy state and thus the resulting film can access a low energy near-equilibrium state. In the context of this hypothesis, the observation that the properties of PVD stable

glass are highly dependent on the deposition temperature and rate is explained as follows: (1) The deposition temperature determines the kinetic surface molecular mobility as well as the thermodynamic driving force for low energy states, while the two variables have opposite trends with deposition temperature and thus there exists an optimal temperature range for achieving the most stable glasses from PVD, for most organic glasses investigated so far this optimal temperature range for deposition is around $0.8-0.85 T_g$; (2) The deposition rate determines the time that coming molecules can spend exploring at the free surface and rearranging before being buried by the next layer, thus the deposition rate will also have an effect on the properties of the resulting PVD stable glasses.

Recent research has developed techniques to directly quantify the surface mobility of molecular glasses such as surface grating decay method[163, 13, 86, 157, 125, 23] and nanorod probe method[162, 159, 160], where the results suggest that the molecules at the free surface move orders of magnitude faster than molecules in the bulk and have a weaker temperature dependence, supporting the main assumption of enhanced surface mobility in the above hypothesis for stable glass formation. Our recent studies using nanorod probe technique have investigated the surface mobility on ultrastable glasses prepared by PVD and have shown that the surface diffusion on molecular glasses is completely independent of the bulk stability or relaxation times and remains constant on stable glasses deposited at different temperatures from PVD. This observation that surface diffusion remains fast on ultrastable glasses on one hand supports the above hypothesis by ensuring efficient surface molecule packing regardless of bulk slow dynamics on previously formed stable layers during deposition, otherwise the physical vapor deposition would be a self-limiting process. However, the invariance of surface diffusion on different stability PVD glasses do not provide a full picture. First, it is not clear how the invariant and always fast surface molecules could translate into glasses with varying bulk stabilities and relaxation dynamics, or in another word how do the surface equilibrium molecules fall out of equilibrium and form a stable glass during vapor deposition is still under question. Another interesting observation cannot be solely answered by fast surface diffusion mediated stable glass formation is that molecules

of various sizes or intermolecular interactions can be made into stable glasses when deposited at similar temperature ranges of $0.8-0.85T_g$ [137, 30, 83]. While studies have shown that surface diffusion strongly depends on molecular size and intermolecular interactions on different molecular glasses[157, 125, 23]. It is not clear why the same optimal deposition temperature range holds true for organic molecules of various sizes or intermolecular interactions.

It is clear from available experimental observations on both stable glass properties and direct surface diffusion measurements that the enhanced surface mobility has an important contribution in stable glass formation by PVD. Yet the current hypothesis does not provide a complete picture, and enhanced surface mobility may not be the only key factor in stable glass formation. We hypothesize that the intermediate layers that are between the mobile surface layer and the bulk slow layer may also have significant roles in stable glass formation. Such layers right underneath the surface mobile layer would have the characteristics of moderate mobility or relaxation times that may accelerate aging rates locally and contribute to the increased stability observed in PVD glasses. In this chapter, we present some interesting observations of ultrathin ($h < 50$ nm) stable glasses prepared by PVD and hope to provide some insights in understanding the exact stable glass forming mechanism by physical vapor deposition.

7.2. Experimental Details

Preparation of ultrathin physical vapor deposited TPD films

All films studied in this Chapter were prepared using physical vapor deposition (PVD) in a custom built high-vacuum (HV) chamber. Silicon (one side polished, 100 plates from Virginia Semiconductor) with 1~2 nm native oxide layer was used as the substrates for all films. A deposition rate of 0.02 nm/s was used for all films. An in-situ quartz crystal microbalance (QCM) was used to monitor film thickness during deposition. After deposition the substrate temperature was brought back to room temperature before the sample was

removed from the chamber. The time it took from removing the sample out of the chamber to the first AFM measurement was around 15 minutes.

Isothermal dewetting and ellipsometry measurements

Isothermal dewetting measurements were performed using atomic force microscopy (AFM, Agilent 5420) equipped with a custom built temperature stage. The details of the setup can be found in Chapter 5. Ultrathin TPD films with thickness ranging from 5 nm to 14 nm were deposited at substrate temperatures ranging from $0.8 T_g$ to T_g with a constant deposition rate of 0.02 nm/s. The morphology evolution of these ultrathin films were monitored *in situ* with AFM. Imaging analysis softwares Gwyddion and ImageJ were used to evaluate the dewetted area from topography images. Spectroscopic ellipsometry was used for thickness and stability measurements. Details of temperature protocol for stable glass transformation and model used to fit raw ellipsometry data were described in Chapter 5.

7.3. Results and Discussion

7.3.1. Effect of deposition temperature on the morphology of as-deposited ultrathin TPD films

In Chapter 5, we have demonstrated that the as-deposited PVD thin films exhibit interesting initial morphologies that are highly dependent on film thickness when deposited at bulk T_g and the roughness of the as-deposited morphology increase with a decrease of film thickness[161]. The rough morphologies in ultrathin PVD films indicate enhanced mobilities in these films during deposition. Here we further test the effect of deposition temperature on the as-deposited morphology of ultrathin PVD films. In Figure 7.1, we show the as-deposited morphology of 12 nm TPD films deposited at five different temperatures relative to bulk T_g , ranging from $0.8 T_g$ to T_g . The morphology becomes rougher when the deposition temperature is increased, suggesting increased mobility during deposition. The root-mean-square roughnesses (RMS) of 8 nm and 12 nm TPD films prepared by PVD were evaluated from AFM images and plotted versus deposition temperature in Figure 7.2. Consistent

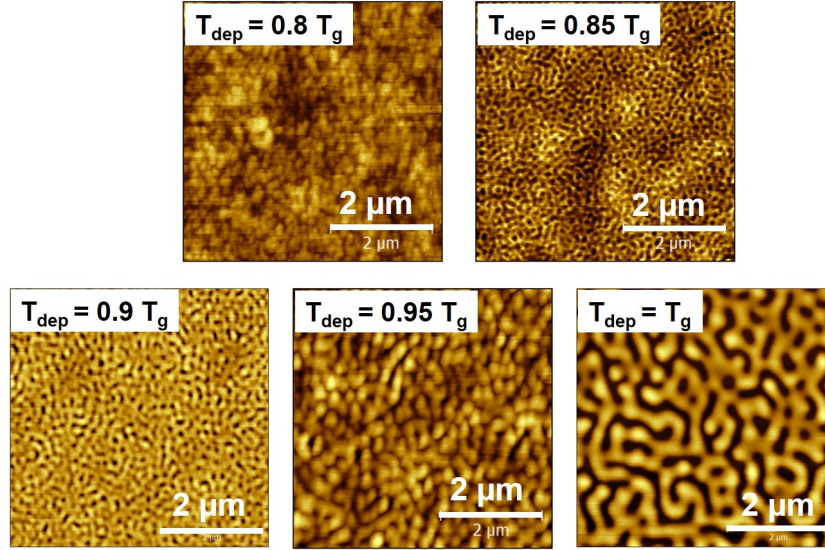


Figure 7.1: The as-deposited morphology of 12 nm TPD films deposited at five different temperatures relative to bulk T_g , deposition rates are 0.02 nm/s.

with Figure 7.1, the roughness decreases rapidly with a decrease in deposition temperature. These observation can be explained as the decreased molecular mobility with decreasing substrate temperature during deposition.

7.3.2. Isothermal dewetting measurements on ultrathin PVD films

When held at a constant temperature even well below bulk T_g , the film morphology will continue to evolve with time. For ultrathin films that are below 14 nm, there are significant further morphology evolution when held isothermally at temperature well below bulk T_g . Similar to the isothermal dewetting measurements described in Chapter 5, AFM was used to track the isothermal dewetting of these ultrathin films deposited at various substrate temperatures. Figure 7.3 shows representative examples of 8 nm TPD films deposited at $0.8T_g$ isothermal dewetting data at five different temperatures, where the dewetting data analysis procedure is the same as previously described in Chapter 5. Similar isothermal dewetting measurements and analysis were performed on films with thicknesses between 5 nm- 14 nm deposited at substrate temperature ranging from $0.8T_g$ to T_g at isothermal

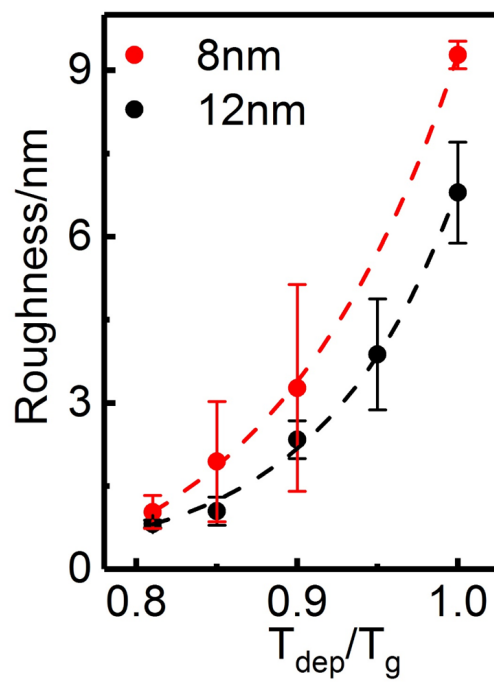


Figure 7.2: RMS of 8 nm and 12 nm TPD films deposited on silicon substrates at different deposition temperatures with a deposition rate of 0.02 nm/s, each data point was averaged from at least 3 samples.

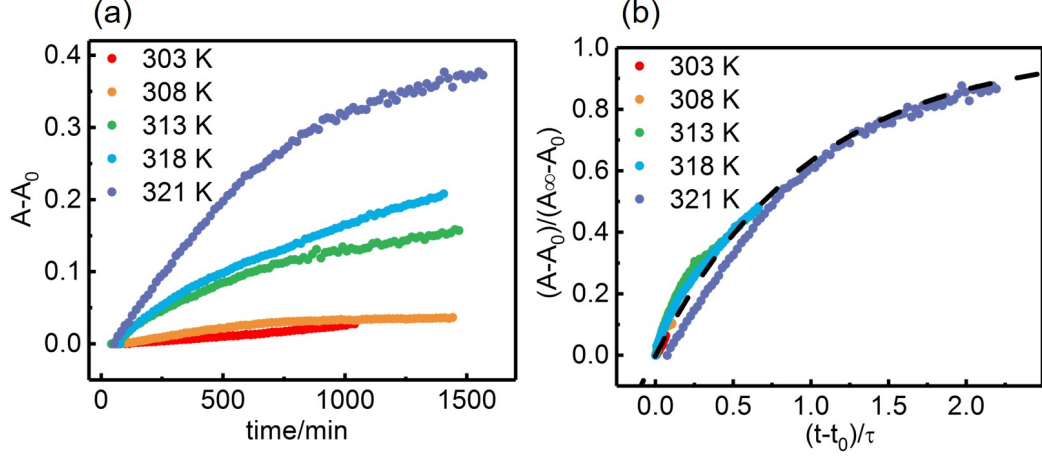


Figure 7.3: Example of isothermal dewetting measurements of 8 nm TPD films deposited at $0.8T_g$. (a) The dewetted area versus time for 8 nm films at different isothermal holding temperatures. (b) Dewetted area at different temperatures collapse onto an universal single exponential curve after scaling time with characteristic dewetting time. The black dashed line is $y = 1 - \exp(-t/\tau)$.

holding temperatures ranging from 303 K to 321 K. The measured apparent activation barrier for each film thickness studied is plotted versus deposition temperature in terms of bulk T_g as shown in Figure 7.4.

There are a few interesting features observed in Figure 7.4. For all ultrathin films investigated, with a decrease in deposition temperature down to $0.85T_g$, the apparent activation energies for dewetting increase, indicating that it takes more energy for the film to dewet when deposited at temperatures below T_g . For 12 nm and 14 nm films, an apparent turnover of the activation energy trend is observed at $0.8T_g$ deposition temperature, which is similar to what has been observed in the non-monotonic stability trend in bulk films with maximum stability happening around the deposition temperature of $0.85T_g$. From these observations, we can at least conclude that the ultrathin films deposited at different substrate temperatures are different in overall dynamics, with slightly slower dynamics when deposited below bulk T_g . This stability difference observed in isothermal dewetting experiments can be of great importance in understanding the formation mechanism of ultrastable glasses as the films studied here are ultrathin and only about 10-15 mono-layers thick, they already show

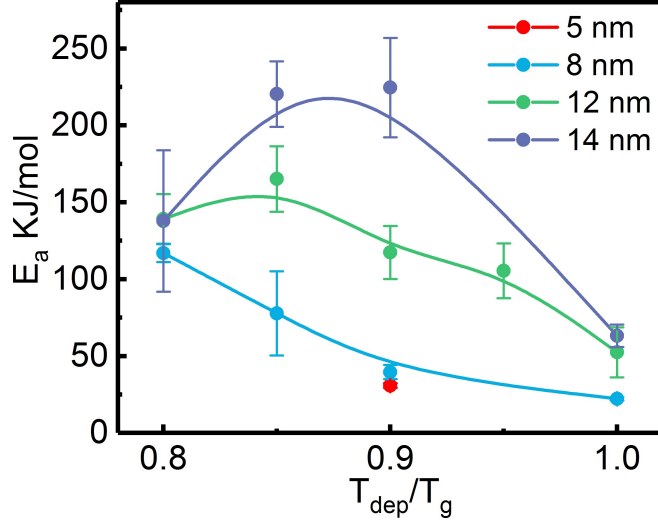


Figure 7.4: Apparent activation barrier evaluated from isothermal dewetting measurements for ultrathin TPD films deposited at different temperatures.

a deposition temperature dependence in stabilities. More importantly, we find that at such ultrathin film regime, the stabilities show a thickness dependence that are not observed in thick stable glass films. For example, the 8 nm stable glasses show a monotonic trend in activation barrier increase with deposition temperature decrease while 14 nm PVD films start to show a non-monotonic trend, it is possible that the overall mobility in 8 nm films are greater than 14 nm films and thus the non-monotonic trend shifts to much lower deposition temperatures. The activation barrier differences observed here in ultrathin PVD films at deposition temperatures that makes ultrastable thick PVD glasses are promising approaches in understanding the early stage stability buildup and forming mechanism of ultrastable glasses from PVD.

However, the preliminary results presented here still have multiple sources of potential errors: (1) The thermal histories of taking these as-deposited ultrathin PVD films out of vacuum chamber may matter and they are not considered in the preliminary measurements, potential aging or rejuvenation may be possible due to their enhanced relaxation dynamics; In the future, *in situ* measurements are needed to exclude such effects. (2) At some of the higher isothermal holding temperatures, the stability in some of the ultrathin films

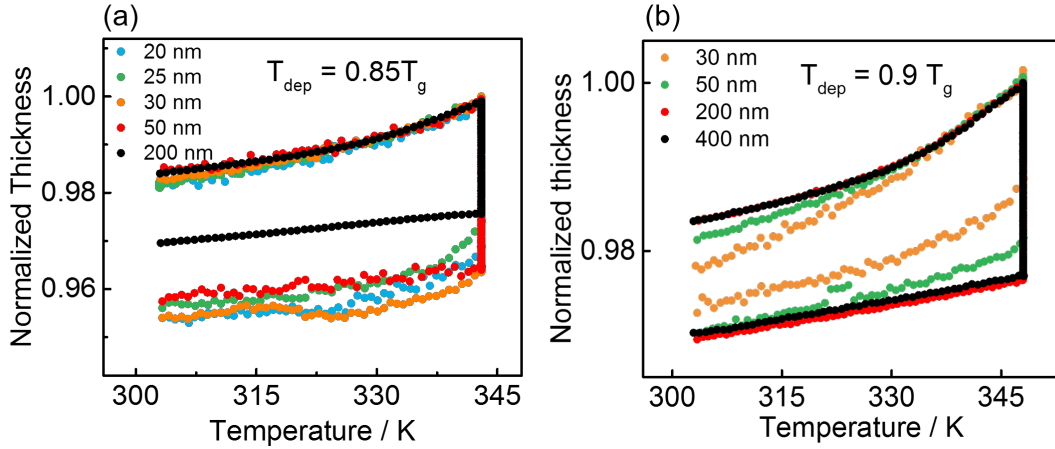


Figure 7.5: (a) Normalized thickness versus temperature upon heating and cooling of various thickness TPD films deposited at $0.85T_g$ with a deposition rate of 0.02 nm/s. (b) Normalized thickness versus temperature upon heating and cooling of various thickness TPD films deposited at $0.9T_g$ with a deposition rate of 0.02 nm/s.

may also be erased/transformed due to their low film T_g s. Thus the isothermal dewetting measurements may not be the best approach in ultrathin PVD film stability determination. In order to have more accurate understanding of these ultrathin film stabilities more careful future measurements are needed.

7.3.3. Stability and density increase in ultrathin PVD films

For ultrathin TPD films vapor deposited on silicon substrates with thicknesses ranging from 20 nm to 50 nm, we also observed interesting thickness dependent density increase in these ultrathin stable glasses. We note that in reported studies on thick stable glasses ($h > 100$ nm), no thickness-dependent stability is observed. For ultrathin films that are below 50 nm, they are in the nanoconfined thickness regime, where the overall dynamics are enhanced and glass transition temperatures are reduced compared to bulk values. It is interesting that when the thickness of PVD films is decreased to such nano-confinement thickness range, the vapor deposited glasses on silicon substrates start to show a thickness dependent stability.

Figure 7.5 shows an example of various thickness ultrathin TPD glasses prepared by PVD at substrate temperatures of $0.85T_g$ and $0.9T_g$. The normalized thickness measured from

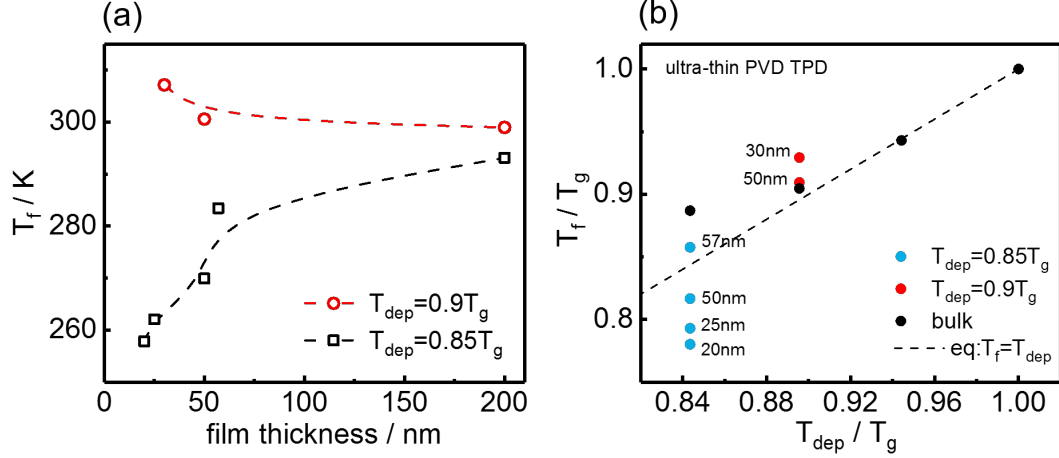


Figure 7.6: (a) Fictive temperature versus film thickness at deposition temperatures of $0.85T_g$ and $0.9T_g$. (b) Normalized fictive temperature versus normalized deposition temperature relative to bulk T_g for ultrathin glasses (colored symbols) and thick glasses (black symbols). The black dashed line is the equilibrium line where fictive temperature equals deposition temperature.

ellipsometry is plotted versus temperature upon heating and cooling ramps on these PVD glasses. In Figure 7.5(a), the preliminary data shows that when deposited at a substrate temperature of $0.85T_g$ films with thickness below 50 nm have greatly increased density when compared to thick 200 nm film. The density increases in ultrathin films below 50 nm can reach 2.8% while the density increase in bulk 200 nm is about 1.4%. The good overlap of the transformed supercooled liquids validates the ellipsometry fit to the ultrathin PVD glasses. Similar observations have been reported in Ref.[78], a 4 nm PVD ultrathin toluene glass exhibited a much higher thermodynamic stability with lower fictive temperature and a lower kinetic stability with lower onset temperature than the bulk PVD toluene glass at deposition temperature of $0.8T_g$. The huge increase in the density of as-deposited ultrathin glasses is surprising and may suggest that there is accelerated aging rates[128] in these ultrathin PVD glasses that result in such high density in as-deposited PVD films. In Figure 7.5(b), however, when we increase the deposition temperature from $0.85T_g$ to $0.9T_g$ the trend reverses, ultrathin PVD glasses have less density increase than the bulk PVD glasses. The trend reverse may be related to the reduced glass transition temperatures of ultrathin

glasses that make $0.9T_{g,bulk}$ not the optimal deposition temperature for achieving high stabilities. The exact reason of such trend reverse still needs further investigation.

To present the thickness dependent stability in a clearer way, the fictive temperature (T_f) of each PVD glass is evaluated as the intercept of supercooled liquid line and the as-deposited glassy line and is plotted as a function of film thickness for two deposition temperatures as shown in Figure 7.6(a). For glasses deposited at $0.85T_g$, fictive temperature decreases with film thickness decrease, indicating more efficient aging in ultrathin PVD glasses at this temperature. When deposited at $0.9T_g$, the fictive temperature increases with film thickness decrease, suggesting less amount of aging in ultrathin glasses. In Figure 7.6(b), the fictive temperature is scaled with bulk T_g and plotted versus scaled deposition temperature. The black symbols are bulk PVD glasses and the black dashed line is the equilibrium line where the fictive temperature equals the deposition temperature. Consistent with various previous studies, at deposition temperatures close to bulk T_g , the bulk PVD glass follows the equilibrium line indicating sufficient aging towards equilibrium during the deposition at high temperatures. When the deposition temperature is decreased below $0.9T_g$, the bulk PVD glasses start to deviate from the equilibrium line suggesting that at lower deposition temperatures the slow kinetics prevent the system from efficient aging towards equilibrium. However, we observed surprising results on ultrathin PVD glasses shown as colored symbols in the plot. Blue data points are ultrathin glasses deposited at $0.85T_g$, surprisingly we find that when the film thickness is decreased from 57 nm to 20 nm, they gradually bypass the equilibrium line. Red data points are ultrathin glasses deposited at $0.9T_g$, when the film thickness is decreased, the ultrathin glasses move further away from the equilibrium line. And here we note that even if we scale the fictive temperature relative to the thin film T_{gs} , the observation of bypassing equilibrium line is still obvious except some slight shift of the data points. The observations that the ultrathin PVD glasses go beyond the equilibrium line is really surprising and worth more careful studies.

The preliminary data presented here motivates future studies on questions of: (1) What

is the cause of enhanced density increase in ultrathin PVD glasses at low deposition temperature? Does this relate to the accelerated aging rates in ultrathin glasses? And how does it relate to the stable glass formation? (2) What is the nature of the bypassing of equilibrium line in ultrathin PVD glasses? Do ultrathin glasses share the same equilibrium line as bulk glasses or is there a new phase towards which the ultrathin glasses age? (3) What is the relation between the ultrathin PVD glass stability deviation from bulk PVD glass and the reduced ultrathin film T_g ? (4) Do the substrate also play an important role in the observations above? As the molecule we studied here TPD has a repulsive interaction with silicon substrate, is it possible that the silicon substrates somehow also accelerate the aging rates in ultrathin glasses? (5) What about the accuracy of the determination of the as-deposited ultrathin PVD glassy line using ellipsometry? Is there any artifact in the thickness modeling due to rich morphological features in ultrathin films?

In order to elucidate some of the above questions, a few experiments can be done: (a) A much more detailed thickness and deposition dependence study needs to be performed to elucidate the thickness range where the stability deviation happens and the deposition temperature's effect on ultrathin PVD glass stability. (b) Use other types of substrates and test the effect of substrate interface on the stability of ultrathin PVD glasses. (c) Perform studies on other organic molecules and test if this is a general case. (d) Perform aging studies on ultrathin glasses at temperatures similar to deposition temperatures and try to correlate physical aging rate with stability generated from PVD. Hopefully such studies can shed light on the forming mechanism of stable PVD glasses from the aspect of ultrathin glasses.

7.3.4. Surface spinodal instability in ultrathin PVD films

In addition to the thickness dependent density increase in ultrathin TPD stable glasses, we also observed surprising surface spinodal instability in the morphology evolution of ultrathin TPD stable glasses (8 nm - 20 nm) that initially fully covered the silicon substrates and then undergo intriguing surface morphological evolutions. We observed three distinct regimes

of the surface evolution. (1) The ultrathin TPD films prepared at temperatures below bulk T_g have initially rough morphologies resulting from the deposition process, the initial deposition resulted roughness will be smoothened out with time mostly due to fast surface diffusion. (2) After the smoothening of the initial roughness, we observe a spontaneous uniform spinodal roughening of the surface. (3) After some period of surface undulation growth, depending on the temperature and the total film thickness, the film either grows holes and dewets or the roughness decays in a very slow rate, possibly due to a competition between ultrathin film instability and surface diffusion, or there exist some form of aging in the underneath layers that prevent further dewetting. In the following, we are going to present the temporal morphology evolution of a 8 nm TPD film deposited at $0.8T_g$ held at 303 K as a representative example of the observed surface spinodal instability phenomena.

Figure 7.10 (c) shows the roughness change of this sample isothermally held at 303 K up to 500 min, time zero was defined as the end of deposition. There is an obvious roughness drop at the beginning of the isothermal hold, the surface smoothening regime is colored in green. Figure 7.7 shows the AFM topography images of the initial flattening process of the as-deposited film, insets show the Fast Fourier Transform (FFT) of the topography. The left image taken at 49 min after the deposition still shows some roughness from the deposition process and the FFT shows a ring-like pattern indicative of a characteristic wavelength existing in the morphology. The initial rough morphology is mostly coming from the first few layer dewetting mediated rough template for later depositions. And the smoothening of the as-deposited morphology is driven by curvature gradients from the roughness and the flow towards flattening is mostly mediated by fast surface diffusion. As at 82 min, the surface is mostly flat, with a root mean square (RMS) roughness less than 0.5 nm. And the FFT image no longer shows a ring-like pattern.

The most striking and surprising morphological evolution feature is the spontaneous roughening that follows the initial surface smoothening described above, as indicated by the rapid increase of roughness in Figure 7.10(c) colored in blue. Figure 7.8 shows three of the rep-

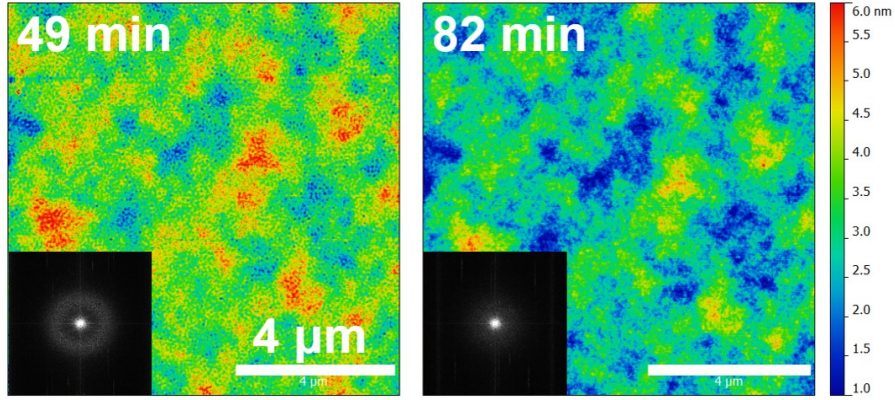


Figure 7.7: AFM topography images of a 8 nm TPD film deposited at $0.8T_g$ with a deposition rate of 0.02 nm/s, this film was held at 303 K. Insets show fast Fourier transform (FFT) pattern of each image.

representative AFM images of the roughening process, where rough features start to emerge spinodal patterns and the height fluctuations grow with time. The roughness increase in this regime can be fit to an exponential growth with a slowing down of roughness that deviate from the exponential growth at around $t_d = 230$ min, the exponential fit is shown as blue dashed line in Figure 7.10(c). After an exponential growth in the amplitude surface undulations, the increase slows down as indicated in the yellow regime. The corresponding AFM images in Figure 7.9 shows a less pronounced amplitude growth in the surface undulations but a more apparent lateral growth of the surface waves. The insets shows the FFT of the corresponding topography images, the ring-like pattern becomes more prominent with the size decreasing, indicative of a growing lateral length scale of the surface undulations.

Here we use the Linearized capillary wave instability model[150] to describe the morphology evolution we observed in ultrathin stable glasses. This model describes the evolution of the capillary instability induced by thermal fluctuations in ultrathin films. Equation 7.1 shows the growth of surface undulation $Z(x, t)$ at time t and the early stage exponential growth of fluctuation amplitude of δh , where in this equation h is the film thickness, q is the wave vector and R is the growth rate. At early stage, the amplitude of the surface fluctuation will increase exponentially with a time independent characteristic wave vector q_M in the

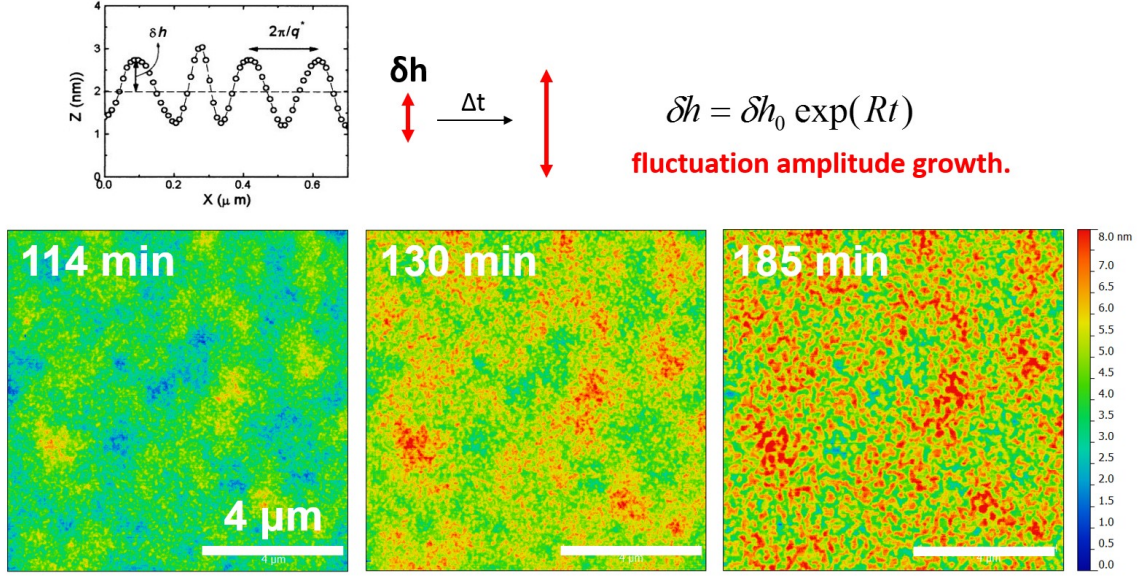


Figure 7.8: AFM topography images of 8 nm TPD film deposited at $0.8T_g$ with deposition rate of 0.02 nm/s, this film was held at 303 K.

morphology, the relation between q_M and fluctuation growth rate R_M at this stage is shown in Equation 7.2. Where γ is the surface tension and η is the viscosity.

$$Z(x, t) = h + \delta h \exp(iqx), \quad \delta h = \delta h_0 \exp(Rt) \quad (7.1)$$

$$q_M = \sqrt{3/2}(a/h^2) = q_c/\sqrt{2}, \quad R_M = 3\gamma a^4/4\eta h^5 \quad (7.2)$$

Fast Fourier Transform was applied on each AFM image and the radial averaging distribution of the FFT image was evaluated. The relative intensity was plotted versus wave vector for each time point imaged in Figure 7.10 (b). A characteristic wave vector q_M can be evaluated as the peak position at each time point. The characteristic wave vector shifts towards lower values with isothermal hold time, indicating an increase in the length scale of surface instability patterns. $\log q_M$ is plotted versus $\log t$ as shown in Figure 7.10 (d), there are two distinct process. The blue regime corresponds to the early stage of the spinodal

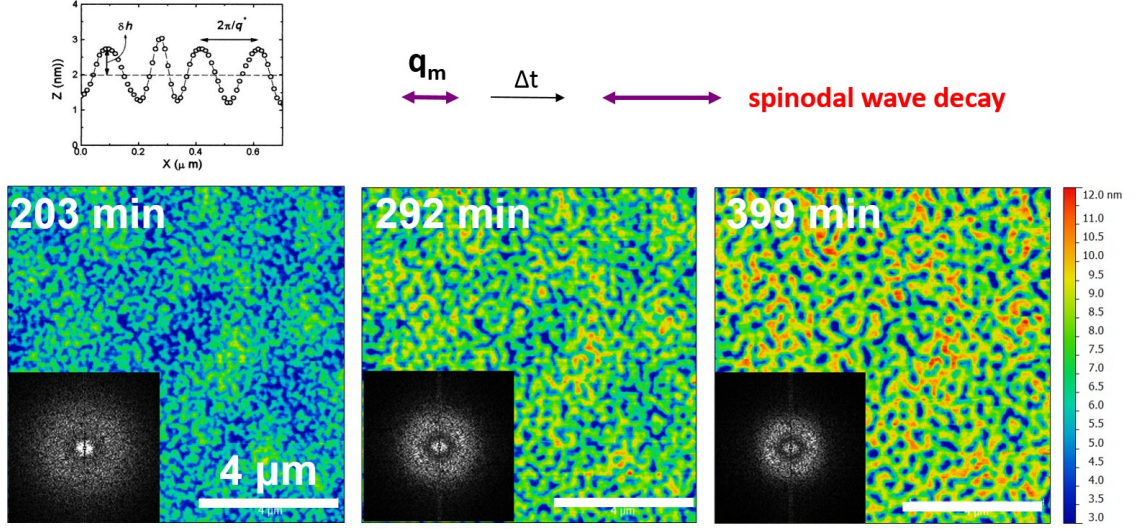


Figure 7.9: AFM topography images of 8 nm TPD film deposited at $0.8T_g$ with deposition rate of 0.02 nm/s, this film was held at 303 K.

instability show nearly time independent q_M with a power law of 0.06, in this regime the dominating mode is the growth of the amplitude of the surface waves with nearly constant characteristic wave vector. In the late stage of the surface instability observed, the dominating mode is the lateral decay of the surface waves or the increase in the characteristic wave vector q_M . As indicated by the yellow regime in Figure 7.10 (d), q_M decays as a function of time with a power law of 0.38, consistent with late stage spinodal decay with a power law of $1/3$ [150]. The transition time t_d from early stage amplitude growth to the late stage wave decay is also consistent with the deviation time of the height fluctuation exponential growth independently evaluated from the roughness change in Figure 7.10 (c), suggesting the validity of the linearized capillary wave instability model.

In order to further test the linearized capillary wave instability model, we compare the 8 nm film morphological instability shown above with another film thickness 12 nm deposited at $0.8T_g$ and isothermally held at the same temperature 303 K. Figure 7.11 shows the temporal evolution of the RMS roughness and the characteristic wave vector in the film, the evolution is qualitatively consistent with what we have observed in the 8 nm film with an early stage amplitude growth and a late stage wave decay. According to Equation 7.2,

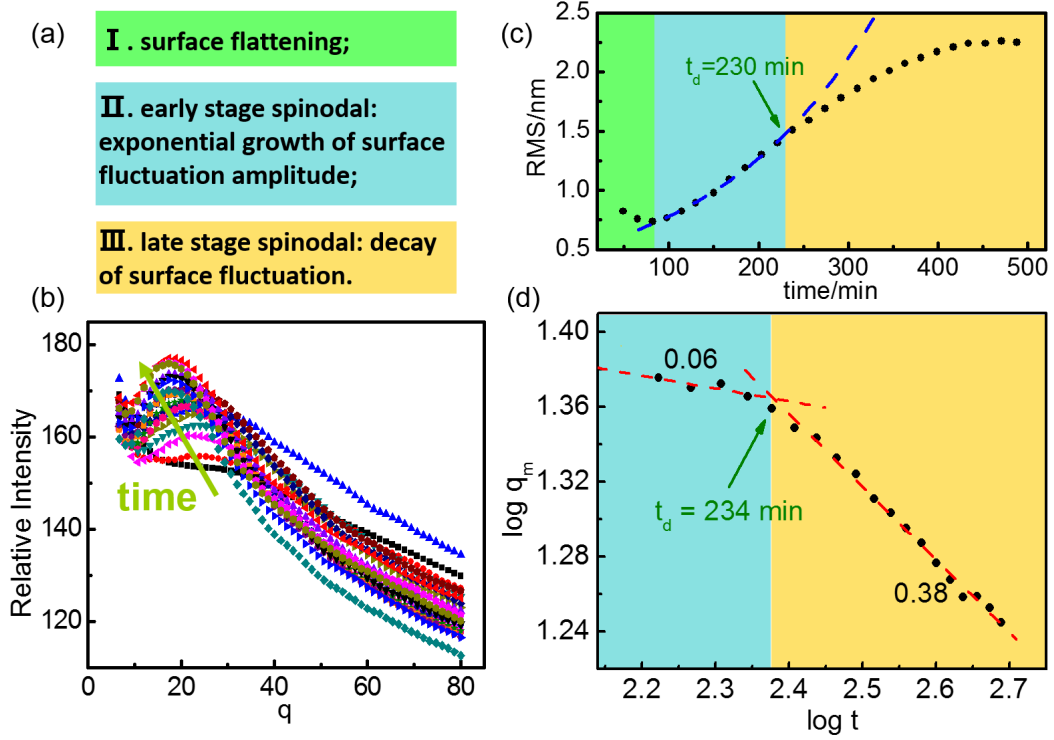


Figure 7.10: (a) The three regimes observed in a 8 nm deposited at $0.8T_g$. (b) The temporal evolution of relative intensity versus wave vector evaluated from the FFT of AFM topography for each time point imaged, green arrow shows the direction of change with isothermal holding time. (c) The RMS roughness of the morphology versus isothermal hold time, each regime colored coded represents each morphological evolution stage as described in (a). The blue dashed line is an exponential fit to the growth of surface roughness or surface undulation. (d) The log-log plot of characteristic wave vector q_M versus time representing the early stage and late stage of the surface spinodal evolution, color codes of each regime consistent with (a) and (c).

in the early stage the time independent characteristic wave vector q_M is only dependent on the film thickness, and one would expect $q_M(h_1)/q_M(h_2) = h_2^2/h_1^2$. From Figure 7.10 and Figure 7.11, we can estimate $q_M(h_1)/q_M(h_2) = 1.32$. From AFM data volume analysis, the $h_2^2/h_1^2 = 1.83$, roughly matches the ratio of q_M , suggesting that the linearized capillary wave instability model fits the surface spinodal instability we observed in these ultrathin stable glass films. We have also investigated several other films and observed similar surface spinodal instabilities. However, at late stages of the surface instabilities, the films either grow holes and dewet or the surface roughness induced from the surface spinodal instability very slowly recovers back to smooth, as already evidenced in Figure 7.11 at around 1000 min of isothermal holding time. The early stage spinodal instability can be explained by the ultrathin nature of the film thickness and the long range interaction of air and substrate tends to dewet the ultrathin film and cause the surface instability. However, the very last stage of the smoothening of the instability induced from early stage is not very well understood, in the situation that we observed here, we also need to consider the possible existence of an underlying very stable or very aged layer from vapor deposition that is preventing the hole nucleations and thus prevents dewetting. It's also worth noting that the maximum surface undulation amplitude of all the ultrathin films investigated falls between 2-3 nm. We hypothesize the possibility that the very surface mobile layer somehow decouples from the underneath stable layer and the surface spinodal instability we measured is driven by the long range interaction of air/substrate and mediated by the very first few layers near the free surface, this may explain why the amplitude of the surface instability growth can only reach as deep as 3 nm. However, the exact mechanism of these surprising morphological evolution worth more careful further measurements and modeling.

If we only focus on the early stage of the surface spinodal instability, according to Equation 7.2, the viscosity that is mediating the surface instability can be expressed in terms of early stage characteristic wave vector q_M and exponential growth rate of the amplitude R_M as $\eta = \gamma q_M^4 h^3 / 3 R_M$. We can calculate the viscosity that is mediating the early stage instability in all the films that we have investigated and the results are shown in Figure

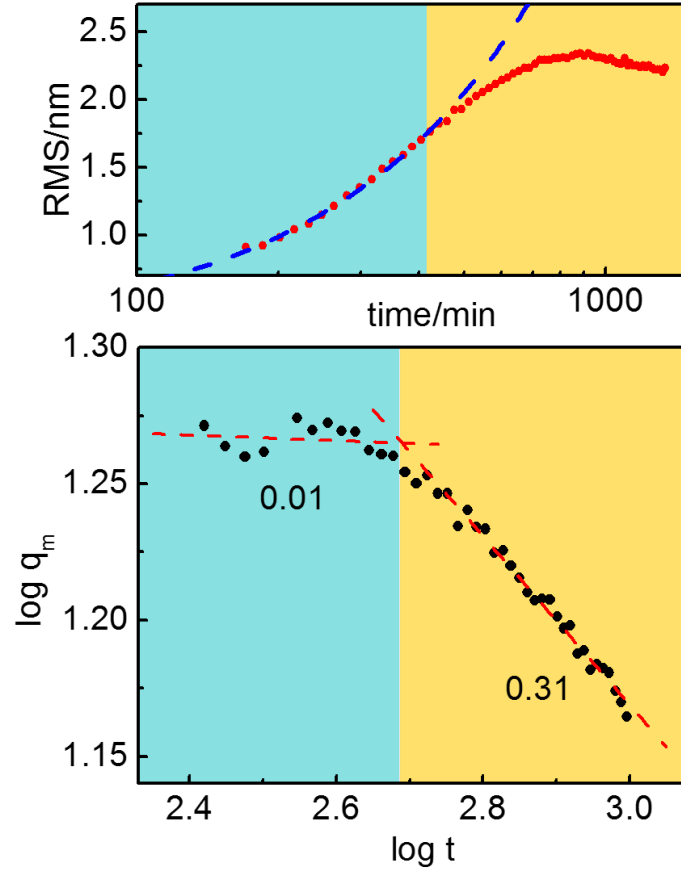


Figure 7.11: The surface spinodal instability in a 12 nm TPD film deposited at $0.8T_g$ isothermally held at 303 K. Top: The temporal evolution of RMS roughness. Bottom: The log-log plot of characteristic wave vector q_M versus time.

7.12. It's interesting to notice that at 303 K the viscosities calculated on different films are very similar and are greatly enhanced than the bulk value. There can be two explanations for this result: (1) The viscosity that is calculated from the surface spinodal instability is the effective viscosity of the entire film, while the thickness range studied here only ranges from 8 nm - 14 nm, it is possible that the effective viscosity of these films does not vary much[161]. (2) The viscosity calculated here corresponds to the viscosity of the very first few layers that show surface spinodal instability which is the first 2 - 3 nm top layers, or the viscosity calculated here can be referred as surface viscosity. In this sense, the invariance of the surface viscosity on different film thickness is reasonable. From our current preliminary data, it's not clear which one is more accurate, but the fact that the surface instability does not exceed 3 nm and the extent of the enhancement of the viscosity in Figure 7.12 compared to bulk matches the extent of the surface diffusion enhancement are important factors to consider. It will be very useful to have a more systematic study of the temperature dependence, thickness dependence, as well as the deposition temperature dependence of the surface spinodal instability phenomenon in these ultrathin stable glasses. It is also necessary to measure the ultrathin stable glasses of other organic molecules to test the generality of such phenomenon. In the case of TPD molecule here, if we hold the film at a slightly higher temperature of 308 K, the surface evolution will be too fast to capture as shown in the example of Figure 7.13, one would observe the three regimes in one single AFM image while it typically takes 15 min to obtain one AFM image. In order to avoid such imaging challenge, a higher T_g molecule can be used.

7.4. Summary and Future Directions

To summarize, in this chapter I have presented some interesting preliminary observations in ultrathin PVD glasses and they are consistent in some ways. For ultrathin PVD glasses with thickness range of 5 nm - 14 nm, isothermal dewetting measurements were performed and the apparent activation energies for dewetting are found to be dependent on the deposition temperatures, suggesting the possibility of stable portion formed in these ultrathin

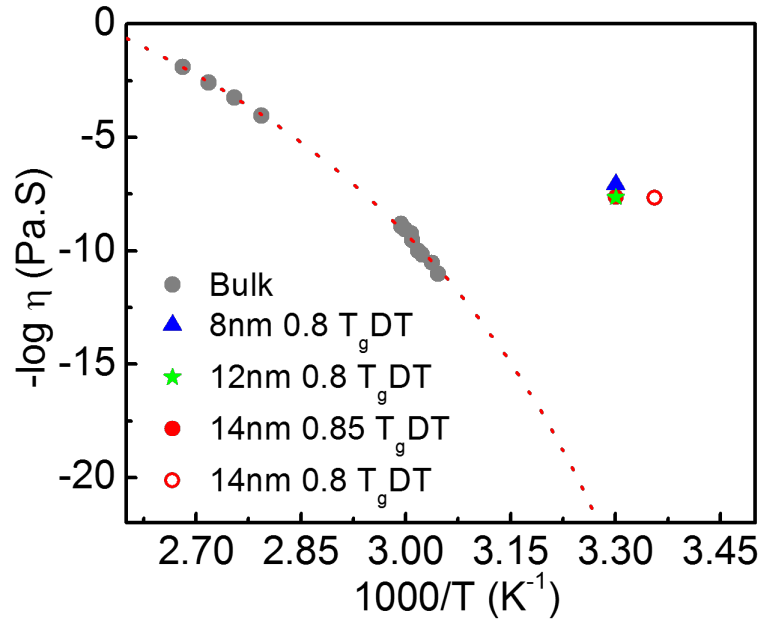


Figure 7.12: The viscosity calculated using linearized capillary wave model on different films (colored symbols) plotted together with bulk viscosity (grey symbols) measured from bulk rheology and shifted bulk CR-T_g data versus inverse temperature.

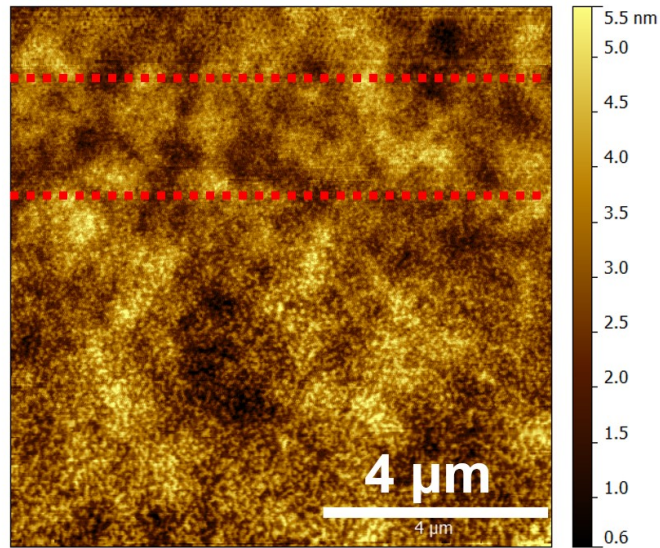


Figure 7.13: The surface evolution of a 8 nm TPD film deposited at 0.8T_g held isothermally at 308 K, the red dashed lines mark the changes in the morphology in one AFM image, from as-deposited rough to smooth to surface spinodal rough again.

glasses during PVD. Ellipsometry thickness measurements were performed on ultrathin PVD glasses with thickness range of 20 nm - 60 nm, where for two deposition temperatures studied, the stabilities of these ultrathin PVD glasses were found to be dependent on the film thickness and such thickness dependence is absent in thick PVD glasses. More strikingly, the ultrathin PVD glasses deposited at low temperatures bypass the equilibrium line and show extremely high thermodynamic stabilities. Lastly, interesting morphological evolutions were observed in ultrathin stable glasses with thickness range of 8 nm - 20 nm. The complex surface instabilities observed in these ultrathin PVD glasses can be qualitatively described with linearized capillary wave instability model and the viscosity that is mediating the surface instability can be calculated and is found to be greatly enhanced than bulk viscosity. Three different types of measurements all suggest that ultrathin PVD glasses have very rich features that may guide the understanding of the formation mechanism for stable PVD glasses. Future studies can focus on these ultrathin thickness regime in order to understand the origin of stable glasses by PVD and possibly suggest ways to make stable glasses with another approach in addition to PVD.

CHAPTER 8 : Summary and Outlook

Here we give a short summary of this thesis as well as some future directions in related research area. The theme of this thesis is to investigate the enhanced dynamics on the surfaces of small molecule organic glasses and the propagation of the free surface induced enhancement in dynamics, and we are interested in the relation between the free surface enhancement and the stable glass formation by physical vapor deposition. In Chapter 2, we first developed a novel technique that use tobacco mosaic virus as a probe to directly measure surface diffusion on liquid-quenched molecular glasses. The surface diffusion on liquid-quenched glasses is orders of magnitude enhanced than bulk diffusion with a weaker temperature dependence. In Chapter 3, we investigated the surface diffusion on stable PVD glasses and physically aged glasses with bulk dynamics suppressed by as large as 13-20 orders of magnitude than liquid-quenched glasses, the results show that the surface diffusion remains fast and invariant on these stable and aged glasses despite the slowing down of the overall dynamics. In Chapter 4, we further investigated the surface diffusion on ultrathin molecular glasses with overall enhanced dynamics that are more similar to the surface enhancement to understand the origin of the invariance of surface diffusion observed on suppressed dynamics. Again, the surface diffusion is found to be independent of ultrathin film thickness where the overall dynamics have been enhanced by 6-14 orders of magnitude. The results from Chapter 2-4 suggest that the surface diffusion on molecular glasses is decoupled from bulk relaxation dynamics and only reflect the lateral diffusion at the free surface. The invariance surface diffusion on glasses of varying bulk dynamics cannot fully explain the formation of stable glasses with varying bulk stabilities by PVD. In the future work, it's interesting to test the relationship between surface diffusion and surface relaxation times, novel techniques need to be developed to probe the latter. As surface diffusion probed using TMV technique mostly comes from the lateral in-plane surface molecular motions, it's important to also develop ways to probe the out-of-plane surface molecular motions and compare the two. In addition, since the surface diffusion is only

dependent on the nature of the molecule investigated, it would be necessary to establish the detailed relationship between surface diffusion and molecule properties, such as size and intermolecular interactions, thus a systematic design of small organic molecules and study of surface diffusion are needed to elucidate the detailed relationships.

In Chapter 5, we combined isothermal dewetting measurements and cooling-rate dependent glass transition temperature measurements to investigate the propagation depth of the surface enhancement effect. As the film thickness is decreased in molecular glasses, the overall film relaxation time or the effective film viscosity decreases, with weaker temperature dependence or a smaller apparent activation barrier for rearrangement. The result also showed a sharp transition in the activation barrier when the film thickness is decreased below 30 nm, indicating long-range correlated dynamics in ultrathin molecular glasses. In Chapter 6, we also investigate the effect of the substrate interface on the propagation depth of free surface enhancement. We find that by changing the film/substrate interaction from repulsive nature to neutral nature, we still observed a sharp transition in the thickness dependent activation barrier with the transition length-scale happening around 30 nm. The increase in the film/substrate interaction didn't change the propagation depth of the surface effect, however it increased the lower limit of the activation barrier of ultrathin films in the transition. Results on polymer glasses in our lab also observed a transition happening near 30 nm for several systems, with slightly smoother transitions in polymeric systems. It's important to question and investigate the origin of this long-range correlation in the dynamics in thin glassy film systems. And studies to connect the experimental observation and glass theories or simulations are also necessary in elucidating the long-range correlated dynamics. In future studies, we can systematically decrease the molecular weight of the polymers and test the transition shapes to see if the transition is in any way related to the size or the intermolecular nature of the system studied. Also, inorganic or metallic glasses can also be investigated to test the generality of the transition and the nature of the length-scale of the transition.

In Chapter 7, we presented some of the interesting preliminary results observed in ultrathin stable PVD glasses with thicknesses below 50 nm. We observed thickness dependent stability in these ultrathin PVD glasses and the behavior is highly dependent on the deposition temperatures. We also observed interesting spontaneous morphological evolutions in these ultrathin stable glasses that can provide a potential way of characterizing near surface viscosity. It's interesting to observed many rich behaviors in ultrathin stable glasses, which may provide important evidence and new directions of understanding the complete formation mechanism of stable glasses. If the intermediate layer right underneath the free surface layer plays an important role in stable glass formation, then the rich behaviors observed in these ultrathin stable glasses are important steps in understanding the problem. In future studies, repeating measurements need to be done to confirm the preliminary results observed in Chapter 7, and more systematic studies can be performed including change of molecules, dependence of ultrathin films stabilities on deposition temperature and rate. More studies have to be done to understand the surface evolution in ultrathin stable glasses. Eventually, it's important to gain insights from the principle and the mechanism of physical vapor deposition and find another route to prepare stable glasses.

BIBLIOGRAPHY

- [1] M. D. Abràmoff, P. J. Magalhães, and S. J. Ram. Image processing with imageJ. *Biophotonics Int.*, 11(7):36–41, 2004. ISSN 10818693. doi: 10.1117/1.3589100.
- [2] G. Adam and J. H. Gibbs. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *The journal of chemical physics*, 43(1):139–146, 1965.
- [3] T. Ala-Nissila, R. Ferrando, and S. Ying. Collective and single particle diffusion on surfaces. *Advances in Physics*, 51(3):949–1078, 2002.
- [4] M. Alcoutlabi and G. B. McKenna. Effects of confinement on material behaviour at the nanometre size scale. *Journal of Physics: Condensed Matter*, 17(15):R461, 2005.
- [5] S. Alexandris, P. Papadopoulos, G. Sakellariou, M. Steinhart, H.-J. Butt, and G. Floudas. Interfacial energy and glass temperature of polymers confined to nanoporous alumina. *Macromolecules*, 49(19):7400–7414, 2016.
- [6] M. Arndt, R. Stannarius, W. Gorbatschow, and F. Kremer. Dielectric investigations of the dynamic glass transition in nanopores. *Physical Review E*, 54(5):5377, 1996.
- [7] R. R. Baglay and C. B. Roth. Communication: Experimentally determined profile of local glass transition temperature across a glassy-rubbery polymer interface with a t_g difference of 80 K, 2015.
- [8] R. R. Baglay and C. B. Roth. Local glass transition temperature $t_g(z)$ of polystyrene next to different polymers: Hard vs. soft confinement. *The Journal of Chemical Physics*, 146(20):203307, 2017.
- [9] U. Bengtzelius, W. Gotze, and A. Sjolander. Dynamics of supercooled liquids and the glass transition. *Journal of Physics C: solid state Physics*, 17(33):5915, 1984.
- [10] M. Benzaquen, P. Fowler, L. Jubin, T. Salez, K. Dalnoki-Veress, and E. Raphaël. Approach to universal self-similar attractor for the levelling of thin liquid films. *Soft Matter*, 10(43):8608–14, 2014.
- [11] L. Berthier and M. D. Ediger. Facets of glass physics. *Physics today*, 69(1):40–46, 2016.
- [12] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L’Hôte, F. Ladieu, and M. Pierno. Direct experimental evidence of a growing length scale accompanying the glass transition. *Science*, 310(5755):1797–1800, 2005.
- [13] C. W. Brian, L. Zhu, and L. Yu. Effect of bulk aging on surface diffusion of glasses. *J. Chem. Phys.*, 140, 2014. ISSN 00219606. doi: 10.1063/1.4863556.

- [14] E. Buck, K. Petersen, M. Hund, G. Krausch, and D. Johannsmann. Decay kinetics of nanoscale corrugation gratings on polymer surface: evidence for polymer flow below the glass temperature. *Macromolecules*, 37(23):8647–8652, 2004.
- [15] M. J. Burroughs, S. Napolitano, D. Cangialosi, and R. D. Priestley. Direct measurement of glass transition temperature in exposed and buried adsorbed polymer nanolayers. *Macromolecules*, 49(12):4647–4655, 2016.
- [16] S. Butler and P. Harrowell. Glassy relaxation at surfaces: The correlation length of cooperative motion in the facilitated kinetic Ising model. *J. Chem. Phys.*, 95(6):4466, Sept. 1991. ISSN 00219606. doi: 10.1063/1.461769.
- [17] S. Butler and P. Harrowell. Glassy relaxation at surfaces: The correlation length of cooperative motion in the facilitated kinetic Ising model. *The Journal of chemical physics*, 95(6):4466–4470, 1991.
- [18] C. Cammarota and G. Biroli. Ideal glass transitions by random pinning. *Proceedings of the National Academy of Sciences*, 109(23):8850–8855, 2012.
- [19] S. Capaccioli, K. L. Ngai, M. Paluch, and D. Prevosto. Mechanism of fast surface self-diffusion of an organic glass. *Phys. Rev. E.*, 86:051503, 2012.
- [20] S. Capponi, S. Napolitano, N. R. Behrnd, G. Couderc, J. Hulliger, and M. Wubbenhorst. Structural Relaxation in Nanometer Thin Layers of Glycerol. *J. Phys. Chem. C*, 114:16696–16699, 2010.
- [21] Y. Chai, T. Salez, J. D. McGraw, M. Benzaquen, K. Dalnoki-Veress, E. Raphaël, and J. A. Forrest. A direct quantitative measure of surface mobility in a glassy polymer. *Science*, 343:994–999, 2014. ISSN 1095-9203. doi: 10.1126/science.1244845.
- [22] D. Chandler and J. P. Garrahan. Dynamics on the way to forming glass: bubbles in space-time. *Annu. Rev. Phys. Chem.*, 61:191–217, 2010.
- [23] Y. Chen, W. Zhang, and L. Yu. Hydrogen bonding slows down surface diffusion of molecular glasses. *The Journal of Physical Chemistry B*, 2016.
- [24] Y. Chua, M. Ahrenberg, M. Tyllinski, M. Ediger, and C. Schick. How much time is needed to form a kinetically stable glass? ac calorimetric study of vapor-deposited glasses of ethylcyclohexane. *J. Chem. Phys.*, 142(5):054506, 2015.
- [25] Y. Z. Chua, M. Ahrenberg, M. Tyllinski, M. D. Ediger, and C. Schick. How much time is needed to form a kinetically stable glass? AC calorimetric study of vapor-deposited glasses of ethylcyclohexane. *J. Chem. Phys.*, 142(5):054506, 2015. ISSN 0021-9606. doi: 10.1063/1.4906806.
- [26] M. T. Cicerone and M. D. Ediger. Enhanced translation of probe molecules in supercooled o-terphenyl: Signature of spatially heterogeneous dynamics? *J. Chem. Phys.*, 104(18):7210–7218, 1996.

- [27] M. T. Cicerone, F. Blackburn, and M. Ediger. How do molecules move near T_g ? molecular rotation of six probes in o-terphenyl across 14 decades in time. *The Journal of chemical physics*, 102(1):471–479, 1995.
- [28] D. Q. M. Craig, P. G. Royall, V. L. Kett, and M. L. Hopton. The relevance of the amorphous state to pharmaceutical dosage forms: Glassy drugs and freeze dried systems. *Int. J. Pharm.*, 179:179–207, 1999. doi: 10.1016/S0378-5173(98)00338-X.
- [29] S. S. Dalal and M. Ediger. Molecular orientation in stable glasses of indomethacin. *The journal of physical chemistry letters*, 3(10):1229–1233, 2012.
- [30] S. S. Dalal, A. Sepúlveda, G. K. Pribil, Z. Fakhraai, and M. Ediger. Density and birefringence of a highly stable α , α , β -trisnaphthylbenzene glass. *The Journal of chemical physics*, 136(20):204501, 2012.
- [31] S. S. Dalal, Z. Fakhraai, and M. Ediger. High-throughput ellipsometric characterization of vapor-deposited indomethacin glasses. *The Journal of Physical Chemistry B*, 117(49):15415–15425, 2013.
- [32] S. S. Dalal, Z. Fakhraai, and M. D. Ediger. High-throughput ellipsometric characterization of vapor-deposited indomethacin glasses. *J. Phys. Chem. B*, 117:15415–15425, 2013. ISSN 15206106. doi: 10.1021/jp405005n.
- [33] S. S. Dalal, D. M. Walters, I. Lyubimov, J. J. de Pablo, and M. Ediger. Tunable molecular orientation and elevated thermal stability of vapor-deposited organic semiconductors. *Proceedings of the National Academy of Sciences*, 112(14):4227–4232, 2015.
- [34] C. R. Daley, Z. Fakhraai, M. D. Ediger, and J. A. Forrest. Comparing surface and bulk flow of a molecular glass former. *Soft Matter*, 8(7):2206–2212, 2012. doi: 10.1039/c2sm06826e.
- [35] K. J. Dawson, K. L. Kearns, M. Ediger, M. J. Sacchetti, and G. D. Zografis. Highly stable indomethacin glasses resist uptake of water vapor. *The Journal of Physical Chemistry B*, 113(8):2422–2427, 2009.
- [36] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer. Stringlike cooperative motion in a supercooled liquid. *Physical review letters*, 80(11):2338, 1998.
- [37] M. Ediger and P. Harrowell. Perspective: Supercooled liquids and glasses. *The Journal of Chemical Physics*, 137(8):080901, 2012.
- [38] M. D. Ediger. Spatially heterogeneous dynamics in supercooled liquids. *Annual review of physical chemistry*, 51(1):99–128, 2000.
- [39] M. D. Ediger and J. A. Forrest. Dynamics near free surfaces and the glass transition

- in thin polymer films: A view to the future. *Macromolecules*, 47(2):471–478, 2014. ISSN 00249297. doi: 10.1021/ma4017696.
- [40] G. Ehrlich and K. Stolt. Surface diffusion. *Annual Review of Physical Chemistry*, 31(1):603–637, 1980.
 - [41] C. Ellison, S. Kim, D. Hall, and J. Torkelson. Confinement and processing effects on glass transition temperature and physical aging in ultrathin polymer films: Novel fluorescence measurements. *The European Physical Journal E: Soft Matter and Biological Physics*, 8(2):155–166, 2002.
 - [42] C. J. Ellison and J. M. Torkelson. The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nat. Mater.*, 2(10):695–700, 2003. ISSN 1476-1122. doi: 10.1038/nmat980.
 - [43] C. J. Ellison, M. K. Mundra, and J. M. Torkelson. Impacts of polystyrene molecular weight and modification to the repeat unit structure on the glass transition- nanoconfinement effect and the cooperativity length scale. *Macromolecules*, 38(5):1767–1778, 2005.
 - [44] Eötvös. *Annalen der Physik*, 27(448), 1886. ISSN 1098-6596.
 - [45] C. M. Evans, H. Deng, W. F. Jager, and J. M. Torkelson. Fragility is a key parameter in determining the magnitude of the g-confinement effects in polymer films. *Macromolecules*, 46(15):6091–6103, 2013.
 - [46] Z. Fakhraai and J. A. Forrest. Probing slow dynamics in supported thin polymer films. *Phys. Rev. Lett.*, 95(July):1–4, 2005. ISSN 00319007. doi: 10.1103/PhysRevLett.95.025701.
 - [47] Z. Fakhraai and J. A. Forrest. Measuring the surface dynamics of glassy polymers. *Science*, 319(5863):600–604, 2008. ISSN 1095-9203. doi: 10.1126/science.1151205.
 - [48] Z. Fakhraai, T. Still, G. Fytas, and M. D. Ediger. Structural variations of an organic glassformer vapor-deposited onto a temperature gradient stage. *J. Phys. Chem. Lett.*, 2:423–427, 2011. ISSN 19487185. doi: 10.1021/jz101723d.
 - [49] A. Farahzadi, P. Niyamakom, M. Beigmohamadi, N. Meyer, D. Keiper, M. Heuken, F. Ghasemi, M. R. Rahimi Tabar, T. Michely, and M. Wuttig. Stochastic analysis on temperature-dependent roughening of amorphous organic films. *EPL (Europhysics Lett.)*, 90(1):10008, 2010. ISSN 0295-5075.
 - [50] H. Fischer. Thermal probe surface treatment of a bulk polymer: Does a surface layer with a lower glass transition than the bulk exist? *Macromolecules*, 35(9):3592–3595, 2002.
 - [51] J. Forrest, K. Dalnoki-Veress, J. Stevens, and J. Dutcher. Effect of free surfaces on

- the glass transition temperature of thin polymer films. *Physical review letters*, 77(10):2002, 1996.
- [52] J. A. Forrest and K. Dalnoki-Veress. The glass transition in thin polymer films. *Adv. Colloid Interface Sci.*, 94:167–196, 2001. ISSN 00018686. doi: 10.1016/S0001-8686(01)00060-4.
 - [53] D. S. Fryer, R. D. Peters, E. J. Kim, J. E. Tomaszewski, J. J. de Pablo, P. F. Nealey, C. C. White, and W.-l. Wu. Dependence of the glass transition temperature of polymer films on interfacial energy and thickness. *Macromolecules*, 34(16):5627–5634, 2001.
 - [54] C. J. Fullerton and R. L. Jack. Investigating amorphous order in stable glasses by random pinning. *Physical review letters*, 112(25):255701, 2014.
 - [55] E. C. Glor and Z. Fakhraai. Facilitation of interfacial dynamics in entangled polymer films. *J. Chem. Phys.*, 141(19):194505, 2014. ISSN 0021-9606. doi: 10.1063/1.4901512.
 - [56] E. C. Glor, R. J. Composto, and Z. Fakhraai. Glass Transition Dynamics and Fragility of Ultrathin Miscible Polymer Blend Films. *Macromolecules*, 48(18):6682–6689, Sept. 2015. ISSN 0024-9297. doi: 10.1021/acs.macromol.5b00979.
 - [57] E. C. Glor, R. J. Composto, and Z. Fakhraai. Glass transition dynamics and fragility of ultrathin miscible polymer blend films. *Macromolecules*, 48(18):6682–6689, 2015.
 - [58] E. C. Glor, G. V. Angrand, and Z. Fakhraai. Exploring the broadening and the existence of two glass transitions due to competing interfacial effects in thin, supported polymer films. *The Journal of Chemical Physics*, 146(20):203330, 2017.
 - [59] P. J. Griffin, J. R. Sangoro, Y. Wang, A. P. Holt, V. N. Novikov, A. P. Sokolov, Z. Wojnarowska, M. Paluch, and F. Kremer. Dynamic crossover and the DebyeStokesEinstein relation in liquid N,N-diethyl-3-methylbenzamide (DEET). *Soft Matter*, 9(43):10373, 2013.
 - [60] E.-m. Han, L.-m. Do, Y. Niidome, and M. Fujihira. Observation of crystallization of vapor-deposited tpd films by afm and ffm. *Chemistry Letters*, (5):969–972, 1994.
 - [61] P. Z. Hanakata, J. F. Douglas, and F. W. Starr. Local variation of fragility and glass transition temperature of ultra-thin supported polymer films. *J. Chem. Phys.*, 137(24):244901, 2012.
 - [62] P. Z. Hanakata, J. F. Douglas, and F. W. Starr. Interfacial mobility scale determines the scale of collective motion and relaxation rate in polymer films. *Nat. Commun.*, 5:4163, 2014. doi: 10.1038/ncomms5163.
 - [63] B. C. Hancock and M. Parks. What is the true solubility advantage for amorphous pharmaceuticals? *Pharmaceutical research*, 17(4):397–404, 2000.

- [64] E. Hempel, G. Hempel, A. Hensel, C. Schick, and E. Donth. Characteristic length of dynamic glass transition near T_g for a wide assortment of glass-forming substances. *The Journal of Physical Chemistry B*, 104(11):2460–2466, 2000.
- [65] G. M. Hocky, T. E. Markland, and D. R. Reichman. Growing Point-to-Set Length Scale Correlates with Growing Relaxation Times in Model Supercooled Liquids. *Phys. Rev. Lett.*, 108(22):225506, June 2012. ISSN 0031-9007.
- [66] G. M. Hocky, T. E. Markland, and D. R. Reichman. Growing point-to-set length scale correlates with growing relaxation times in model supercooled liquids. *Physical review letters*, 108(22):225506, 2012.
- [67] I. Hodge. Effects of annealing and prior history on enthalpy relaxation in glassy polymers. 6. adam-gibbs formulation of nonlinearity. *Macromolecules*, 20(11):2897–2908, 1987.
- [68] S. Hutcheson and G. McKenna. Nanosphere embedding into polymer surfaces: A viscoelastic contact mechanics analysis. *Phys. Rev. Lett.*, 94(7):076103, 2005.
- [69] M. Ilton, D. Qi, and J. Forrest. Using nanoparticle embedding to probe surface rheology and the length scale of surface mobility in glassy polymers. *Macromolecules*, 42(18):6851–6854, 2009.
- [70] C. L. Jackson and G. B. McKenna. The glass transition of organic liquids confined to small pores. *Journal of Non-Crystalline Solids*, 131:221–224, 1991.
- [71] K. L. Kearns, S. F. Swallen, M. Ediger, T. Wu, and L. Yu. Influence of substrate temperature on the stability of glasses prepared by vapor deposition. *The Journal of chemical physics*, 127(15):154702, 2007.
- [72] K. L. Kearns, S. F. Swallen, M. Ediger, T. Wu, Y. Sun, and L. Yu. Hiking down the energy landscape: Progress toward the kauzmann temperature via vapor deposition. *J. Phys. Chem. B*, 112(16):4934–4942, 2008.
- [73] K. L. Kearns, M. Ediger, H. Huth, and C. Schick. One micrometer length scale controls kinetic stability of low-energy glasses. *The Journal of Physical Chemistry Letters*, 1(1):388–392, 2009.
- [74] K. L. Kearns, T. Still, G. Fytas, and M. Ediger. High-modulus organic glasses prepared by physical vapor deposition. *Advanced Materials*, 22(1):39–42, 2010.
- [75] K. L. Kearns, P. Krzyskowski, and Z. Devereaux. Using deposition rate to increase the thermal and kinetic stability of vapor-deposited hole transport layer glasses via a simple sublimation apparatus. *The Journal of Chemical Physics*, 146(20):203328, 2017.
- [76] J. L. Keddie, R. A. L. Jones, and R. A. Corey. Size-dependent depression of the glass transition temperature in polymer films. *Europhys. Lett.*, 27(1):59–64, 1994.

- [77] T. Koga, N. Jiang, P. Gin, M. Endoh, S. Narayanan, L. Lurio, and S. Sinha. Impact of an irreversibly adsorbed layer on local viscosity of nanoconfined polymer melts. *Physical review letters*, 107(22):225901, 2011.
- [78] E. Leon-Gutierrez, G. Garcia, A. Lopeandia, M. Clavaguera-Mora, and J. Rodríguez-Viejo. Size effects and extraordinary stability of ultrathin vapor deposited glassy films of toluene. *The Journal of Physical Chemistry Letters*, 1(1):341–345, 2009.
- [79] E. Leon-Gutierrez, A. Sepúlveda, G. Garcia, M. T. Clavaguera-Mora, and J. Rodríguez-Viejo. Stability of thin film glasses of toluene and ethylbenzene formed by vapor deposition: an in situ nanocalorimetric study. *Phys. Chem. Chem. Phys.*, 12(44):14693–14698, 2010. ISSN 1463-9076. doi: 10.1039/c0cp00208a.
- [80] E. Leutheusser. Dynamical model of the liquid-glass transition. *Physical Review A*, 29(5):2765, 1984.
- [81] C. Lim and W. Stronge. Normal elastic-plastic impact in plane strain. *Mathematical and computer modelling*, 28(4-8):323–340, 1998.
- [82] T. Liu, K. Cheng, E. Salami, F. Gao, E. Glor, M. Li, P. Walsh, and Z. Fakhraai. Synthesis and High-Throughput Characterization of Structural Analogues of Molecular Glassformers: 1,3,5-Trisarylbenzenes. *Soft Matter*, 11(38):7558–7566, 2015. ISSN 1744-683X. doi: 10.1039/C5SM01044F.
- [83] T. Liu, K. Cheng, E. Salami-Ranjbaran, F. Gao, C. Li, X. Tong, Y.-C. Lin, Y. Zhang, W. Zhang, L. Klinge, P. J. Walsh, and Z. Fakhraai. The effect of chemical structure on the stability of physical vapor deposited glasses of 1,3,5-triarylbenzene. *J. Chem. Phys.*, 143(8):084506, Aug. 2015. ISSN 0021-9606. doi: 10.1063/1.4928521.
- [84] V. Lubchenko and P. G. Wolynes. Theory of structural glasses and supercooled liquids. *Annu. Rev. Phys. Chem.*, 58:235–266, 2007.
- [85] B. Mahltig, H. Böttcher, K. Rauch, U. Dieckmann, R. Nitsche, and T. Fritz. Optimized UV protecting coatings by combination of organic and inorganic UV absorbers. *Thin Solid Films*, 485(1):108–114, 2005. ISSN 00406090. doi: 10.1016/j.tsf.2005.03.056.
- [86] R. Malshe, M. Ediger, L. Yu, and J. De Pablo. Evolution of glassy gratings with variable aspect ratios under surface diffusion. *J. Chem. Phys.*, 134(19):194704, 2011.
- [87] J. D. McGraw, T. Salez, O. Bäümchen, E. Raphaël, and K. Dalnoki-Veress. Self-similarity and energy dissipation in stepped polymer films. *Phys. Rev. Lett.*, 109(12):128303, sep 2012.
- [88] J. C. Meredith, A. P. Smith, A. Karim, and E. J. Amis. Combinatorial materials science for polymer thin-film dewetting. *Macromolecules*, 33(26):9747–9756, 2000. ISSN 00249297. doi: 10.1021/ma001298g.

- [89] G. F. Meyers, B. M. DeKoven, and J. T. Seitz. Is the molecular surface of polystyrene really glassy? *Langmuir*, 8(9):2330–2335, 1992.
- [90] S. Mirigian and K. S. Schweizer. Unified theory of activated relaxation in liquids over 14 decades in time. *The Journal of Physical Chemistry Letters*, 4(21):3648–3653, 2013.
- [91] S. Mirigian and K. S. Schweizer. Communication: Slow relaxation, spatial mobility gradients, and vitrification in confined films. *J. Chem. Phys.*, 141:161103, 2014.
- [92] S. Mirigian and K. S. Schweizer. Elastically cooperative activated barrier hopping theory of relaxation in viscous fluids. i. general formulation and application to hard sphere fluids. *The Journal of chemical physics*, 140(19):194506, 2014.
- [93] S. Mirigian and K. S. Schweizer. Theory of activated glassy relaxation, mobility gradients, surface diffusion, and vitrification in free standing thin films. *J. Chem. Phys.*, 143:244705, 2015.
- [94] C. T. Moynihan, A. J. Easteal, M. A. BOLT, and J. Tucker. Dependence of the fictive temperature of glass on cooling rate. *Journal of the American Ceramic Society*, 59(1-2):12–16, 1976.
- [95] W. W. Mullins. Flattening of a Nearly Plane Solid Surface due to Capillarity. *J. Appl. Phys.*, 30(1):77, 1959.
- [96] D. Musumeci, C. T. Powell, M. D. Ediger, and L. Yu. Termination of Solid-State Crystal Growth in Molecular Glasses by Fluidity. *J. Phys. Chem. Lett.*, 5(10):1705–10, may 2014.
- [97] S. Napolitano, E. Glynos, and N. B. Tito. Glass transition of polymers in bulk, confined geometries, and near interfaces. *Reports on Progress in Physics*, 80(3):036602, 2017.
- [98] M. L. F. Nascimento and E. D. Zanotto. Mechanisms and dynamics of crystal growth, viscous flow, and self-diffusion in silica glass. *Physical Review B*, 73(2):024209, 2006.
- [99] D. Nečas and P. Klapetek. Gwyddion: an open-source software for SPM data analysis. *Cent. Eur. J. Phys.*, 10(1):181–188, 2012. ISSN 1895-1082.
- [100] K. Ngai and K. Y. Tsang. Similarity of relaxation in supercooled liquids and interacting arrays of oscillators. *Physical Review E*, 60(4):4511, 1999.
- [101] T. D. Nguyen, J.-M. Y. Carrillo, M. A. Matheson, and W. M. Brown. Rupture mechanism of liquid crystal thin films realized by large-scale molecular simulations. *Nanoscale*, 6(6):3083–3096, 2014. ISSN 2040-3364.
- [102] P. O’Connell and G. McKenna. Dramatic stiffening of ultrathin polymer films in

- the rubbery regime. *The European Physical Journal E: Soft Matter and Biological Physics*, 20(2):143–150, 2006.
- [103] A. Oron and S. G. Bankoff. Long-scale evolution of thin liquid films. *Rev. Mod. Phys.*, 69(3):931–980, 1997. ISSN 0034-6861.
 - [104] K. Paeng, S. F. Swallen, and M. D. Ediger. Direct measurement of molecular motion in freestanding polystyrene thin films. *J. Am. Chem. Soc.*, 133(22):8444–8447, 2011. ISSN 00027863. doi: 10.1021/ja2022834.
 - [105] K. Paeng, C. T. Powell, L. Yu, and M. D. Ediger. Fast Crystal Growth Induces Mobility and Tension in Supercooled o-Terphenyl. *J. Phys. Chem. Lett.*, 3(18):2562–7, 2012.
 - [106] K. Paeng, R. Richert, and M. Ediger. Molecular mobility in supported thin films of polystyrene, poly (methyl methacrylate), and poly (2-vinyl pyridine) probed by dye reorientation. *Soft Matter*, 8(3):819–826, 2012.
 - [107] R. M. Papaleo, R. Leal, W. H. Carreira, L. Barbosa, I. Bello, and A. Bulla. Relaxation times of nanoscale deformations on the surface of a polymer thin film near and below the glass transition. *Phys. Rev. B*, 74(9):094203, 2006.
 - [108] C. H. Park, J. H. Kim, M. Ree, B.-H. Sohn, J. C. Jung, and W.-C. Zin. Thickness and composition dependence of the glass transition temperature in thin random copolymer films. *Polymer*, 45(13):4507–4513, 2004.
 - [109] B. A. Pazmiño Betancourt, P. Z. Hanakata, F. W. Starr, and J. F. Douglas. Quantitative relations between cooperative motion, emergent elasticity, and free volume in model glass-forming polymer materials. *Proc. Natl. Acad. Sci.*, 112(10):2966–2971, 2015. ISSN 0027-8424. doi: 10.1073/pnas.1418654112.
 - [110] I. L. Pegg. Turning nuclear waste into glass. *Physics Today*, 68(2):33–39, 2015.
 - [111] N. G. Perez-de Eulate, M. Sferrazza, D. Cangialosi, and S. Napolitano. Irreversible adsorption erases the free surface effect on the T_g of supported films of poly (4-tert-butylstyrene). *ACS Macro Letters*, 6(4):354–358, 2017.
 - [112] D. Pires, J. L. Hedrick, A. De Silva, J. Frommer, B. Gotsmann, H. Wolf, M. Despont, U. Duerig, and A. W. Knoll. Nanoscale three-dimensional patterning of molecular resists by scanning probes. *Science*, 328(5979):732–735, 2010. doi: 10.1126/science.1187851.
 - [113] D. J. Plazek, C. A. Bero, and I.-C. Chay. The recoverable compliance of amorphous materials. *Journal of non-crystalline solids*, 172:181–190, 1994.
 - [114] R. D. Priestley, L. J. Broadbelt, and J. M. Torkelson. Physical aging of ultrathin polymer films above and below the bulk glass transition temperature: Effects of attractive

- vs neutral polymer- substrate interactions measured by fluorescence. *Macromolecules*, 38(3):654–657, 2005.
- [115] R. D. Priestley, C. J. Ellison, L. J. Broadbelt, and J. M. Torkelson. Structural relaxation of polymer glasses at surfaces, interfaces, and in between. *Science*, 309(5733):456–459, 2005. doi: 10.1126/science.1112217.
 - [116] R. D. Priestley, D. Cangialosi, and S. Napolitano. On the equivalence between the thermodynamic and dynamic measurements of the glass transition in confined polymers. *Journal of non-crystalline solids*, 407:288–295, 2015.
 - [117] J. E. Pye and C. B. Roth. Two simultaneous mechanisms causing glass transition temperature reductions in high molecular weight freestanding polymer films as measured by transmission ellipsometry. *Physical review letters*, 107(23):235701, 2011.
 - [118] J. E. Pye, K. A. Rohald, E. A. Baker, and C. B. Roth. Physical aging in ultrathin polystyrene films: Evidence of a gradient in dynamics at the free surface and its connection to the glass transition temperature reductions. *Macromolecules*, 43(19):8296–8303, 2010. ISSN 00249297. doi: 10.1021/ma101412r.
 - [119] D. Qi, C. R. Daley, Y. Chai, and J. A. Forrest. Molecular weight dependence of near surface dynamical mechanical properties of polymers. *Soft Matter*, 9(37):8958, 2013.
 - [120] S. Rath and H. Port. Dewetting of thin UHV-deposited organic films. *Chem. Phys. Lett.*, 421:152–156, 2006. doi: 10.1016/j.cplett.2006.01.080.
 - [121] R. Richert. Evidence for dynamic heterogeneity near T_g from the time-resolved inhomogeneous broadening of optical line shapes. *The Journal of Physical Chemistry B*, 101(33):6323–6326, 1997.
 - [122] C. Roth, A. Pound, S. Kamp, C. Murray, and J. Dutcher. Molecular-weight dependence of the glass transition temperature of freely-standing poly (methyl methacrylate) films. *The European Physical Journal E*, 20(4):441–448, 2006.
 - [123] C. B. Roth and J. Dutcher. Glass transition temperature of freely-standing films of atactic poly (methyl methacrylate). *The European Physical Journal E: Soft Matter and Biological Physics*, 12:103–107, 2003.
 - [124] C. B. Roth, K. L. McNerny, W. F. Jager, and J. M. Torkelson. Eliminating the enhanced mobility at the free surface of polystyrene: fluorescence studies of the glass transition temperature in thin bilayer films of immiscible polymers. *Macromolecules*, 40(7):2568–2574, 2007.
 - [125] S. Ruan, W. Zhang, Y. Sun, M. Ediger, and L. Yu. Surface diffusion and surface crystal growth of tris-naphthyl benzene glasses. *The Journal of Chemical Physics*, 145(6):064503, 2016.

- [126] E. V. Russell and N. Israeloff. Direct observation of molecular cooperativity near the glass transition. *Nature*, 408(6813):695–698, 2000.
- [127] T. Salez, J. D. McGraw, S. L. Cormier, O. Bäumchen, K. Dalnoki-Veress, and E. Raphaël. Numerical solutions of thin-film equations for polymer flows. *Eur. Phys. J. E. Soft Matter*, 35(11):114, nov 2012.
- [128] A. Sepúlveda, E. Leon-Gutierrez, M. Gonzalez-Silveira, C. Rodríguez-Tinoco, M. T. Clavaguera-Mora, and J. Rodríguez-Viejo. Accelerated aging in ultrathin films of a molecular glass former. *Phys. Rev. Lett.*, 107(2):025901, 2011. ISSN 00319007. doi: 10.1103/PhysRevLett.107.025901.
- [129] A. Shavit and R. A. Riggleman. Influence of backbone rigidity on nanoscale confinement effects in model glass-forming polymers. *Macromolecules*, 46(12):5044–5052, 2013. ISSN 00249297. doi: 10.1021/ma400210w.
- [130] A. Shavit and R. A. Riggleman. Physical aging, the local dynamics of glass-forming polymers under nanoscale confinement. *J. Phys. Chem. B*, 118:9096, 2014.
- [131] Y. Shirota and H. Kageyama. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chem. Rev.*, 107(4):953–1010, 2007. doi: 10.1021/cr050143.
- [132] S. Singh and J. J. De Pablo. A molecular view of vapor deposited glasses. *J. Chem. Phys.*, 134(2011):194903, 2011. ISSN 00219606. doi: 10.1063/1.3586805.
- [133] C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. VanLandingham, H.-C. Kim, W. Volksen, R. D. Miller, and E. E. Simonyi. A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nature materials*, 3(8):545–550, 2004.
- [134] J. D. Stevenson and P. G. Wolynes. On the surface of glasses. *J. Chem. Phys.*, 129(23):234514, 2008. doi: 10.1063/1.3041651.
- [135] L. C. E. Struik. *Physical aging in amorphous polymers and other materials*. PhD thesis, TU Delft, Delft University of Technology, 1977.
- [136] Y. Sun, L. Zhu, K. L. Kearns, M. D. Ediger, and L. Yu. Glasses crystallize rapidly at free surfaces by growing crystals upward. *Proceedings of the National Academy of Sciences*, 108(15):5990–5995, 2011.
- [137] S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. S. Kim, R. J. McMahon, M. D. Ediger, T. Wu, L. Yu, and S. Satija. Organic glasses with exceptional thermodynamic and kinetic stability. *Science*, 315(5810):353–356, 2007. ISSN 0036-8075. doi: 10.1126/science.1135795.
- [138] S. F. Swallen, K. L. Kearns, S. Satija, K. Traynor, R. J. McMahon, and M. Ediger.

- Molecular view of the isothermal transformation of a stable glass to a liquid. *The Journal of chemical physics*, 128(21):214514, 2008.
- [139] C. W. Tang and S. A. Vanslyke. Organic electroluminescent diodes. *Appl. Phys. Lett.*, 51(12):913–915, 1987. ISSN 00036951. doi: 10.1063/1.98799.
 - [140] J. H. Teichroeb and J. A. Forrest. Direct imaging of nanoparticle embedding to probe viscoelasticity of polymer surfaces. *Phys. Rev. Lett.*, 91(1):016104, 2003.
 - [141] S. Timoshenko and J. Goodier. Theory of elasticity,(1970), 433.
 - [142] A. Q. Tool. Relation between inelastic deformability and thermal expansion of glass in its annealing range. *Journal of the American Ceramic society*, 29(9):240–253, 1946.
 - [143] J. Torres, P. Nealey, and J. De Pablo. Molecular simulation of ultrathin polymeric films near the glass transition. *Physical Review Letters*, 85(15):3221, 2000.
 - [144] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess. Length scale of dynamic heterogeneities at the glass transition determined by multi-dimensional nuclear magnetic resonance. *Physical Review Letters*, 81(13):2727, 1998.
 - [145] J. H. van Zanten, W. E. Wallace, and W.-l. Wu. Effect of strongly favorable substrate interactions on the thermal properties of ultrathin polymer films. *Physical Review E*, 53(3):R2053, 1996.
 - [146] J. G. C. Veinot and T. J. Marks. Toward the ideal organic light-emitting diode. The versatility and utility of interfacial tailoring by cross-linked siloxane interlayers. *Acc. Chem. Res.*, 38(8):632–643, 2005. ISSN 00014842. doi: 10.1021/ar030210r.
 - [147] D. M. Walters, R. Richert, and M. D. Ediger. Thermal stability of vapor-deposited stable glasses of an organic semiconductor. *J. Chem. Phys.*, 142(13):134504, 2015. ISSN 0021-9606. doi: 10.1063/1.4916649.
 - [148] M. Wuttig and N. Yamada. Phase-change materials for rewriteable data storage. *Nature materials*, 6(11):824–832, 2007.
 - [149] X. Xia and P. G. Wolynes. Fragilities of liquids predicted from the random first order transition theory of glasses. *Proceedings of the National Academy of Sciences*, 97(7):2990–2994, 2000.
 - [150] R. Xie, A. Karim, J. Douglas, C. Han, and R. Weiss. Spinodal dewetting of thin polymer films. *Phys. Rev. Lett.*, 81(6):1251, 1998.
 - [151] J. Xu, L. Ding, J. Chen, S. Gao, L. Li, D. Zhou, X. Li, and G. Xue. Sensitive characterization of the influence of substrate interfaces on supported thin films. *Macromolecules*, 47(18):6365–6372, 2014.

- [152] Z. Yang, Y. Fujii, F. K. Lee, C.-H. Lam, and O. K. C. Tsui. Glass transition dynamics and surface layer mobility in unentangled polystyrene films. *Science*, 328(5986):1676–1679, 2010. ISSN 1095-9203.
- [153] L. Yu. Amorphous pharmaceutical solids: preparation, characterization and stabilization. *Adv. Drug Deliv. Rev.*, 48(1):27–42, may 2001.
- [154] L. Yu. Surface mobility of molecular glasses and its importance in physical stability. *Adv. Drug Deliv. Rev.*, jan 2016.
- [155] C. Zhang, Y. Fujii, and K. Tanaka. Effect of long range interactions on the glass transition temperature of thin polystyrene films. *ACS Macro Letters*, 1(11):1317–1320, 2012.
- [156] J. Zhang, G. Liu, and J. Jonas. Effects of confinement on the glass transition temperature of molecular liquids. *The Journal of Physical Chemistry*, 96(8):3478–3480, 1992.
- [157] W. Zhang and L. Yu. Surface Diffusion of Polymer Glasses. *Macromolecules*, 49(2):731–735, jan 2016.
- [158] W. Zhang, C. W. Brian, and L. Yu. Fast Surface Diffusion of Amorphous o-Terphenyl and Its Competition with Viscous Flow in Surface Evolution. *J. Phys. Chem. B*, 119(15):5071–5078, 2015. doi: 10.1021/jp5127464.
- [159] Y. Zhang and Z. Fakhraai. Invariant fast diffusion on the surfaces of ultrastable and aged molecular glasses. *Physical Review Letters*, 118(6):066101, 2017.
- [160] Y. Zhang and Z. Fakhraai. Decoupling of surface diffusion and relaxation dynamics of molecular glasses. *Proceedings of the National Academy of Sciences*, page 201701400, 2017.
- [161] Y. Zhang, E. C. Glor, M. Li, T. Liu, K. Wahid, W. Zhang, R. A. Riggleman, and Z. Fakhraai. Long-range correlated dynamics in ultra-thin molecular glass films. *J. Chem. Phys.*, 145(11):114502, sep 2016.
- [162] Y. Zhang, R. Potter, W. Zhang, and Z. Fakhraai. Using tobacco mosaic virus to probe enhanced surface diffusion of molecular glasses. *Soft Matter*, 12:9115–9120, 2016.
- [163] L. Zhu, C. W. Brian, S. F. Swallen, P. T. Straus, M. D. Ediger, and L. Yu. Surface self-diffusion of an organic glass. *Phys. Rev. Lett.*, 106(25):256103, 2011. ISSN 00319007.