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Abstract

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Keywords

droplets, potassium hydroxides, microscopy, images, aqueous solutions, graphite, mica, adsorption, sorptive properties, ambient temperature, wetting

Comments

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Imaging and manipulation of nanometer-size liquid droplets by scanning polarization force microscopy

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Using atomic force microscopy in noncontact mode, we have imaged nanometer-size liquid droplets of KOH water solutions on the surfaces of highly oriented pyrolytic graphite and mica. On graphite the droplets prefer to be adsorbed on atomic step edges. Droplets on the same step tend to be evenly spaced and of similar size. The droplets can be manipulated by the atomic force microscopy tip allowing the controllable formation of droplet patterns on the surface. © 1996 American Vacuum Society.

I. INTRODUCTION

Liquid droplets on solids can be observed in everyday life, such as dew drops forming on plant leaves, sweat on our skin, and a foggy glass window in winter. The behavior of liquid droplets on a solid is very important in determining the processes of spreading or wetting and in the study of the interactions between the three basic interfaces: gas–liquid, gas–solid, and liquid–solid. Practical applications such as paints, lubrication, gluing, plant treatment, cosmetology, etc., are governed by droplet behavior. Research has been carried out in this field since the early nineteenth century and the laws governing the macroscopic processes are well known; however, the understanding at the mesoscopic and microscopic scale is still incomplete.^{1,2} Progress has been impeded by a lack of experimental techniques capable of providing information at such small scales. Several decisive advances have been achieved in the past decade because of the development of techniques such as surface scattering methods, ellipsometry, and x-ray reflectivity, which make possible the detailed investigation of the properties of thin liquid films with the thickness of even one molecular layer.² However, the lateral resolution of these techniques is at best in the micrometer range, which is insufficient for a detailed understanding of droplet formation and behavior.

We have recently shown that the atomic force microscope (AFM), operated in a noncontact electrostatic mode, using dc or ac biased AFM tips, can be used for nondestructive imaging of liquids.³ This mode of operation is known as scanning polarization force microscopy (SPFM) since the tip–sample interaction is due to polarization forces. Briefly, when a voltage is applied to the AFM tip, the strong electric field around its apex induces a polarization of the charge distribution on the nearby sample surface. Due to the long range nature of electrostatic interactions, the force can be detected at distances of several hundred Å from the surface. By maintain-

ing this force constant by feedback control of the gap between the tip and the surface, a constant force image can be obtained. In our previous work,⁴ SPFM was used to image the condensation and evaporation of molecularly thin films of water on mica with nanometer resolution. This method can also be used to image thicker liquid structures such as liquid droplets or bulk liquid surfaces.

In this article we report results utilizing this new technique to study the behavior of liquid droplets of KOH water solutions at the nanometer scale on atomically flat surfaces of highly oriented pyrolytic graphite (HOPG) and mica. KOH solution was chosen because it remains in its liquid phase at the humidities used throughout our measurements. HOPG and mica are ideal substrates because their cleaved surfaces are atomically flat over length scales of thousands of Å or more, thus reducing the influence of substrate roughness and heterogeneity.

II. EXPERIMENT

A macroscopic drop of roughly 10 μ l of solution was deposited onto a freshly cleaved surface of HOPG or mica. Micrometer- to nanometer-size droplets could be formed by blowing with a jet of compressed gas or by absorbing with a filter paper to produce a surface that visually appears dry. The density of droplets could be controlled by changing the initial concentration of KOH in the water solution; however, the droplets equilibrate with ambient humidity which determines the final KOH concentration. On HOPG, solutions with high initial concentration (2 M) produced a high droplet density, while solutions with low initial concentration (0.1 M) produced a low droplet density. This is possibly due to the higher wettability of more concentrated KOH solution on HOPG. The experiments were performed in an environmental chamber containing a homemade AFM⁵ head where the relative humidity (RH) could be controlled. We used a commercial electronic control unit (RHK Technology, Rochester Hills, MI) and cantilever (Digital Instruments, Santa Barbara, CA). The nominal force constant of the cantilevers is

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FIG. 1. A $6 \times 6 \mu\text{m}^2$ image of liquid droplets prepared by 2 M KOH water solution on the surface of HOPG. The imaging conditions are: tip bias +5 V; force 16 nN (gap $\sim 400 \text{ \AA}$); and relative humidity 50%.

0.58 N/m. The cantilevers are made of Si_3N_4 and were coated with a 100- $\text{\AA}$ -thick Pt layer. All the experiments were performed at room temperature.

III. RESULTS AND DISCUSSION

A. Imaging droplets

Figure 1 is a typical SPFM image ($6 \times 6 \mu\text{m}^2$) of KOH droplets on the surface of HOPG. The apparent size of the droplets ranges from hundreds to thousands of $\text{\AA}$. The apparent height is typically tens to hundreds of $\text{\AA}$. The exact dimensions of the droplets cannot be determined unless the tip shape is known and a quantitative analysis performed. The apparent dimensions will nonetheless be of the correct order of magnitude.

Although droplets can be found in the flat areas between steps, they strongly prefer to adsorb on the step edges. Figure 2 further demonstrates this phenomenon in the case of low droplet density. All the droplets are found on step edges. Although it is well known that macroscopic roughness can contribute to the trapping of liquid drops on surfaces,² it is still surprising that atomic steps can also anchor drops as large as a few thousand $\text{\AA}$.

In addition, along a given step the size of the droplets is nearly uniform, as is their separation. This is possibly a result of hydrodynamic instabilities. As the liquid film is being displaced by an air jet or removed by osmotic transfer to the filter paper, it first breaks down into disconnected fragments on the surface which are in the form of strips attached to steps. Further liquid removal thins out the strips to the point that their surface tension is too high, and thus break into droplets as seen in the images.

Droplets can be imaged on insulating surfaces as well. Figure 3 shows droplets of various sizes on the mica surface.

FIG. 2. A $10 \times 10 \mu\text{m}^2$ images of droplets prepared by 0.1 M KOH solution on HOPG. The imaging conditions are: tip bias +5 V; force 16 nN (gap $\sim 400 \text{ \AA}$); and relative humidity 50%.

We found that producing droplets on mica is not as easy as on graphite. This is probably due to the lack of steps and high hydrophilicity.

B. Manipulating droplets

The attractive force between the tip and a droplet can be increased to the point where the entire droplet can be moved on the surface. This is accomplished by reducing the tip-sample gap at constant bias voltage, or by increasing the bias voltage while maintaining the gap. The scanning speed is also critical in this process. Slow scanning facilitates effective displacement while fast scanning tends to be ineffective. Figures 4(a)–(c) show an example of this process. Figure 4(a) is an image obtained with a tip bias of +6 V and a constant force of 20 nN with a scanning speed of $20 \mu\text{m/s}$ in

FIG. 3. An $8 \times 8 \mu\text{m}^2$ image of droplets prepared by 2 M KOH solution on mica surface. The imaging conditions are: tip bias +6 V; force 16 nN; and relative humidity 48%.

FIG. 4. (a) $2.5 \times 2.5 \mu\text{m}^2$ image of droplets of KOH solution on HOPG at relative humidity 95%. Tip bias is +6 V, force 20 nN (gap $\sim 500 \text{ \AA}$), scan speed $20 \mu\text{m/s}$ in the x direction and $0.04 \mu\text{m/s}$ in the y direction. (b) $2 \times 2 \mu\text{m}^2$ image in the center area of (a). Tip bias is +6 V, force 22 nN (gap $\sim 300 \text{ \AA}$), scan speed $10 \mu\text{m/s}$ in the x direction, and $0.02 \mu\text{m/s}$ in the y direction. (c) $2.5 \times 2.5 \mu\text{m}^2$ image in the same area as in (a). Tip bias is +6 V, force 20 nN (gap $\sim 500 \text{ \AA}$), scan speed $20 \mu\text{m/s}$ in the x direction, and $0.04 \mu\text{m/s}$ in the y direction.

the x direction and $0.04 \mu\text{m/s}$ in the y direction. All the droplets remained stationary under these imaging conditions. If the force is increased to 22 nN with the same bias while scanning at a slower scanning speed of $10 \mu\text{m/s}$ in x and $0.02 \mu\text{m/s}$ in y , three of the droplets are moved by the tip. They move nearly along the slow scan direction, which show up as three streaks in Fig. 4(b). With the same force but faster scanning, no droplet displacement is observed. Figure 4(c) shows the new arrangement of the droplets imaged at a lower force.

The mechanism of droplet displacement is explained as follows. If the horizontal component of the attractive force between the tip and the droplet is larger than the shear force (friction) between the droplet and the solid substrate, the droplet will be pulled along with the tip. The force necessary to do this depends upon the size of the droplet, and can be controlled by the gap or bias voltage. If the tip is scanning too fast, the inertia of the droplet prevents it from following the tip and results in no displacement as evident in Fig. 4.

Thus, by controlling either gap or bias, droplets can be manipulated at will. Figures 5(a)–(f) depict the manipulation of several KOH liquid droplets on a HOPG surface at a relative humidity of 95%. The initial droplet configuration is shown in Fig. 5(a). We then moved the tip over the position of a droplet at the lower left-hand corner, lowered the gap, slowly moved the tip to the lower right-hand corner, stopped the tip, increased the gap to the normal value, and acquired another image [Fig. 5(b)], which shows that the droplet has been moved by the tip to the lower right-hand corner. Following a similar procedure we rearranged the droplets into a new pattern as shown in Fig. 5(f).

It was found that the droplets were difficult to manipulate at low humidity. This may be due to the fact that at low humidity the KOH droplets are highly concentrated and are

FIG. 5. Images showing the process of manipulation of droplets of KOH solution on HOPG at relative humidity of 95%. The arrows indicate the moving directions of manipulated droplets. The tip bias is +6 V for both imaging and manipulation, but the force is 18 nN (gap $\sim 700 \text{ \AA}$) for imaging and 23 nN (gap $\sim 250 \text{ \AA}$) for manipulation.

more viscous. It is also observed that droplets adsorbed on steps are difficult to move even at high humidity which means that the liquid–solid interaction on the steps is larger than that on flat regions of the surface. If a droplet being moved by the tip crosses a step, it becomes irreversibly pinned. This is consistent with the observation that the deposited droplets are more likely to adsorb on steps.

IV. CONCLUSIONS

We have been able to image nanometer-sized droplets of a liquid on solid surfaces. This provides new possibilities for studying the wetting process in the mesoscopic and microscopic range. The manipulation of liquid droplets at the nanometer scale has also been achieved.

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