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Abstract

The surface potential of a multidomain BaTiO$_3$ (001) surface was imaged in the presence and absence of ultraviolet (UV) illumination. The UV radiation induces a decrease in the surface potential contrast between c+ and c– domains with a time constant of a few seconds due to redistribution of photocarriers and screening. A slower process of recovery was observed after illumination. In addition, scanning a conducting atomic force microscopy tip in contact under UV illumination destabilizes some ferroelectric domains.

Photoinduced charge dynamics on BaTiO$_3$ (001) surface characterized by scanning probe microscopy

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The surface potential of a multidomain BaTiO$_3$ (001) surface was imaged in the presence and absence of ultraviolet (UV) illumination. The UV radiation induces a decrease in the surface potential contrast between $c+$ and $c-$ domains with a time constant of a few seconds due to redistribution of photocarriers and screening. A slower process of recovery was observed after illumination. In addition, scanning a conducting atomic force microscopy tip in contact under UV illumination destabilizes some ferroelectric domains. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2348776]

Super-band-gap light illumination on a semiconducting ferroelectric surface induces various interesting charge effects related to the spontaneous polarization.[1] It is well known that photoexcitation causes increased surface conductivity, domain imprint, and changes in dielectric constant and piezoelectric coefficient. The underlying mechanism is the redistribution of photoexcited charge carriers in a ferroelectric domain driven by the depolarization field to form intrinsic screening layers. Consistent with this picture is the reported domain orientation-dependent local photochemical reactivity on ferroelectric surfaces, i.e., reduction occurs on out-of-the-plane polarized domains and oxidation on into-the-plane polarized domains.[2] This discovery led to domain controlled photocatalysis and opened a pathway to the directed assembly of nanoparticles with engineered domain structures.[3,4] Understanding the charge dynamics is critical for applications of ferroelectric materials in electro-optical storage and sensor devices. Extensive experimental studies on the photoinduced charge effects using the macroscopic parallel-plate capacitor configurations[5] have been done. Currently several electrical scanning probe techniques with nanometer spatial resolution and high sensitivity to electric fields at this length scale make direct observation of photocarriers on individual domains possible, which is the subject of this letter. Local imaging by a scanning probe provides information about an electrode-free ferroelectric surface; thus screening charge is from either intrinsic charge and/or adsorbates rather than from carriers in electrodes as in the case of parallel-plate capacitor measurements.

Scanning probe imaging of domains and measurement of local hysteresis loops in ferroelectrics have been carried out routinely by many researchers.[6] Only Gruverman *et al.* reported the UV light-induced shift in hysteresis loops and domain pinning using piezoresponse force microscopy (PFM).[7] PFM, a powerful imaging tool, differentiates domains based on the contrast in the phase shift of the cantilever oscillation. To detect the relative amount of surface charge on domains, however, scanning surface potential microscopy (SSPM) (also referred to as scanning Kelvin probe microscopy)[8] is used in this study. SSPM is implemented in noncontact mode, in which case charge transfer between tip

and surface is minimal. PFM, in contrast, is in contact mode with a conductive tip as an electrode. This difference may lead to different effects on a ferroelectric surface under UV light, which is also investigated in this work.

A BaTiO$_3$ single crystal ($5 \times 5 \times 1$ mm^3, $T_C = 130$ °C, MTI Corp.) with an epi-polished (001) surface was heated on a hot plate to 150 °C (above the Curie temperature) and then cooled to room temperature on a copper plate. Surface corrugations due to ferroelectric domains are visible under reflected light. Atomic force microscopy (AFM) topography, SSPM, and PFM measurements were performed on a commercial Dimension 3100 AFM system with a gold-coated silicon cantilever with spring constant $k \approx 7$ N/m. In SSPM, the topography is acquired by intermittent contact mode with the tip oscillating at resonance, $f_0 = 202.3$ kHz. For subsequent PFM imaging of the same location, the same AFM tip was used and the AFM control switched to contact mode. A 5 V p.p., 50 kHz ac signal was applied to the tip. The first harmonic amplitude and phase shift of the induced piezoelectric sample oscillation are detected by a lock-in amplifier. The domains with different orientations can be distinguished from the contrast in the phase image. UV illumination was carried out by fixing an 11SC-1 pencil style UV lamp (primary line of 254 nm, 4.5 mW/cm^2 at 2.54 cm) within 2 cm of the BaTiO$_3$ sample with the angle between the lamp and the surface normal less than 30° to ensure sufficient intensity.

Shown in Fig. 1(a) is the topography image of the BaTiO$_3$ (001) surface with corrugations corresponding to the tilting of adjacent a and c domains. a and c domains are identified by the shape of the domain walls in the SSPM and
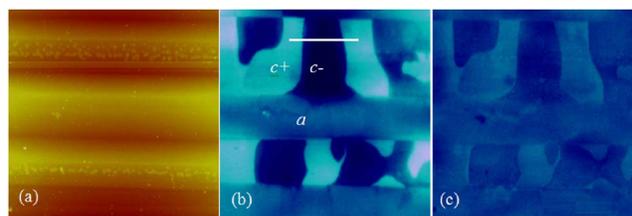

FIG. 1. (Color online) (a) AFM topography of a BaTiO$_3$ (001) surface that shows three corrugations due to a-c domain walls. z scale is 200 nm. (b) The surface potential image of the same area as shown in (a) shows c domains with curved domain walls. z scale is 0.25 V (c) The surface potential image when the UV light is on. z scale is 0.25 V.

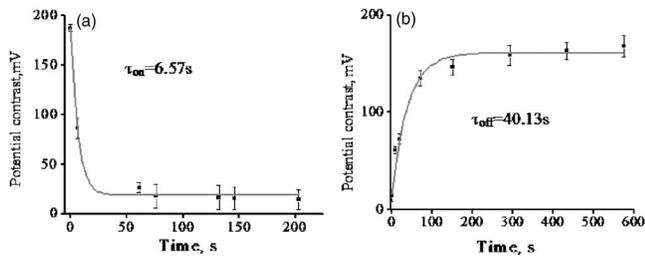[a)]Electronic mail: bonnell@lrsm.upenn.edu

FIG. 2. Time dependence of surface potential contrast between $c+$ and $c-$ domains immediately after UV light is switched (a) on and (b) off.

PFM images [Figs. 1(b) and 1(d)]: 90° a-c domain walls intersect the (001) surface along straight lines while 180° c domain walls intersect (001) plane along curves. Since the surface of a $c+$ domain terminates with positive polarization charge and that of a $c-$ domain with negative polarization charge, curved regions with higher potential should be $c+$ domains, as will be further discussed later. The surface potential contrast is the largest between $c+$ and $c-$ domains and we denote this value as $\Delta V_{c+,c-}$. The measured $\Delta V_{c+,c-}$ in this experiment is 150–200 mV.

When the sample was illuminated, a significant and gradual decrease in $\Delta V_{c+,c-}$ to 10 mV was observed within a few seconds [Fig. 1(c)]. When the UV is switched off, $\Delta V_{c+,c-}$ gradually increases back to the original value at a slower rate. Clearly the surface potential contrast is strongly influenced by UV illumination, indicating that screening of the polarization bound charge on the domain surfaces is involved. By scanning repeatedly along a single line, indicated in Fig. 1(b), at a rate of 0.5 Hz, the kinetics of the surface charge relaxations in the presence and absence of light were monitored (Fig. 2). The potential contrast changes $\Delta\varphi$ in both processes are exponentially dependent on time with an associated time constant, i.e., $\Delta V_{c+,c-}=A+B\exp(-t/\tau)$. The time constants extracted from the data are $\tau_{on}=6.5$ s for light-on processes and $\tau_{off}=40.1$ s for light-off processes. Since the electrons and holes are generated at the same location and are equal in number, they do not cause the potential contrast change upon generation. The exponential decays must originate from the spatial redistribution and retrapping of photocarriers. Because of the large cross section of photoexcitation in the UV range, photogenerated electron-hole pairs initially only exist in the surface layer. In a $c+$ domain, which has a polarization vector out of the surface plane, the internal polarization field drives positive charge (holes) away into the bulk while retaining electrons near the surface. Some redistributed photocarriers are trapped in vacant trap states. Thus a space-charge field opposing the polarization field increases until the space-charge field equals the polarization field or the rate of electron-hole pair generation equals that of recombination. When the light is switched off, the trapped carriers are thermally activated and diffuse along the concentration gradient to eventually recombine. With carrier mobility in BaTiO$_3$ on the order of 1 cm^2/(V s), the vertical length of a domain about 10 μm, and the polarization field about 10 kV/cm, the time of carrier drift is extremely short. Therefore, the light-on and light-off processes are limited by the rate of photoexcitation and that of thermal excitation, respectively. Relaxation time constants are given by $\tau=\varepsilon_0\varepsilon/\sigma$, where ε is the dielectric constant of BaTiO$_3$ and σ is the conductivity. So the ratio between light conductivity and dark conductivity is $\sigma_L/\sigma_D=6.1$.
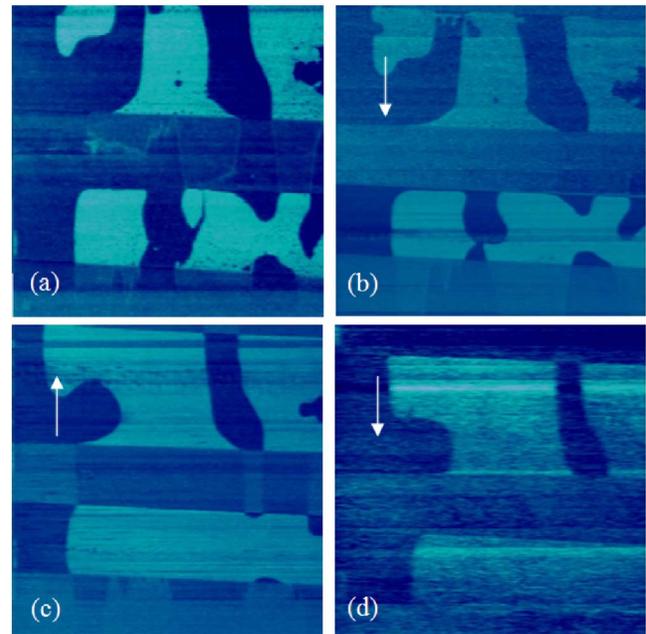

FIG. 3. (Color online) (a) PFM phase image of domains in BaTiO$_3$. [(b)–(d)] Consecutive images showing the motion of 180° domain walls during UV illumination as imaged with PFM. The arrows indicate the slow scan direction. The scan rate is 2 min and 50 s per frame. z scale is 4°. All images are 50×50 μm^2 in size.

Some previous studies considered extrinsic screening on ferroelectric surfaces, in which case determination of $c+$ and $c-$ domains from the contrast in a SSPM image is complicated.[9,10] Depending on the amount of adsorbate, the sign of $\Delta V_{c+,c-}$ can be either positive when the surface is partially screened or negative when the surface is completely screened. In the case where physisorbed charge completely screens the surface, the very low desorption energies (~1 kJ/mol) (Ref. 11) of ambient adsorbates would result in immediate desorption upon light illumination, leading to a reversal of the sign of $\Delta V_{c+,c-}$. This is, however, not observed in the experiment. In addition, the dynamics of extrinsic adsorption has a time constant 30–100 times longer than the ones measured here. Thus, screening by adsorbates does not play a dominant role in our experiment.

Although the domain potential contrast variations due to charge redistribution were observed on UV illumination, change in the domain structure did not occur. This confirms that illumination did not reorient the ferroelectric domains. Furthermore the domain structure did not change during SSPM imaging for a variety of imaging conditions (lift height, drive amplitude, etc.). Subsequently, PFM imaging at the same location was done in the absence of UV light [Fig. 3(a)]. The domain pattern matches that imaged by SSPM, except for a reversed contrast. Note that, in principle, domain orientation is determined from PFM phase; ideal piezoelectric coupling results in a phase shift between $c+$ to $c-$ domains of +180°. For the images in Fig. 3, the contrast in the phase image is less than 4°, which indicates that electrostatic coupling plays a larger role. Also note that the phase contrast fluctuates slightly and slowly (Fig. 3), which cannot be easily attributed to piezoelectric properties. This indicates that the magnitude of the phase shift in PFM is a critical parameter for image interpretation and should always be reported. Nevertheless, the PFM imaged domain pattern is sufficiently clear to examine domain stability.

When the UV light is switched on during imaging in contact mode, rapid 180° domain wall motion is visible in consecutive PFM images [Figs. 3(b)–3(d)]. The image acquisition time is 2.8 min. The domain wall velocity increases with the curvature, indicating a clear tendency for coarsening. The conducting AFM tip, in contact with the surface, has destabilized the domain pattern. It is known that the surface conductivity of a ferroelectric is enhanced by super-band-gap light and, as discussed above, a screening layer of photocarriers exists on the surface that stabilizes the domain structure. The AFM tip with only a small amplitude high frequency ac voltage is effectively a grounding electrode. Thus the most likely cause of the destabilization is the removal of screening charge.

The curvature of a domain wall is $1/R$, where R is the local radius of curvature. For simplicity, we consider the stability of a small cylindrical $c+$ domain with radius R embedded in a large $c-$ domain, or vice versa. Stability of a domain without screening is established, when $2E_C P + \sigma_{dw} + \sigma_{dp} \geq 0$, where E_C is the resistance to depolarization generally denoted as coercive field, P is the polarization vector, σ_{dw} is the domain wall stress due to wall energy γ, and σ_{dp} is the stress due to depolarization field.[12] A lower bound for R of a stable domain is given by $R > 4\gamma E_C P$. Screening charge reduces P by σ_{sc} which is the surface charge density, and thus the lower bound for R decreases. So c domains with a crucial value of curvature are stable if screened but will shrink if screening charge is removed by the AFM cantilever.

An alternative explanation is that the imaging voltage in PFM destabilizes domain polarization. To clarify this, we scanned the surface under UV radiation without applying an ac bias. Contact induced domain wall motion was still observed. It should be noted that in the absence of UV illumination, PFM images acquired consecutively do not exhibit any change in domain structure. In addition, no change in 90° domain walls was found, which indicates that, although c domains can reverse polarization upon charge removal, they do not easily transform into a domains because of the large energy associated with crystallographic strain.[13]

The above observation implies that PFM implemented in contact mode with a conducting tip strongly interacts with the ferroelectric surface, which can alter the properties of the sample. As a result, PFM imaging on the evolution of domain structures in semiconducting ferroelectric surfaces needs to take into account the possibility of any charge transfer induced destabilization. A clear understanding of charge transfer between the cantilever and the surface is necessary to quantify PFM on semiconducting ferroelectrics.

In summary, SSPM was used to directly observe photocarrier screening on a BaTiO$_3$ (001) surface. Surface potential contrast of c domains is significantly reduced by UV illumination and recovers after the illumination is switched off. Both relaxation processes are found to be characteristic of charging and discharging due to photocarriers. While domain structure does not change under UV during SSPM imaging, a rapid domain wall motion takes place during PFM scanning which is attributed to domain destabilization due to the removal of the screening photocarriers by the conducting AFM tip.

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