Surface Conduction on Insulating BaTiO$_3$ Crystal Suggesting an Intrinsic Surface Electron Layer

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We report conduction measurements on the clean, free surface of transparent insulating BaTiO$_3$ single crystals in high vacuum. We find that the insulating BaTiO$_3$ crystals exhibit surface conductance that is dependent on the spontaneous polarization, whereas no conduction perpendicular to the surface is observed. The surface conduction shows semimetallic temperature dependence and persists down to at least 100 K. The observations suggest a two-dimensional electron on a clean, free ferroelectric surface that may be regarded as a ferroelectric metal. The results have important implications for understandings of the fundamental properties of ferroelectrics, the size effect, and ferroelectric devices.

The surface of the ferroelectric, which significantly influences its size effect [1–3], is unique among those of the condensed matters because that is where the macroscopic electric charges caused by the ferroelectric spontaneous polarization appear. The electric field created by the surface charges is enormous when they are unshielded. This field, called the depolarization field, has been considered a dominant controlling factor of the unusually large size effect [3], the domain configuration, and limitations of the performance of ferroelectric field-effect transistors [4]. On the other hand, there has been speculation that such an enormous field may form a special layer on the free surface of the ferroelectric [5,6]. If such a layer exists, it will change our understanding of the fundamental properties as well as of the limitations of the ferroelectric such as the domain configuration of a very small ferroelectric, because the layer can be regarded as a natural electrode spontaneously formed on the insulating ferroelectric. However, no direct observation of the surface electron layers has been reported so far, and the surface electrons have been usually regarded as trapped and immobile, if they exist at all. Here we show that the atomically well-defined free surface of poled transparent insulating single crystals of a prototype ferroelectric system, BaTiO$_3$, conducts current in high vacuum, and that a surface electron layer exists.

Typical ferroelectric perovskite oxides such as BaTiO$_3$ and PbTiO$_3$ are usually regarded as insulators, having a spontaneous polarization P_S. The macroscopic electric charges due to P_S appear only at the surface, the interface, or the domain boundary. Therefore, various properties have been explained in a way similar to that of magnetism by comparing P_S with the magnetization M_S. For example, the 180° domain configuration [Fig. 1(a)] is usually explained by a Kittel model for the 180° magnetic domains [7]. When the surface of the ferroelectric is electrodeless, it is conventionally thought that an enormous depolarization field appears and is minimized by forming a multidomain structure. Consequently, in a very thin ferroelectric, the ferroelectric phase is expected to exist only

in a certain range of domain width, which poses severe constraints on the switching of P_S and the minimum size of the stable ferroelectric phase [3].

On the other hand, theories considering a finite band gap of the ferroelectric predict a carrier layer on the ferroelectric surface that relaxes these limitations [6,8,9], which may be supported partly by the recent observations of the field effects in the perovskite oxides having a band gap close to those of conventional semiconductors [10]. However, this prediction is usually considered to be a shear theoretical possibility and has not received serious attention, because the ferroelectrics have been studied as the lattice dynamics systems and ferroelectric perovskites possess a band gap of 3–4 eV, which requires larger band bending and, therefore, may induce other screening mechanisms. Indeed, despite the importance of nanometer-scale ferroelectrics, the physical nature of a clean ferroelectric
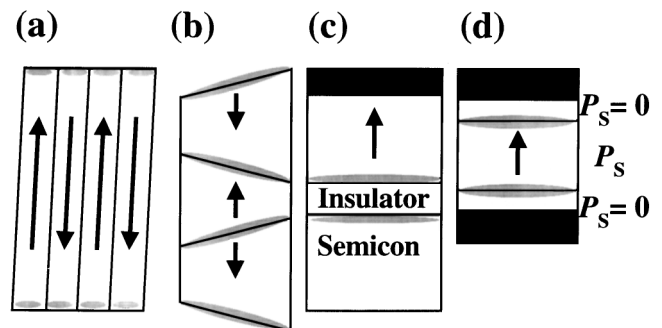

FIG. 1. Typical domain configurations. (a) Cross sectional view of 180° stripe domains. (b) Head-on domains. The arrows indicate the direction of P_S, and the shaded areas indicate the locations where the carrier is possibly generated. The dark shaded area corresponds to the metal electrode. (c) Carrier generation in a typical heterostructure used for field effect transistors. (d) Modeling of a capacitor structure (metal/ferroelectric/metal) where P_S has surface relaxation and the carrier generation. The ferroelectric layer is modeled by an insulator ($P_S = 0$)/ferroelectric (bulk value P_S)/insulator ($P_S = 0$).

surface remains unclear [11,12], and the direct experimental study of such a layer has been missing so far. Therefore, we have investigated the basic nature of the hypothetical electron layer on the atomically well-defined surface of BaTiO$_3$.

Surface conduction that is not due to adsorption and defects is measurable only on a clean surface of a high-quality single crystal in a high vacuum or at the domain boundaries [6]. It is predicted that the accumulation of electrons at the BaTiO$_3$ surface in positively poled states and a weak inversion of hole carriers in negatively poled states. As-grown single crystals of BaTiO$_3$ grown by a flux method, which were lightly yellowish, transparent, and insulating, were used to avoid polishing procedures and possible surface damage. We confirmed that the surface is atomically well defined by observing steps of one lattice height by an atomic force microscope (AFM). We have developed a procedure of controlling P_S at the electrodeless surface of a ferroelectric, using a pair of T-shaped Pt electrodes sputtered on the top surface of the crystals and one on the bottom surface. To reduce contamination and damage, the electrodes were deposited via the holes of a metal mask of which peripherals are completely shielded by sticking polymers, thus eliminating the diffusion of sputtered materials into the gap area and minimizing the mechanical contact of the area [13]. The adsorbed water is removed by annealing the samples in high vacuum at 150 °C that is low enough to avoid making the adsorbed hydrocarbon semiconductive.

The results below are for a crystal with a thickness of 0.34 mm and a shiny smooth surface. The surface conductance is obtained by measuring the current between two top electrodes. The gaps between the top electrodes and the width of the electrodes are 0.36 and 2.7 mm, respectively. To control P_S, we build first a randomly oriented state by a temperature cycling across the Curie temperature T_C of 130 °C, and identify it by a polarized-light optical microscope. Then, we apply a dc electric field, e.g., 800 V/cm, between the two top electrodes and the bottom electrode slightly above T_C, and allow it to cool. The resulting state is optically isotropic in-plane below T_C, indicating that the optical axis and, therefore, P_S are perpendicular to the surface. The validity of the procedure is further confirmed by measuring a pyroelectric current on a small electrode to which the same procedure is applied. The remnant polarization P_r of the small electrode estimated from the pyroelectric current yielded an expected polarity and agreed with P_r estimated from the displacement-electric field (D-E) hysteresis curves (20 μC/cm^2). No change or deposition was detected on the surface of the gap area by an optical microscope after many poling procedures. Unless stated otherwise, all the measurements and the processes below were performed at a pressure of 3×10^{-8} torr in darkness. The results below are obtained after several temperature cycles between room temperature and 150 °C in vacuum. The conductance and the current below are probably lower than an intrinsic value due to the Schottky contact resistance.

The surface conductance is measured each time after orienting the polarization of the gap area randomly and then poling the area either positive (negative bias on the top surface) or negative (positive bias on the top surface). The measurements are performed at 70 °C directly after the poling to obtain the conductance of a fresh surface. The current-voltage (I-V) characteristics of the positively poled state exhibit an Ohmic relation and a 10 times higher conductance than a negatively poled and a randomly oriented state (Fig. 2). The current-time (I-t) characteristics at a fixed voltage indicate that the current is not transient due to the trap emission or the dielectric response. The polarization dependence is extremely small and irreproducible when the surface conductance is measured in air. In addition, the conductance is much lower than the above results when the poling is performed in air and measured in vacuum. The surface conduction of the positively poled state decreased after 12 days in vacuum but remained higher than that of the other states. All these observations indicate that the conduction takes place on the surface and is controlled by the polarization. Furthermore, we did not observe these phenomena in pure and reduced SrTiO$_3$ single crystals that are paraelectric, which shows that these observations were not due to the change of the Schottky contacts by the current [14].

The surface conductance shows activation-type conduction from 200 °C to a temperature below room temperature.
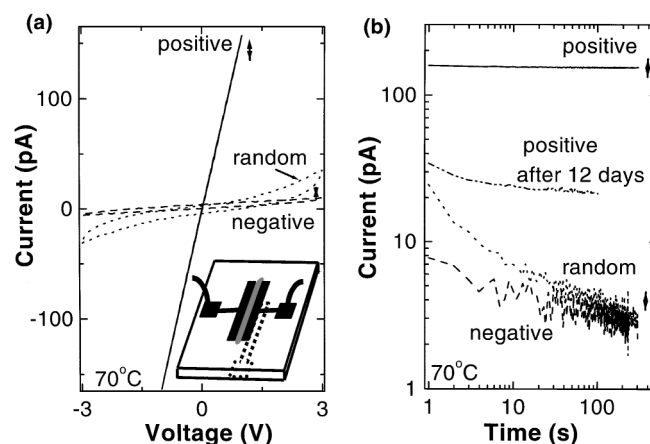

FIG. 2. Polarization dependence of the surface current by two terminal measurements. (a) Current-voltage characteristics. (b) Time dependence of current at a fixed voltage of 1 V at 70 °C. Solid lines, dashed lines, and dotted lines correspond to a positively ↑, a negatively ↓, and a randomly polarized state, respectively. The dash-dotted lines in Fig. 2(b) correspond to the state that is kept 12 days in vacuum after positive poling. The small arrows ↕ represent the reproducibility for each poling state, when the poling state was changed in the order of random, ↓, random, ↓, random, ↑, random, and ↑. Inset shows sample configuration: Two T-shaped metal electrodes are deposited on the top surface and one (shown by the dotted line) is deposited on the bottom surface of a BaTiO$_3$ single crystal. The gap area (shaded) is poled.

Figure 3(a) is an example of a temperature dependence of the positively poled state in which only approximately 50% of the gap area can be poled due to the increase of the coercive field after many repetitions of the poling. The temperature dependence between 0 and $-100\,°C$ is similar to that of bulk conduction of heavily doped or semimetallic $BaTiO_3$, and the activation energy estimated from the slope is 45 meV, which is extraordinarily small if it is due to simple impurity levels in $BaTiO_3$. The instrumental noise level is below 0.1 pA, and, therefore, the spikes and the noisy features are attributed to the pyroelectric current and the trap emission. The surface conduction at $-170\,°C$ shows Ohmic I-V characteristics and does not decrease with time [Fig. 3(b)]. A marked observation is the increase of the surface conductance below $-140\,°C$ as seen in the zoomed view in Fig. 3(a), which eliminates the ion conduction and the hopping conduction between the trap levels as the origin of the surface conduction. On the other hand, the conduction between the top and bottom electrodes, which is regarded as the conduction through the bulk, shows only the current due to the dielectric response, which diminishes with time [Fig. 3(b)]. The temperature dependence of the negatively poled state, which is almost 100% expressed in terms of an area ratio, is more remarkable [Fig. 3(c)]. The conductance at $-170\,°C$ is higher than that at room temperature. The surface conduction exhibits Ohmic I-V characteristics up to 3 V at all temperatures between -170 and $200\,°C$ and decreases only slightly with time [Fig. 3(c)].

The preceding results are consistent with the picture that an electron layer is formed at the free ferroelectric surface. We expect also that the electron layer can form at the domain boundaries (Fig. 1). Indeed, one of the randomly polarized states formed during 30 poling cycles exhibited an appreciable conduction between the top and bottom electrodes at $-170\,°C$. The observations suggest conduction by the percolation of the current path at the domain boundaries. In this view, the hysteresis and relaxation of the current in the randomly oriented state, which are larger than those in the poled state in Fig. 2, can be explained as the carrier emission from the domain boundary. However, it is worthwhile to reemphasize that in the poled states the conduction between the top and bottom electrodes is always lower than the surface conduction.

The above results support the existence of the surface conduction, which is probably due to a surface carrier layer formed by P_S [15]. Figure 4 shows an example of the self-consistently calculated carrier distribution by incorporating the relaxation of P_S near the surface (∇P) [12] and the quantization of the motion perpendicular to the surface [16]. The surface electron layer with a thickness of a few nanometers is calculated to exist a few lattice constants below the surface. This surface may not necessarily be a physical surface but, in a more exact definition, a location where P_S effectively terminates. Therefore, the possibility arises to observe conduction due to the surface electron layer even in an ordinary high vacuum. The theoretical maximum carrier density in the absence of traps is approximately 10^{21} cm^{-3}, the total charge of which is close to P_S (Fig. 4), which suggests that the surface electron may exhibit the metallic temperature dependence of conduction. Using the present experimental surface conductivity and
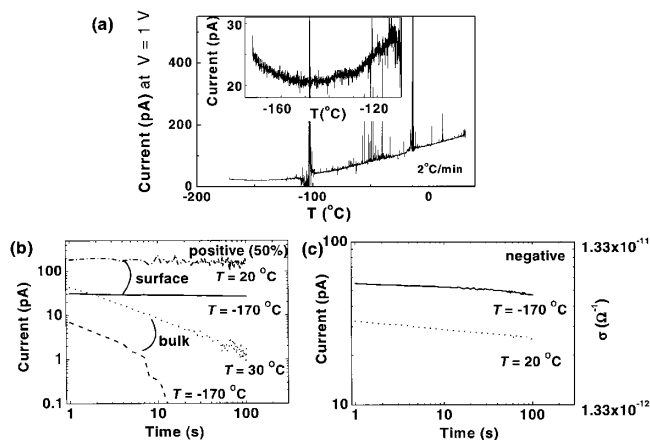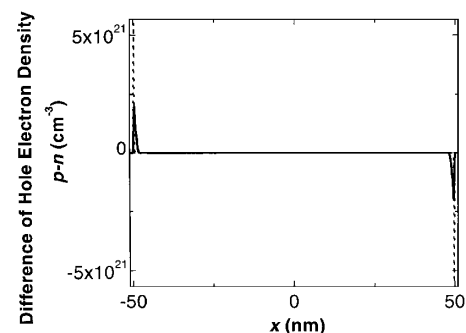

FIG. 3. Temperature dependence of the surface conduction and comparison with bulk conduction. (a) Temperature dependence of current at a fixed voltage of 1 V with an enlarged view of a low-temperature region (inset). Approximately 50% of the gap area is positively poled. The big spikes near -100 and $0\,°C$ are due to the pyroelectric current at the successive phase transitions. Other spikes are probably due to trap emission. (b) Time dependence of the current at a fixed voltage of -1 V of the same state as in (a). The solid, dashed, dotted, and the dash-dotted lines correspond to the surface conduction at $-170\,°C$, the bulk conduction at $-170\,°C$, the bulk conduction at $30\,°C$, and the surface conduction at $20\,°C$, respectively. (c) Time dependence of the surface current at a fixed voltage of -1 V of a negatively poled state. The solid and dotted lines correspond to the surface conduction at $-170\,°C$ and at $20\,°C$ after cooling, respectively.

FIG. 4. Self-consistently calculated electron hole distributions in an electrodeless, single domain, 100 nm thick, pure $BaTiO_3$ platelet with P_S perpendicular to the surface at 300 K and $P_S = 0$ at $\|x\| > 50$ nm. These example distributions are for different free parameter values of η in the Ginzburg-Landau free energy $F_F = \alpha P_S^2 + \beta P_S^4 + \gamma P_S^6 + \eta(dP_S/dx)^2$, where the last term represents the energy for the bending of P_S. The solid and dotted lines show the carrier distributions that yield the minimum free energy that is the sum of F_F, electrostatic energy, and kinetic energy for a given value of $\sqrt{\eta/2\alpha} = 2$ and 7 nm, respectively. The surface carrier layer is 2 nm thick and is located 0.5 nm below the effective ferroelectric surface ($\|x\| = 50$ nm). As surface relaxation increases, the width of the surface carrier layer increases and the maximum carrier concentration decreases.

the reported value of bulk mobility of 1 cm^2/V s [17], the carrier density per area is estimated to be 10^8 cm^{-2}. For a surface layer with thickness of a few nanometers, the carrier density is 10^{15} cm^{-3}. These experimental numbers should be regarded as the minimum values, because the mobility is expected to be reduced significantly by the scattering at the surface and the coupling with P_S. Moreover, in the present sample, the surface still contains many traps, and, therefore, most of the carriers are probably trapped. From this, we may conclude that a surface electron or hole layer exists that has an enormous surface carrier density which is close to P_S, and that a fraction of these electrons or holes exists as free carriers.

The present surface carrier layer donates the freedom and the moving capability to the domains, especially 180° domains, that determine the macroscopic and the mesoscopic properties of the electrodeless ferroelectric. The result can explain the natural formation of head-on domains [18] [Fig. 1(b)] and a successful modeling of the 90° domain configuration by stress and strain without electrostatistics [2], and supports the switching capability and the phase stability of a ferroelectric in metal/ferroelectric/insulator/semiconductor structures used for ferroelectric field-effect transistors [Fig. 1(c)] [19]. Furthermore, the surface carrier layer can relax the limitation posed by the ∇P effect that is considered to be an important mechanism of the destabilization of the small ferroelectrics and be also present on electroded ferroelectric surfaces [12]. This is because a simple modeling of this effect is the tri-layer structure of the ferroelectric consisting of thin insulating surface layers with $P_S = 0$ and a layer having a bulk value of P_S [Fig. 1(d)]. Therefore, the present results provide a theoretical basis for the wide applications of ultrasmall ferroelectrics and could also imply that the ferroelectric surface has various possible applications including catalyst.

[1] A. V. Bune et al., Nature (London) **391**, 874 (1998); Ph. Ghoosez and K. M. Rabe, Appl. Phys. Lett. **76**, 2767 (2000).

[2] N. A. Pertsev and A. G. Zembilgotov, J. Appl. Phys. **80**, 6401 (1996); S. P. Aplay et al., J. Appl. Phys. **85**, 3271 (1999).

[3] W. Y. Shih, W. H. Shih, and I. A. Aksay, Phys. Rev. B **50**, 15 575 (1994).

[4] I. P. Batra, P. Wurfel, and B. D. Silverman, Phys. Rev. B **8**, 3257 (1973).

[5] W. Känzig, Phys. Rev. **98**, 549 (1955); (for example) G. I. Rosenman et al., Appl. Phys. Lett. **56**, 689 (1990).

[6] Y. Watanabe, Phys. Rev. B **57**, 789 (1998).

[7] M. E. Lines and A. M. Glass, Principles and Application of Ferroelectrics and Related Materials (Clarendon Press, Oxford, 1977).

[8] B. M. Vul, G. M. Guro, and I. I. Ivanchik, Sov. Phys. Semicond. **4**, 128 (1970).

[9] R. E. Cohen, Ferroelectrics **194**, 323 (1997).

[10] J. Mannhart, D. G. Schlom, J. G. Bednorz, and K. A. Müller, Phys. Rev. Lett. **67**, 2099 (1991); Y. Watanabe, Appl. Phys. Lett. **66**, 1770 (1995).

[11] J. Padilla and D. Vanderbilt, Phys. Rev. B **56**, 1625 (1997); V. Ravikumar, D. Wolf, and V. P. Dravid, Phys. Rev. Lett. **74**, 960 (1995).

[12] W. R. Kretschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979); D. R. Tilley and B. Zeks, Solid State Commun. **49**, 823 (1984).

[13] The surface was examined by an optical reflectance by using polarization microscope at normal and 45° incidence and AFM. Among them, the friction force scanning force microscopy that detects the difference of the topmost atomic layer indicated that the top surface of the gap area is not Pt.

[14] A. Beck, J. G. Bednorz, Ch. Gerber, C. Rossel, and D. Widmer, Appl. Phys. Lett. **77**, 139 (2000).

[15] Alternatively, the conduction between the electrodes on the top surface that is ascribed to the surface conduction may be due to the surface oxygen vacancies formed in the vacuum or the resistance degradation by poling. This effect as the primary origin is excluded by the following arguments: (A) The annealing above 800 °C over 10 h in a high vacuum is needed to introduce oxygen deficiency of 0.1%–0.001% into BTO (tetragonal/cubic BaTiO$_3$) crystals of a similar size. Compared with this, the 150 °C in a high vacuum used before the measurements in Figs. 2, 3(a), and 3(b) is an extremely mild condition. (B) The reduced BTO in (A) is black or dark brown, whereas the sample in Figs. 2 and 3 stayed transparent. However, the surface current of the reduced BTO is 120 pA in the similar measurement. Such a small value of the BTO surface that is far more reduced than the surface in Figs. 2 and 3 cannot explain the current ($>$150 pA) in the positively poled state (Figs. 2 and 3). (C) In Fig. 2 no systematic increase of current with the poling sequence was found (it decreased very slightly). (D) The observation that the surface conduction decreased after the holding in an ultrahigh vacuum for 12 days [Fig. 2(b)] is inconsistent with the explanation by the oxygen vacancy effect. (E) The electric field for the poling is only 0.79 kV/cm in Figs. 2 and 3(c) that is far below the voltage for the resistance degradation, e.g., $0.1-1$ MV/cm of BaTiO$_3$ films. Additionally, the largest field concentrates on the electrode, not on the gap area.

[16] T. Ando, A. B. Fowler, and F. Stern, Rev. Mod. Phys. **54**, 437 (1982).

[17] C. N. Berglund and W. S. Baer, Phys. Rev. **157**, 358 (1967).

[18] L. M. Eng, H.-J. Güntherodt, G. A. Schneider, U. Köpke, and J. Muñoz Saldaña, Appl. Phys. Lett. **74**, 233 (1999).

[19] For example, K. Sugibuchi, Y. Kurogi, and N. Endo, J. Appl. Phys. **46**, 2877 (1975).