

Research Report

Surface conduction on a transparent BaTiO₃ crystal suggesting a possible surface electron layer

Yukio Watanabe and Motochika Okano

Kyushu Institute of Technology
Department of Electrical Engineering
Sensui 1-1, Tobata
Kitakyushu
Fukuoka 804-8550
Japan

LIMITED DISTRIBUTION NOTICE

This report has been submitted for publication outside of IBM and will probably be copyrighted if accepted for publication. It has been issued as a Research Report for early dissemination of its contents. In view of the transfer of copyright to the outside publisher, its distribution outside of IBM prior to publication should be limited to peer communications and specific requests. After outside publication, requests should be filled only by reprints or legally obtained copies (e.g., payment of royalties). Some reports are available at <http://domino.watson.ibm.com/library/Cyberdig.nsf/home>.



Research
Almaden • Austin • Beijing • Delhi • Haifa • T.J. Watson • Tokyo • Zurich

Surface conduction on a transparent BaTiO₃ crystal suggesting a possible surface electron layer

Yukio Watanabe and Motochika Okano

Kyushu Institute of Technology, Department of Electrical Engineering, Sensui 1-1, Tobata, Kitakyushu, Fukuoka 804-8550, Japan

Abstract - The increasing demand to incorporate miniature ferroelectrics in large-scale integrated circuits (LSI) has triggered a renewed interest in their size effect¹⁻⁸. The surface of the ferroelectric, which influences the size effect significantly, is unique because that is where the macroscopic electric charges caused by the ferroelectric spontaneous polarization appear. There has been speculation that such a field may form a special layer on the free ferroelectric surface⁹⁻¹². If such a layer exists, it will change our understanding of the fundamental properties and of the limitations of a very small ferroelectric, because the layer can be regarded as a natural electrode. However, its direct observation has not been reported so far, and the surface electrons have been usually regarded as immobile, if they exist at all. Here, we report conduction measurements on the clean, free surface of insulating single crystals of a prototype ferroelectric system, BaTiO₃, in high vacuum. We find that the BaTiO₃ crystals exhibit surface conductance that is dependent on the spontaneous polarization and shows semimetallic temperature dependence. The observations provide evidence of a two-dimensional electron or hole layer on a clean, free ferroelectric surface that may be regarded as a ferroelectric metal.

1. Introduction

Typical ferroelectric perovskite oxides such as BaTiO₃ and PbTiO₃ are usually regarded as insulators, one of whose most basic property is a spontaneous polarization P_S that is reversible by an external electric field. 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. 1a), is usually explained by a Kittel model for the 180° magnetic domains¹³. 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. 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 , or destabilizes the ferroelectric phase in an extreme case, limiting the minimum size of the ferroelectric phase.

These textbook concepts may be changed, especially in miniature ferroelectrics, if we consider the electrons originating from the finite energy band gap of the ferroelectrics because the depolarization field can be screened by these electrons. As seen in Figs. 2a and b, the situation of the free ferroelectric surface is similar to the SiO₂/Si interface in the metal/oxide/Si (MOS) diode under the electric field, suggesting a possible carrier generation at the ferroelectric surface by the depolarization field. Indeed, several observations are puzzling if no mobile charges exist at the ferroelectric surface. For example, the natural formation of head-on domains¹⁴ (Fig. 1b), a successful explanation of the 90° domain configuration (Fig. 1c) by stress and strain without electrostatics^{5,6}, and the switching and the phase stability of a ferroelectric in metal/*ferroelectric/insulator/semiconductor* structures⁸ (Fig. 1d) contradict the expectations based on the conventional electrostatics of ferroelectrics¹⁵. On the other hand, theories considering a finite band gap of the ferroelectric explain these observations and predict a carrier layer on the ferroelectric surface^{12,16,17}. Indeed, the electric field induces carriers in a superconducting perovskite oxide¹⁸. Furthermore, the P_S -induced mobile carriers persist for more than 10 months on the surface of a perovskite oxide, having a band gap of 2 eV¹⁹. These observations suggest a possibility of the carrier generation in ferroelectric perovskites, although they possess a band gap of 3 - 4 eV, which requires larger band bending and may induce other screening mechanisms. Namely, a two-dimensional electron gas may exist near the free surface of the ferroelectric and improve significantly the size limit of the ferroelectric phase without electrodes. However, the physical nature of a clean ferroelectric surface remains unclear²⁰⁻²³, and the direct experimental study of such a layer has been missing so far. To identify the existence and the basic nature of the hypothetical electron layer, we have investigated the current transport on the clean, free surface of BaTiO₃.

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 boundaries¹². As-grown single crystals of BaTiO₃ grown by a flux method, which were lightly yellowish, transparent, and insulating, were used to avoid polishing procedures and possible surface damage. We have developed a technique that allows the control of P_S at the electrodeless surface of a ferroelectric. This is achieved by a pair of T-shaped Pt electrodes sputtered on the top surface of the crystals and one on the bottom surface (Fig. 2c). To avoid contamination and damage, the electrodes were defined by masks instead of a lithography process, thus avoiding mechanical contact of the gap area during the process. We confirmed the absence of the sputtered materials in the gap area.

The results below are for a crystal shown in Fig. 2c with a shiny smooth surface. 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 top two 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. 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 conductance data below were measured at a pressure of 3×10^{-8} torr in a vacuum chamber in darkness. The results below are obtained after several temperature cycles between room temperature and 150 °C in vacuum.

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 shortly after the poling procedure 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. 3). 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. Furthermore, the surface conductance in air is usually lower than that of all the polarization states in vacuum. 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 SrTiO₃ single crystals that are paraelectric. In addition, we have confirmed that these observations were not due to the change of the Schottky contacts by the current.

The surface conductance shows activation-type conduction from 200 °C to a temperature below room temperature. Figure 4a is an example of a temperature dependence of the positively poled state in which only approximately 50% of the gap area can possibly be poled due to the increase of the coercive field. The temperature dependence between 0 and -100 °C is similar to that of bulk conduction of heavily doped or semimetallic BaTiO₃. The spike in the curve is due 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. 4b). A marked observation is the increase of the surface conductance below -140 °C as seen in the zoomed view in Fig. 4a, 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. 4b). The temperature dependence of the negatively poled state, which is almost 100% expressed in terms of an area ratio, is more remarkable (Fig. 4c). The conductance at -170 °C is higher than that at room temperature.

The preceding results are consistent with the picture that an electron layer is formed at the free ferroelectric surface. Theoretically, the electron layer can also form at the domain boundaries such as the head-on or the 90° domain boundaries if the charges are not completely screened by ions at these boundaries (Fig. 1c). Indeed, one of the randomly polarized states formed during 30

poling cycles exhibited an appreciable conduction between the top and bottom electrodes that was comparable to the surface conduction and was observed at $-170\text{ }^{\circ}\text{C}$. 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. 3, 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 . Such a 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 ferroelectric. For example, the ferroelectric field-effect transistors⁸ can have a switching capability, and the ferroelectric phase in these structures is stabilized (Fig. 1d). Furthermore, the relaxation of P_S near the surface (∇P) is considered to be an important mechanism of the destabilization of the small ferroelectrics, which can also be present on a electroded ferroelectric surface^{22,23}. The simple modeling of this effect is the tri-layer structure of the ferroelectric consisting of two thin insulating surface layers with $P_S = 0$ and the layer having a bulk value of P_S (Fig. 1e). Therefore, the surface electron layer can solve various limitations posed by surface relaxation.

A theoretical calculation predicts the existence of a two-dimensional carrier layer on a ferroelectric surface¹². The accumulation of electrons at the surface is expected in positively poled states, whereas a weak inversion of whole carriers is expected in negatively poled states. When the quantization of the motion perpendicular to the surface is considered²⁴, the surface electron layer with a thickness of a few nanometers is predicted to exist a few lattices constants below the surface²⁵. This surface may not necessarily be a physical surface but, in a more exact definition, a location where P_S effectively terminates. The maximum charge density in the absence of traps is estimated to be 10^{21} - 10^{22} cm^{-3} , the total charge of which is approximately the same as P_S . Using the reported value of bulk mobility of $1\text{ cm}^2/\text{Vs}$ and the experimental surface conductivity, 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 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 contains many traps and adsorbents 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 conductance can be further increased, however, by improving the BaTiO_3 surface.

References

- 1 Bune, A.V. *et al.* Two-dimensional ferroelectric films. *Nature* **391**, 874-877 (1998).
- 2 Ghoosez, Ph. & Rabe, K. M. Microscopic model of ferroelectricity in stress free PbTiO_3 ultra-thin films. *Appl. Phys. Lett.* **76**, 2767-2769 (2000).
- 3 Shaw, T. M. *et al.* The effect of stress on the dielectric properties of barium strontium titanate thin films. *Appl. Phys. Lett.* **75**, 2129-2131 (1999).
- 4 Ganpule, C. S. *et al.* Scaling of ferroelectric properties in thin films. *Appl. Phys. Lett.* **75**, 409-411 (1999).
- 5 Pertsev, N. A. & Zembilgotov, A. G. Domain populations in epitaxial ferroelectric thin films: Theoretical calculations and comparison with experiment. *J. Appl. Phys.* **80**, 6401-6406 (1996).

- 6 Aplay, S. P. *et al.* Effect of the electrode layer on the polydomain structure of epitaxial $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films, *J. Appl. Phys.* **85**, 3271-3277 (1999).
- 7 Shih, W. Y., Shih, W. H. & Aksay, I. A. Size dependence of the ferroelectric transition of small BaTiO_3 particles: Effect of depolarization, *Phys. Rev. B* **50**, 15575-15585 (1994).
- 8 Batra, I. P., Wurfel, P. & Silverman, B. D. Phase transition, stability, and depolarization field in ferroelectric thin films, *Phys. Rev. B* **8**, 3257- 3265 (1973).
- 9 Känzig, W. Space charge layer near the surface of a ferroelectric, *Phys. Rev.* **98**, 549-550 (1955).
- 10 Rosenman, G. I. *et al.* Emission of electrons on switching of the $\text{Gd}_2(\text{MoO}_4)_3$ ferroelectric-ferroelastic in electric field. *Appl. Phys. Lett.* **56**, 689-691 (1990).
- 11 Geissler, K., Gundel, H., Riege, H. & Handerek, J. Intense laser-induced electron emission from prepoled lead-lanthanum-zirconium-titanate ceramics. *Appl. Phys. Lett.* **56**, 895-897 (1990).
- 12 Watanabe, Y. Theoretical stability of the polarization in a thin semiconducting ferroelectric. *Phys. Rev. B* **57**, 789 – 804 (1998).
- 13 Lines, M. E. & Glass, A. M. Principles and application of ferroelectrics and related materials (Clarendon Press, Oxford, 1977).
- 14 Eng, L. M., Güntherodt, H.-J., Schneider, G. A., Köpke, U. & Muñoz Saldaña, J. Nanoscale reconstruction of surface crystallography from three-dimensional polarization distribution in ferroelectric barium-titanate ceramics. *Appl. Phys. Lett.* **74**, 233-235 (1999).
- 15 Vul, B. M., Guro, G. M. & Ivanchik, I. I. Field effect at the contact between a semiconductor and a c-domain ferroelectric, *Sov. Phys. Semicond.* **4**, 128-131 (1970).
- 16 Cohen, R. E. Surface effect in ferroelectrics: Periodic slab computations for BaTiO_3 , *Ferroelectrics* **194**, 323-342 (1997).
- 17 Sugibuchi, K., Kurogi, Y. & Endo, N. Ferroelectric field-effect memory device using $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film. *J. Appl. Phys.* **46**, 2877-2881 (1975).
- 18 Mannhart, J., Schlom, D. G., Bednorz, J. G. & Müller, K. A. Influence of electric fields on pinning in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films, *Phys. Rev. Lett.* **67**, 2099-2101 (1991).
- 19 Watanabe, Y. Epitaxial all-perovskite ferroelectric field effect transistor with a memory retention. *Appl. Phys. Lett.* **66**, 1770-1772 (1995).
- 20 Padilla, J. & Vanderbilt, D. *Ab initio* study of BaTiO_3 surfaces. *Phys. Rev. B* **56**, 1625-1631 (1997).
- 21 Ravikumar, V., Wolf, D. & Dravid, V. P. Ferroelectric-monolayer reconstruction of the SrTiO_3 (100) surface. *Phys. Rev. Lett.* **74**, 960-963 (1995).
- 22 Kretschmer, W. R. & Binder, K. Surface effects on phase transitions in ferroelectrics and dipolar magnets. *Phys. Rev. B* **20**, 1065-1076 (1979).
- 23 Tilley, D. R. & Zeks, B. Landau theory of phase transitions in thick films, *Solid State Commun.* **49**, 823-827 (1984).
- 24 Ando, T. Fowler, A. B. & Stern, F. Electronic properties of two-dimensional systems, *Rev. Mod. Phys.* **54**, 437-672 (1982).
- 25 Berglund, C. N. & Baer, W. S. Electron transport in a single-domain, ferroelectric Barium Titanate. *Phys. Rev.* **157**, 358-365 (1967).

Acknowledgments

We acknowledge S. W. Cheong for his kind help with the BaTiO_3 single crystals growth, T. Shigesue and T. Obara for technical assistance and J. G. Bednorz for useful discussions and proofreading. This work was supported in part by the Asahi Glass Foundation.

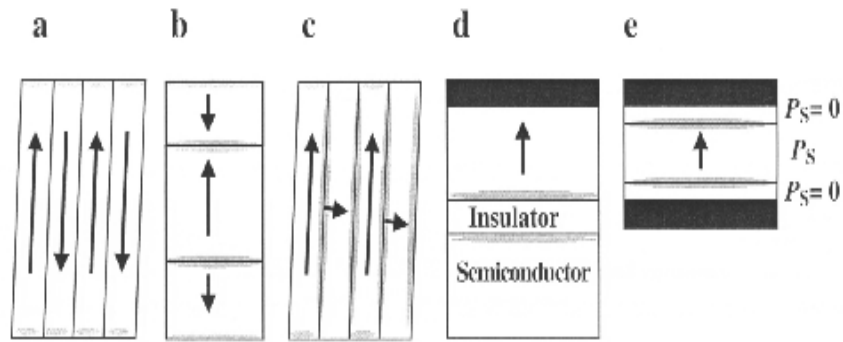


Figure 1 Typical domain configurations. Cross sectional view of 180° stripe domains, **a**. Head-on domains, **b** and 90° (a/c) domains, **c**. The arrows indicate the direction of P_S , and the shaded areas indicate the locations where the carrier is possibly generated. The dark shaded area corresponds to the metal electrode. 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, **e**. The ferroelectric layer is modeled by an insulator ($P_S = 0$)/ferroelectric (bulk value P_S)/insulator ($P_S = 0$).

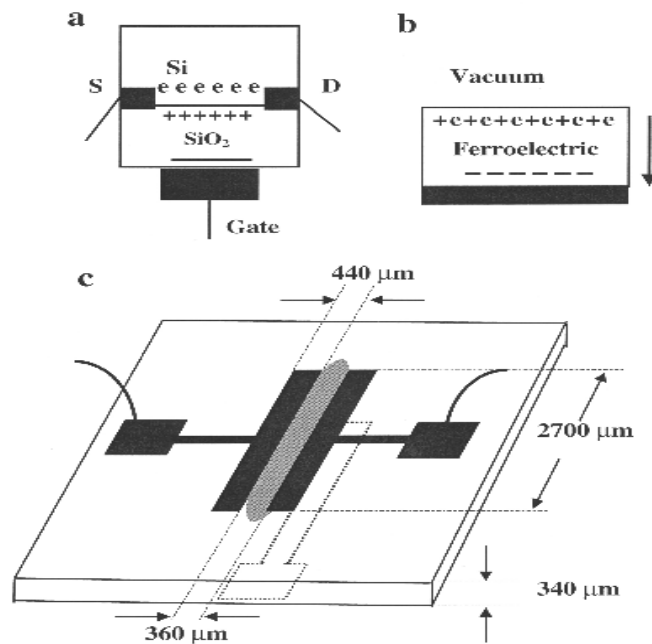


Figure 2 Sample and the comparison of the field effect in a metal/oxide/Si diode, where the field effect is due to spontaneous polarization in the ferroelectric. Inverted view of the conventional metal/oxide/Si (MOS) diode, **a**. The current from S to D is controlled by the voltage at the metal gate electrode, because SiO_2 is polarized as shown by positive and negative charges and induces the electrons (e) at the SiO_2/Si interface. Schematic diagram of the ferroelectric with one side covered with metal and the other side in contact with the vacuum **b**. The origin of the carrier accumulation is similar to that in MOS, and the charge distribution in **c** is similar to that in **b**, except that the carriers are now located in the ferroelectric. The difference is the location of the carrier that is in the ferroelectric. Schematic diagram of the sample, **c**. 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.

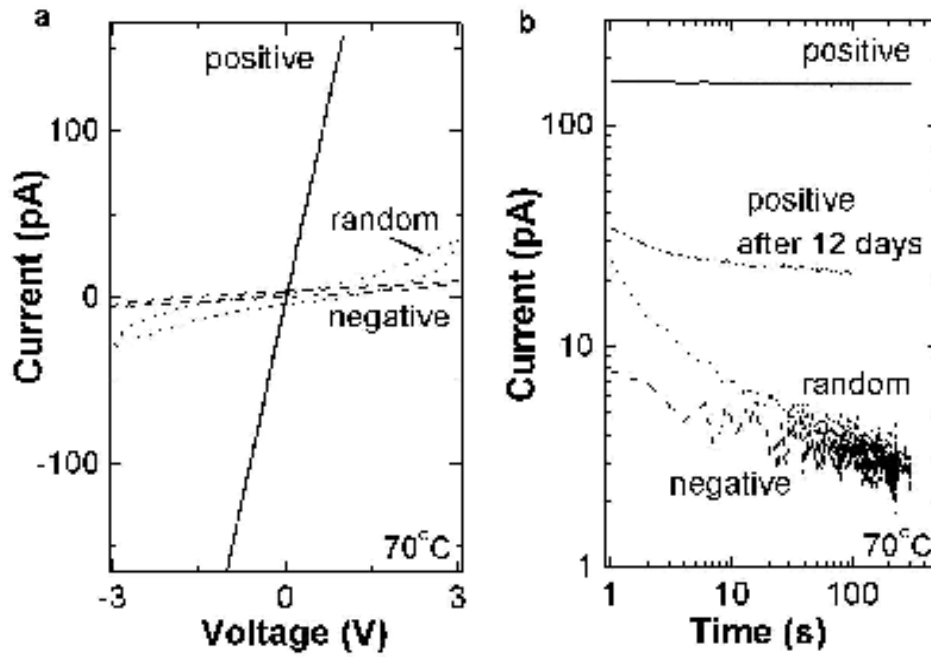


Figure 3 Polarization dependence of the surface current. Current-voltage characteristics, **a**. Time dependence of current at a fixed voltage of 1 V at 70 °C, **b**. Solid lines, dashed lines, and dotted lines correspond to a positively, a negatively, and a randomly polarized state, respectively. The dash-dotted lines in Fig. 3b correspond to the state that is kept 12 days in vacuum after positive poling.

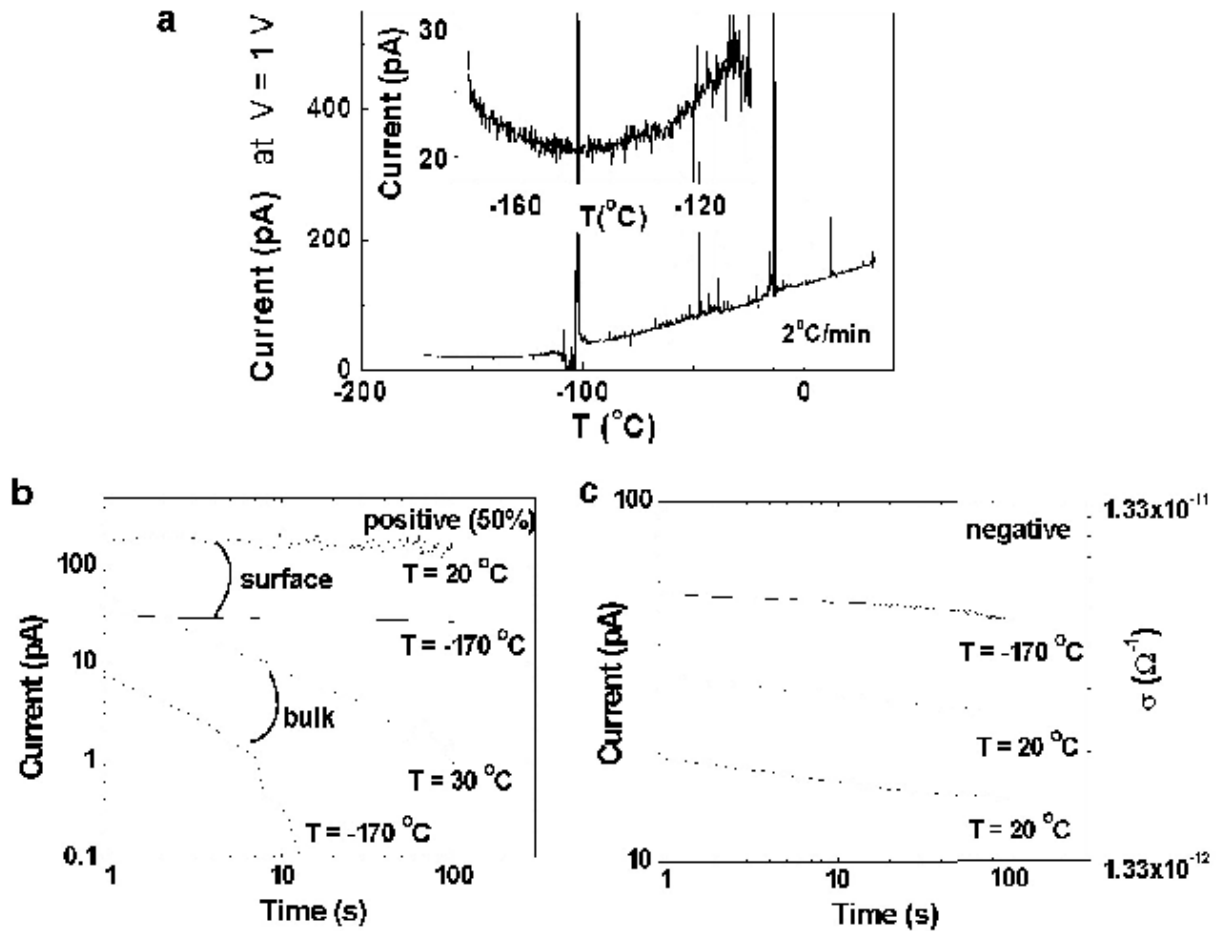


Figure 4 Temperature dependence of the surface conduction and comparison with bulk conduction.

Temperature dependence of current at a fixed voltage of 1 V with an enlarged view of a low-temperature region (inset), **a**. 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. Time dependence of the current at a fixed voltage of -1 V, **b**, of the same state as in Fig. 4a. 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. Time dependence of the surface current at a fixed voltage of -1 V of the negatively poled state, **c**. The solid, dashed, and dotted lines correspond to the surface conduction at -170°C , before cooling, and at 20°C after cooling, respectively.