Nonlinear positive temperature coefficient of resistance of BaTiO_3 film

Okano, Motochika
Department of Physics, Kyushu University

Watanabe, Yukio
Department of Physics, Kyushu University

Cheong, Sang-Wook
Bell Laboratories

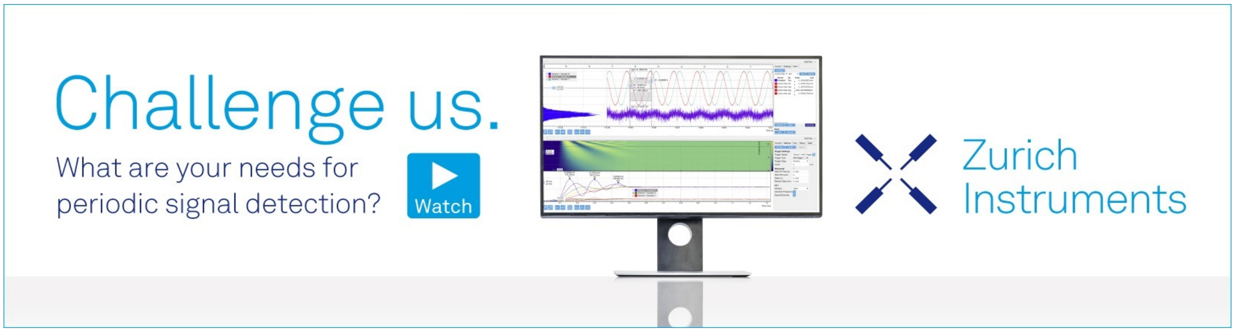
出版情報：Applied Physics Letters. 82 (12), pp.1923-1925, 2003-03-24. American Institute of Physics
バージョン：

Applied Physics Letters

Nonlinear positive temperature coefficient of resistance of $BaTiO_3$ film

Cite as: Appl. Phys. Lett. **82**, 1923 (2003); https://doi.org/10.1063/1.1563061
Submitted: 13 September 2002 . Accepted: 27 January 2003 . Published Online: 18 March 2003

Motochika Okano, Yukio Watanabe and Sang-Wook Cheong



Nonlinear positive temperature coefficient of resistance of $BaTiO_3$ film

Motochika Okano[a)] and Yukio Watanabe[b)]
Kyushu University, Hakozaki, Fukuoka, Japan 812-8581

Sang-Wook Cheong
Bell Laboratories, Murray Hill, New Jersey 07974-0636

(Received 13 September 2002; accepted 27 January 2003)

Conductance decreasing with increasing temperature (T) above a characteristic T (T_0) is found in the reverse-diode characteristics of metal contacts on strained $BaTiO_3$ epitaxial films. The conduction mechanisms below and above T_0 near the Curie temperature of the bulk $BaTiO_3$ are distinctly different. Marked similarities to these characteristics are found in the surface conduction on $BaTiO_3$ single crystal in a high vacuum. By comparing the observations with the positive temperature coefficient of resistance (PTCR) effect in ceramics, we suggest that the anomaly is regarded as a PTCR effect at metal/ferroelectric contact, and discuss the origin of the effect in thin films and single crystals. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1563061]

The positive temperature coefficient of resistance (PTCR) effect has been widely used.[1] Although the PTCR effect in ceramics is attributed to the change of the potential barrier at grain boundaries due to the ferroelectric–paraelectric phase transition,[2] the details are still controversial. It has also been observed in single crystals[3] and single-grain ferroelectrics.[4] However, no PTCR effect in thin films has been reported,[5] except for a similar effect in a paraelectric $Ba_{0.5}Sr_{0.5}TiO_3$ polycrystalline film and those at low T.[6] This is partly because of the suppression of the phase transition by the strain caused by the substrate.[7,8] Here, we found a PTCR-like anomalous conduction in $BaTiO_3$ (BTO) epitaxial films, by examining very small reverse current through the Schottky contact on the BTO films. We report also similar phenomena in the surface conduction of a BTO single crystal in a high vacuum.

BTO films are epitaxially grown on 0.5-wt % Nb-doped $SrTiO_3$ (STON) that serves an ohmic bottom contact. We concentrate on a 100-nm-thick Au electrode (0.2 mm^2) deposited near 25 °C on a 230-nm-thick BTO film that shows well-defined diode properties and a remnant polarization of 1–2 $\mu C/cm^2$. The samples are annealed beforehand in air at the highest T of each experiment to exclude extraneous T dependences, such as the chemical change of the contact electrode. X-ray diffractometry shows that the c-axis lattice constant increases from the bulk value of 4.036 to 4.092 Å, and its ratio to the a-axis lattice constant increases from 1.01 to 1.03. The estimated two-dimensional strain is approximately 2.98 GPa. According to the Ginzburg–Landau theory, this leads to the enhanced Curie temperature T_C, which is over 600 °C in a crude estimation, disregarding the effects of the thermal expansion and the inhomogeneity. The real part of the static permittivity ε increases monotonically with temperature (T), at least to 150 °C, consistently with the estimated T_C enhancement (Fig. 1).

The current–voltage characteristics exhibit Schottky diode properties (Fig. 2). The conductance both in the forward high voltage and the low-voltage ohmic region increases monotonically with T. However, the reverse-bias current density I_R decreases with T between 80 and 150 °C (Fig. 3). Most of the measured Au and Pt electrodes exhibit similar anomalies. The $I-V$ characteristics measured afterwards show that I_R increases rapidly above 180 °C. The hysteresis in $I-V$ curves are due to the capacitive response or the emission/absorption of the trapped carriers (dielectric relaxation), because I_R during the increase of the absolute voltage $|V|$ $[I^+(V)]$ is higher than I_R during the decrease of $|V|$ $[I^-(V)]$[9] and the hysteresis decreases by reducing the voltage sweep speed. The net dc conduction component at V approximated by $[I^+(V)+I^-(V)]/2$ is shown in Fig. 3,[10] and an effective permittivity ε_{eff} is deduced from the capacitive response $[I^+(V)-I^-(V)]/2$ (inset of Fig. 1). T at which the T dependence changes (T_0) is 80 °C in Fig. 3 and T_0 tends to increase and become less well defined with repeated experiments. This may be due to the change of the strain at the surface by the unintended annealing effect.

The observed T dependence resembles the PTCR effect in ceramics. Figure 4 shows that T_0 shifts toward a higher T with decreasing $|V|$. Indeed, this characteristic is observed in the PTCR effect in single-grain samples, whose conductance starts to decrease from 30–40 °C below T_C.[11]

The T dependence of the conductance in the ohmic re-

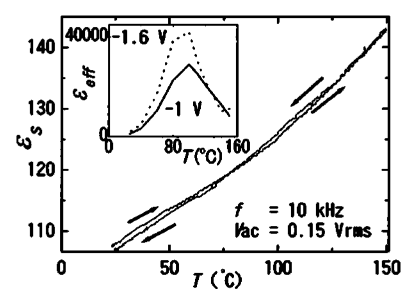


FIG. 1. T dependence of the real part of the permittivity ε at 10 kHz of Au/BTO/STON from 25 to 150 °C and from 150 to 26 °C. The arrows show the direction of the T change. Inset shows an ε_{eff} at −1 and −1.6 V, whereas the absolute value has little physical significance.

[a)]Present address: Toshiba Corp.
[b)]Author to whom correspondence should be addressed; electronic mail: ynab7scp@mbox.nc.kyushu-u.ac.jp

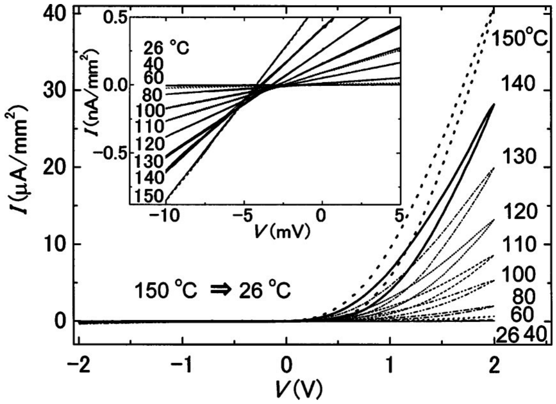


FIG. 2. $I-V$ characteristics of Au/BTO/STON during cooling. Similar characteristics are observed during heating. The inset shows the $I-V$ characteristics for a low-bias voltage swing of 10 mV, in which the curves shift upward with increasing T.

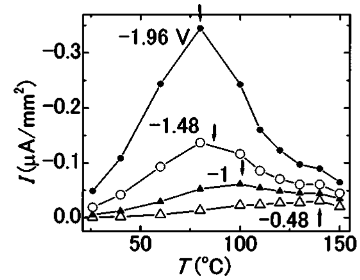


FIG. 4. T dependence of the reverse current density I_R at −0.48 V (open triangles), −1 V (filled triangles), −1.48 V (open circles), and −1.96 V (filled circles) extracted from the net dc current component in Fig. 3. The arrows show the peak positions.

gion is ordinary, which shows that the bulk properties, such as the mobility and the carrier density, possess a normal T dependence. However, the diode-like $I-V$ characteristics prove that the nonlinear conduction is limited by the surface, at least, at one polarity. Figure 5 confirms that the reverse-bias current below T_0 is limited by the surface: the $I-V$ characteristics below T_0 is markedly well explained by the Schottky emission model $I_R \propto T^2 \exp(-q\phi/kT - q\sqrt{qE/4\pi\varepsilon_d}/kT)$, where q, k, ϕ, ε_d, and E are the elementary charge, the Boltzmann constant, the barrier height without the barrier lowering effect, the dynamic permittivity, and the electric field ($\propto V$), respectively.[12] Moreover, the T dependence is explicable by kT in this formula with a constant ε_d below T_0 [inset of Fig. 5(b)]. Figures 5(a) and 5(b) indicate that the conduction mechanism changes at T_0, and no standard conduction mechanisms explain the conduction above T_0. On the other hand, the forward-bias current between +1 and +2 V shows the ordinary activation-type T dependence, with the activation energy 0.55–0.58 eV for 25–150 °C. With increasing T, its $I-V$ characteristics become fitted well by the space-charge-limited-current model[12] that is applied to the bulk conduction, which explains the absence of the anomaly. This is because the Schottky barrier becomes conductive enough for the forward bias current due to the factor $\exp(qV/kT)$.

The PTCR effect in ceramics is conventionally explained by the change of the barrier height at T_C.[2] Similarly, the preceding results suggest that the decrease of conductance is due to the increase of an effective barrier height above T_0. Its possible origin can be ion segregation due to the increased ion mobility at high T, the change of the surface state by the spontaneous polarization P_S, or the change of the leakage current path by the change of P_S and the domain configuration. The first possibility is improbable, because the $I-V$ characteristics are observed at the same T during both cooling and heating. Therefore, we examine the last two origins, which are related to the ferroelectric phase transition at the surface.

T_0 is 40–50 °C below T_C of the bulk BTO (i.e., 120–130 °C), similar to the PTCR effect of the single-grain samples.[11] The observed $\varepsilon-T$ characteristics in Fig. 1 would not contradict the diffuse phase transition at the surface,[13] if $t_{surf} < t_{rest}$ and $\varepsilon_{surf} > \varepsilon_{rest}$, because $1/\varepsilon = [t_{surf}/\varepsilon_{surf} + (t - t_{surf})/\varepsilon_{rest}]/t$, where t and ε are the thickness and the permittivity of the BTO film, respectively, and the quantities with the subscripts "surf" and "rest" are

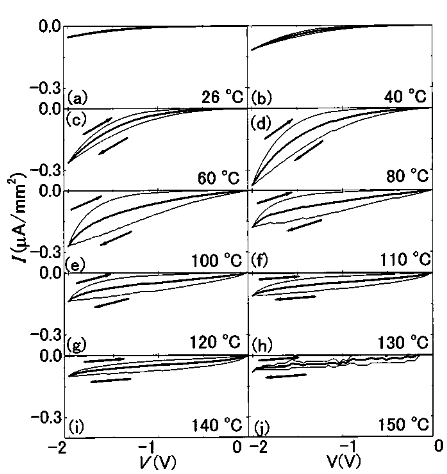


FIG. 3. Enlarged replots of $I-V$ characteristics at reverse bias (negative voltage on the Au electrode) from Fig. 2. Thick lines in the middle of each $I-V$ hysteresis curve show the net dc current component density. The arrows show the direction of the change. The T dependence during heating is the same, except for T of the minimum conductance occurring at 130 and 150 °C.

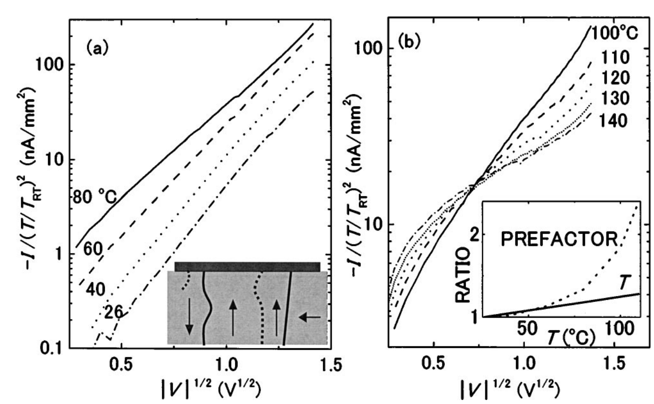


FIG. 5. Schottky plot ($\log I - \sqrt{V}$) of the $I-V$ characteristics at reverse bias below (a) and above T_0 (b) replotted from Fig. 3. Different lines correspond to 80 °C (100 °C), 60 °C (110 °C), 40 °C (120 °C), 26 °C (130 °C), and (140 °C), respectively. $T_{RT} = 298$ K. The characteristics above T_0 are inexplicable by such other established models as space conduction, Poole–Frenkel, and the Fowler–Nordheim tunneling model. Inset in (a) illustrates the model of the domains and the conduction passes. Inset in (b) shows the ratios of T to 299 K = 26 °C (solid lines) and the prefactor of $\sqrt{E}$ in $\exp(q\sqrt{qE/4\pi\varepsilon_d}/kT)$ (dotted lines) obtained by curve fitting to the data, where its ratio is mostly given by $T/\sqrt{\varepsilon_d}$.

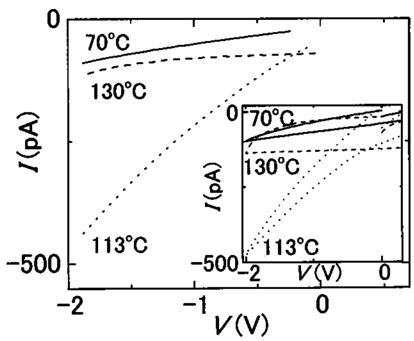


FIG. 6. Conduction on BTO surface in a high vacuum at 70, 113, and 130 °C. T_C estimated by the polarization microscope is between 113 and 130 °C. The main figure shows net dc current with zero bias current corrected. The inset is the original data showing the large capacitive response near T_C.

those of the top surface and the bulk/bottom-surface, respectively. We expect $t_{surf} < t_{rest}$ and $\varepsilon_{surf} > \varepsilon_{rest}$, because the strain that is expected to reduce ε[7,8] is highest at the bottom surface and relaxes toward the top surface.

Indeed, the inset of Fig. 1 shows a marked increase of the dielectric response ε_{eff} that peaks near the bulk T_C, which is probably associated with the domain wall motion as reported for the ferroelectric superlattice.[14] Therefore, the T dependence of ε_{eff} supports the variableness of P_S and the domain wall near T_0. Additionally, the nonlinear dielectric response or the domain wall motion near T_0 may explain the deviation of the $I-V$ characteristics from the standard conduction mechanisms.

The observations indicate consistently that the anomaly starting at T_0 is related to the ferroelectric phase transition and, therefore, can be regarded as a PTCR effect. However, the present results are insufficient to identify detailed mechanisms. One of the possible origins is the change of ϕ by P_S, which is not supported, at least, by the experiments at 25 °C.[9] Another explanation is based on the assumption that the current is injected from the special locations at the surface such as the domain boundaries or the dislocations [inset of Fig. 5(a)], which is indicated by the measurement of nanometer-scale contacts.[15] Therefore, the possibility arises that the change of the crystallographic structure by the phase transition induces strain that concentrates at these locations and subsequently changes their electronic state.

An idealized model of these locations is the *c*-surface of BTO single crystal. Indeed, the $I-V$ characteristics of the surface conduction on an insulating BTO single crystal near T_C exhibit a remarkable similarity to Fig. 3 (see Fig. 6).[16] Here, these $I-V$ characteristics should be regarded as reverse-bias characteristics, because Pt/BTO-surface/Pt is a double Schottky diode and the current is limited by the most resistive part, that is a reverse-biased contact. Actually, the $I-V$ characteristics of the surface conduction slightly below T_C, for example, at 100 °C, are well explained by the Schottky emission model. These observations invoke a speculative mechanism: the density of the carriers that possibly exist at the $a-c$ or the head-on domain boundaries decreases near T_C, as shown in Ref. 16, leading to the increase of ϕ. This model appears also consistent with Fig. 5.

In summary, we report the reverse-bias conductance decreasing with increasing T above T_0, which we regard as a PTCR effect at the metal/ferroelectric contact. We suggest that the reduction of the PTCR effect in thin films is probably due to the current limitation by the Schottky contact instead of the ferroelectric/ferroelectric contact, the diffuse phase transition, and the suppression of the domain wall population.

KAKENHI's Nos. 12134208, 13640334, and 14038235 are acknowledged.

[1] See, for example, Q. Jianquan, Z. Qing, W. Yongli, W. Yajing, and L. Longtu, Solid State Commun. **120**, 505 (2001); M. M. Gallego and A. R. West, J. Appl. Phys. **90**, 394 (2001).
[2] W. Heywang, Solid-State Electron. **3**, 51 (1961); G. H. Jonker, *ibid.* **7**, 895 (1964).
[3] I. Ueda and S. Ikegami, J. Phys. Soc. Jpn. **20**, 546 (1965); S. Ikegami, I. Ueda, and Y. Ise, *ibid.* **16**, 572 (1961); J. B. MacChesney and J. F. Potter, J. Am. Ceram. Soc. **48**, 81 (1965).
[4] M. Kuwarabara, K. Morino, and T. Matsunaga, J. Am. Ceram. Soc. **79**, 997 (1996).
[5] N. Lemée, C. Dubourdieu, G. Delabouglise, J. P. Sénateur, and R. Laroudie, J. Cryst. Growth **235**, 347 (2002); M. N. Khan, H.-T. Kim, T. Kusawake, H. Kudo, K. Ohsima, and H. Uwe, J. Appl. Phys. **86**, 2307 (1999).
[6] C. S. Hwang, B. T. Lee, H. J. Cho, K. H. Lee, C. S. Kang, H. Horii, S. I. Lee, and M. Y. Lee, Appl. Phys. Lett. **71**, 371 (1997); Y. Watanabe, Phys. Rev. B **57**, R5563 (1998).
[7] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
[8] Y. Watanabe and A. Masuda, Jpn. J. Appl. Phys. **40**, 5610 (2001).
[9] Y. Watanabe, Phys. Rev. B **59**, 11257 (1999).
[10] During each $I-V$ measurement, the steps of $V(dV)$ and $t(dt)$ (t: time) are kept constant. Therefore, the capacitive response $I_d = C(V)\ dV/dt$ (C: capacitance) is removed $C(V)$ is approximately given by $[I^-(V) - I^+(V)]/2/(dV/dt)$.
[11] K. Hamamoto and M. Kuwabara, Jpn. J. Appl. Phys. **40**, L1163 (2001).
[12] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
[13] C. B. Parker, J.-P. Maria, and A. I. Kingon, Appl. Phys. Lett. **81**, 340 (2002).
[14] A. Erbil, Y. Kim, and R. A. Gerhardt, Phys. Rev. Lett. **77**, 1628 (1996).
[15] Y. Watanabe, D. Sawamura, and M. Okano, Appl. Phys. Lett. **72**, 2415 (1998).
[16] Y. Watanabe, M. Okano, and A. Masuda, Phys. Rev. Lett. **86**, 332 (2001). Details of the experimental condition are similar to those in this Ref.