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Okano, Motochika Department of Physics, Kyushu University

Watanabe, Yukio Department of Physics, Kyushu University

Cheong, Sang-Wook Bell Laboratories

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## Nonlinear positive temperature coefficient of resistance of BaTiO<sub>3</sub> film

Motochika Okano<sup>a)</sup> and Yukio Watanabe<sup>b)</sup> Kyushu University, Hakozaki, Fukuoka, Japan 812-8581

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

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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<sub>3</sub> epitaxial films. The conduction mechanisms below and above  $T_0$  near the Curie temperature of the bulk BaTiO<sub>3</sub> are distinctly different. Marked similarities to these characteristics are found in the surface conduction on BaTiO<sub>3</sub> 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.<sup>1</sup> Although the PTCR effect in ceramics is attributed to the change of the potential barrier at grain boundaries due to the ferroelectricparaelectric phase transition,<sup>2</sup> the details are still controversial. It has also been observed in single crystals<sup>3</sup> and singlegrain ferroelectrics.<sup>4</sup> However, no PTCR effect in thin films has been reported,<sup>5</sup> except for a similar effect in a paraelectric  $Ba_{0.5}Sr_{0.5}TiO_3$  polycrystalline film and those at low T.<sup>6</sup> This is partly because of the suppression of the phase transition by the strain caused by the substrate.<sup>7,8</sup> Here, we found a PTCR-like anomalous conduction in BaTiO<sub>3</sub> (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<sub>3</sub> (STON) that serves an ohmic bottom contact. We concentrate on a 100-nm-thick Au electrode (0.2 mm<sup>2</sup>) 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 Tdependences, 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  $T_{\rm C}$ , 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  $\varepsilon$  increases monotonically with temperature (T), at least to  $150 \,^{\circ}$ C, consistently with the estimated  $T_{\rm C}$  enhancement (Fig. 1).

The current-voltage characteristics exhibit Schottky di-

ode 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  $I_{\rm R}$  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  $I_{\rm R}$  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  $I_{\rm R}$  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 Vapproximated by  $[I^+(V)+I^-(V)]/2$  is shown in Fig. 3,<sup>10</sup> and an effective permittivity  $\varepsilon_{eff}$  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  $T_{\rm C}$ .<sup>11</sup>

The T dependence of the conductance in the ohmic re-



FIG. 1. *T* dependence of the real part of the permittivity  $\varepsilon$  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  $\varepsilon_{\rm eff}$  at -1 and -1.6 V, whereas the absolute value has little physical significance.

<sup>&</sup>lt;sup>a)</sup>Present address: Toshiba Corp.

<sup>&</sup>lt;sup>b)</sup>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*.

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  $I_{\rm R} \propto T^2 \exp(-q\phi/kT - q\sqrt{qE/4\pi\varepsilon_d}/kT)$ , where  $q, k, \phi, \varepsilon_d$ , 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.<sup>12</sup> Moreover, the T dependence is explicable by kT in this formula with a constant  $\varepsilon_d$  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 spacecharge-limited-current model<sup>12</sup> that is applied to the bulk



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. 4. *T* dependence of the reverse current density  $I_{\rm R}$  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.

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  $T_{\rm C}$ .<sup>2</sup> 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  $P_{\rm S}$ , or the change of the leakage current path by the change of  $P_{\rm S}$  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.<sup>11</sup> The observed  $\varepsilon - T$  characteristics in Fig. 1 would not contradict the diffuse phase transition at the surface,<sup>13</sup> 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  $\varepsilon$  are the thickness and the permittivity of the BTO film, respectively, and the quantities with the subscripts "surf" and "rest" are



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.  $T_{\rm RT} = 298$  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.  $T_{\rm C}$  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  $T_{\rm C}$ .

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  $\varepsilon^{7,8}$  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  $\varepsilon_{\rm eff}$  that peaks near the bulk  $T_{\rm C}$ , which is probably associated with the domain wall motion as reported for the ferroelectric superlattice.<sup>14</sup> Therefore, the *T* dependence of  $\varepsilon_{\rm eff}$  supports the variableness of  $P_{\rm S}$  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  $\phi$  by  $P_s$ , which is not supported, at least, by the experiments at 25 °C.<sup>9</sup> 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 nanometerscale contacts.<sup>15</sup> 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  $T_{\rm C}$  exhibit a remarkable similarity to Fig. 3 (see Fig. 6).<sup>16</sup> 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  $T_{\rm C}$ , 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  $T_{\rm C}$ , as shown in Ref. 16, leading to the increase of  $\phi$ . 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.

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