# The electronic conduction mechanism in barium strontium titanate thin films

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In the literature, the Schottky emission equation is widely used to describe the conduction mechanism in perovskite-type titanate thin films. Though the equation provides a good fit to the leakage current data, the extracted values of the Richardson and dielectric constants are inconsistent with their experimental values. In this work, a modified Schottky equation is applied. This equation resolves the difficulties associated with the standard Schottky equation. Also, the electronic mobility in thin films of barium strontium titanate is reported. © *1998 American Institute of Physics.*
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Thin films of perovskite-type titanates such as $Ba_{1-x}Sr_xTiO_3$ (BST), $SrTiO_3$, and $BaTiO_3$ are of great interest for a variety of integrated devices such as dynamic random access memory (DRAM),[1] decoupling capacitors,[2] pyroelectric infrared (IR) sensors,[3] and piezoelectric microactuators.[4] To successfully use these films for technological applications, the material and electrical properties of these films need to be better understood. Consequently, these films have been the focus of extensive research in the last several years.

An important property of perovskite-type titanate thin films is the charge transport or conduction mechanism. In recent years, several studies have investigated the dependence of the measured leakage current on voltage, temperature, and electrode materials in these films.[5–9] The measured current is observed to be interface limited and the Schottky emission equation[10] is widely used to describe the conduction mechanism. Although the Schottky equation gives a good fit to the data, the extracted parameters such as the Richardson and dielectric constants are inconsistent with their experimental values. The extracted value of the Richardson constant is 3–5 orders of magnitude smaller than its value of 120 A/cm$^2$ K$^2$ for the free-electron mass.[5–7,9] Since the effective mass is about five times heavier than the free-electron mass in crystalline perovskite-type titanates,[11,12] this discrepancy cannot be attributed to the effective electron mass. In addition, the optical dielectric constant obtained from the Schottky equation varies between 0.5 and 1.8;[5–7,9] these values are much smaller than that determined by optical methods.[13] These discrepancies indicate that the Schottky emission equation does not provide a satisfactorily description of the conduction mechanism in thin perovskite-type titanate films. In this letter, a modified Schottky equation[14] is applied to the leakage current data for thin-film $Ba_{0.5}Sr_{0.5}TiO_3$ capacitors with platinum electrodes. Using the modified equation, the discrepancies in the extracted values of the Richardson and dielectric constants are resolved. Also, the electronic mobility in thin films of BST is reported.

We commence by reviewing the standard Schottky equation that was originally derived for a metal/vacuum interface.[10] This equation is widely applied to the leakage current data for perovskite-type titanate thin films and is written as

$$J = A^*T^2 \exp(-\phi_b/kT)\exp(\beta\sqrt{E_0}),$$
$$A^* = (4\pi em^*k^2/h^3), \tag{1}$$

where $J$ is the current density, $\beta = (e/kT)(e/4\pi\epsilon_0\epsilon)^{1/2}$, $\epsilon_0$ is the permittivity of free space, $\epsilon$ is the optical dielectric constant, $E_0$ is the electric field at the metal/insulator interface, $e$ is the electronic charge, $k$ is the Boltzmann constant, $h$ is the Planck constant, $\phi_b$ is the barrier height at the cathode, $A^*$ is the Richardson constant, and $m^*$ is the effective electron mass.

Simmons showed[14] that the above equation is applicable to insulators only if the electronic mean-free path in the insulator is equal to or greater than the thickness of the insulator. For insulators in which the electronic mean-free path is less than the insulator thickness, Eq. (1) is modified and written as

$$J = \alpha T^{3/2}E_0\mu(m^*/m_0)^{3/2}\exp(-\phi_b/kT)\exp(\beta\sqrt{E_0}), \tag{2}$$

where $\alpha = 3\times10^{-4}$ A s/cm$^3$ K$^{3/2}$, $\mu$ is the electronic mobility in the insulator, and $m_0$ is the free-electron mass; the rest of the symbols have been defined earlier. Since $\mu$ is weakly dependent on temperature in $BaTiO_3$ and $SrTiO_3$ single crystals,[11,15–17] $\mu$ is assumed to be a constant in the present study. It may also be noted that there is no clear distinction between bulk and electrode limited conduction mechanisms in Eq. (2) because each plays a part in the conduction process. The density of the free carriers at the interface is electrode limited while the mobility is a bulk property.

Current measurements were performed on $Ba_{0.5}Sr_{0.5}TiO_3$ capacitors with platinum (Pt) electrodes using source measurement units (HP 4657); the voltage was applied at the top electrode. The BST films were sputter deposited at 550 °C in an ambient of oxygen and argon gases. The BST film thickness is 600 Å as determined by the ellipsometry; the capacitor areas ranged from $1\times10^{-5}$ to $5.3\times10^{-5}$ cm$^2$.
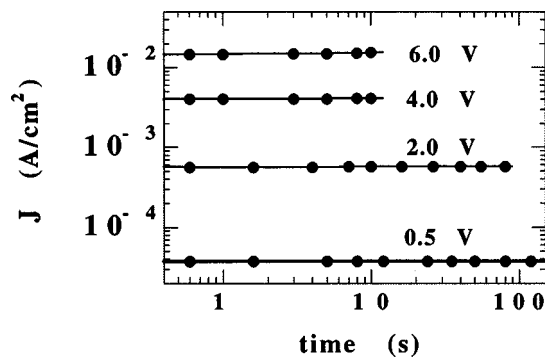
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FIG. 1. The dependence of current density on time ($t$) as a function of applied voltages at 142 °C, measurements were performed on a Pt/BST/Pt capacitor.

Figure 1 shows the dependence of the current density on time as a function of applied voltage for a BST capacitor; measurements were made at 142 °C. As shown in Fig. 1, the current density remains constant with time and is a measure of the steady-state current density. Currents were measured for $\leqslant 100$ s because at longer times, particularly at higher voltages, the current density starts to increase with the onset of resistance degradation. Similar measurements were also performed at other temperatures. In the present study, the current density is observed to reach its steady-state value within seconds for temperatures $> 75$ °C. It should be pointed out that this behavior of currents reaching steady state within a few seconds is not always observed for BST thin films. As reported in the literature,[5,6,14] the current density is observed to decay with time over hundreds of seconds in some BST capacitors. This decay of the current density is voltage polarity dependent and does not have a power-law dependence on time with power $\approx -1.0$, and therefore, cannot be identified with dielectric relaxation currents. This slowly decaying current is identified with the ionic current associated with oxygen vacancies and is discussed in detail elsewhere.[18] Since the electronic mobility is much greater than the ionic mobility, the current density would reach its steady-state value in a few seconds only in those samples in which the dominant conduction mechanism is electronic and not ionic. Therefore, in the present study with its focus on the electronic conduction mechanism, only those samples are studied in which the electronic current is the dominant component as indicated by the absence of transients in current versus time curves.

The voltage dependence of the steady-state current density ($J$) for BST capacitors is shown in Fig. 2; the voltage is of positive polarity applied at the top electrode. In Fig. 2(a), the data is analyzed using the Schottky equation [Eq. (1)]. Figure 2(a) shows the dependence of the steady-state current density on the square root of the applied voltage measured at sample temperatures of 75 and 142 °C. The Schottky equation provides a good fit to the data as indicated by the solid lines. The slope of the fit provides an estimate of the optical dielectric constant ($\epsilon$). The extracted values of $\epsilon$ are show in Fig. 2(a) and the mean $\epsilon = 1.7$. Hence, the extracted optical dielectric constant is about a factor of 3 lower than the optically determined value of 4.8.[13] This discrepancy in the extracted $\epsilon$ can be resolved by the modified Schottky equation [Eq. (2)]. The above data are replotted in accordance with
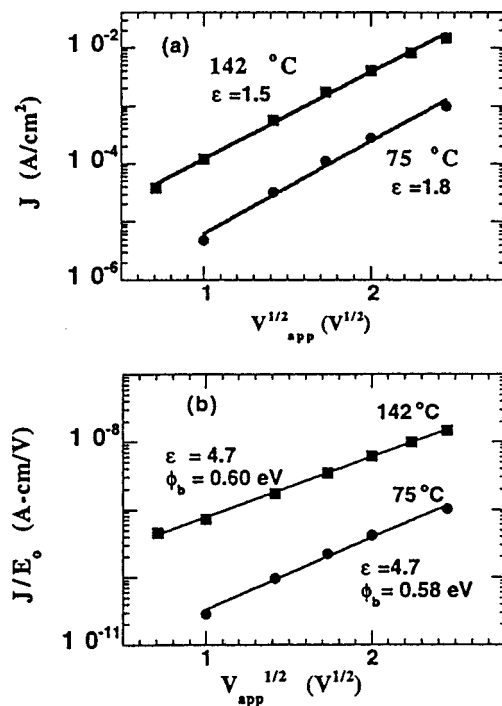


FIG. 2. Dependence of steady-state current density ($J$) on applied voltage ($V_{app}$) at 75 and 142 °C for Pt/BST/Pt structures. Symbols are the measurements and solid lines are fits to the data; $\epsilon$ is the optical dielectric constant extracted from the slope of the fit. (a) Data are plotted in accordance with Eq. (1); (b) data are plotted in accordance with Eq. (2); $\phi_b$ is the barrier height.

Eq. (2) in Fig. 2(b). In Fig. 2(b), $J/E_0$ is plotted versus the square root of applied voltage in Fig. 2(b), where $E_0$ is the field at the cathode interface. Since several studies indicate that BST thin-film capacitors are completely depleted,[6,9] we set $E_0 = V_{app}/d$, where $d$ is the BST film thickness. The modified Schottky equation provides a good fit to the data, as indicated by solid lines. The slope of the fit provides an estimate of the optical dielectric constant ($\epsilon$): $\epsilon$ is estimated to be 4.7 at both 75 and 142 °C. This extracted value of $\epsilon$ agrees within 5% with the optically determined value of 4.8.[13] Hence, unlike Eq. (1), the modified Schottky equation [Eq. (2)] provides a satisfactory description of $\epsilon$.

We will now discuss the difficulty associated with the extracted Richardson constant using the Schottky equation [Eq. (1)]. The steady-state current density ($J$) was measured as a function of temperature ($T$) for two different applied voltages. In Fig. 3(a), $J/T^2$ is plotted versus $1/T$ in accordance with Eq. (1). The Schottky equation provides a good fit to the data, as indicated by solid lines. The preexponential factor of the fit is a measure of the Richardson constant ($A^*$). As shown in Fig. 3(a), the extracted value of $A^*$ is 0.01 A/cm$^2$ K$^2$. From Eq. (1), this extracted value of $A^*$ implies that the effective electron mass $m^* \approx 0.0001 m_0$, where $m_0$ is the free-electron mass. In comparison, $A^* \approx 600$ A/cm$^2$ K$^2$ with $m^* \approx 5 m_0$ in crystalline BaTiO$_3$ (Ref. 11) and SrTiO$_3$.[12] Hence, Schottky equation analysis yields $A^*$ and $m^*$ values that are five orders of magnitude smaller than those observed in crystalline BaTiO$_3$ and SrTiO$_3$. This incompatibility can be resolved by the application of the modified Schottky equation as discussed below.

The data shown in Fig. 3(a) are replotted in Fig. 3(b). In Fig. 3(b), the data are plotted in accordance with the modi-

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pendent current density data are plotted in accordance with Eq. (2) in Fig. 2(b). In Fig. 2(b), the preexponential factor provides an estimate of $\phi_b$, provided $\mu$ and $m^*$ are known. As discussed above, $m^* = 5m_0$ and $\mu = 0.001$ cm²/V s. Using these values of $\mu$ and $m^*$, $\phi_b$ is estimated to be 0.58 and 0.60 eV at 75 and 142 °C, respectively, and is shown in Fig. 2(b). Hence, voltage-dependent data yield mean $\phi_b = 0.59$ eV. We now estimate $\phi_b$ from the temperature-dependent data shown in Fig. 3(b). In Fig. 3(b), the slope of the fit provides an estimate of $\phi_b$ provided the optical dielectric constant ($\epsilon$) is known. From Fig. 2(b), $\epsilon = 4.7$. Using this value of $\epsilon$, the temperature-dependent data yield mean $\phi_b = 0.71$ eV as shown in Fig. 3(b). In summary, the estimated $\phi_b$ is 0.6 and 0.7 eV from the voltage and temperature dependent data, respectively. These $\phi_b$ values differ by 16% and the modified Schottky equation is self-consistent within the experimental error.

In conclusion, we have applied a modified Schottky equation to the current data in thin films of BST. In comparison to the standard Schottky equation, this equation provides a more satisfactory description of the electronic conduction mechanism in thin BST films.
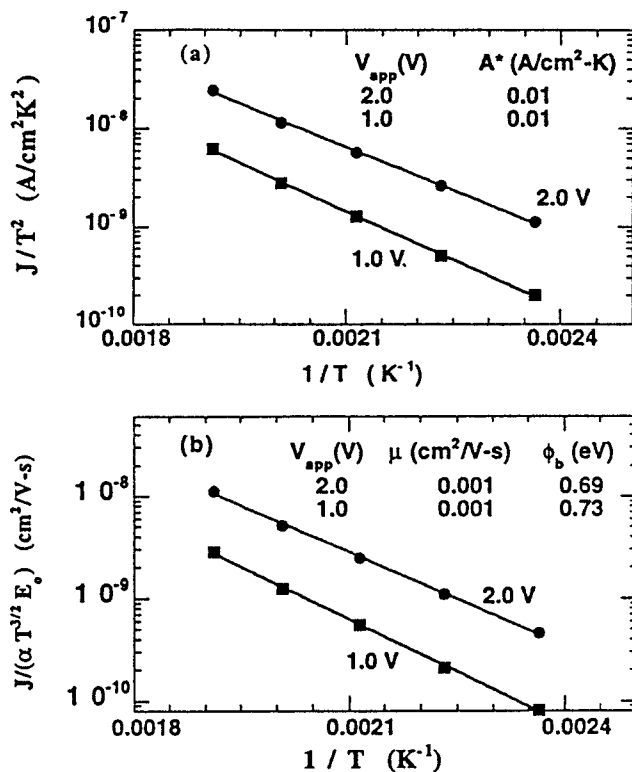
FIG. 3. Dependence of steady-state current density ($J$) on temperature ($T$) at constant applied voltage ($V_{app}$) for Pt/BST/Pt structures; symbols are the measurements and solid lines are the fits. (a) Data are fitted in accordance with Eq. (1) and the Richardson constant ($A^*$) is obtained from the preexponential factor of the fit. (b) data are plotted in accordance with Eq. (2) with $\alpha = 3 \times 10^{-4}$ A s/cm³ K$^{3/2}$ and $E_0$ is the applied electric field; the electronic mobility ($\mu$) the barrier heights ($\phi_b$) are extracted from the fits.

fied Schottky equation [Eq. (2)]: $J/(\alpha T^{3/2} E_0)$ is plotted versus $1/T$; where, $\alpha = 3 \times 10^{-4}$ A s/cm³ K$^{3/2}$ and $E_0 = V_{app}/d$. The modified Schottky equation provides a good fit to the data, as indicated by the solid lines. The preexponential factor of the fit is equal to $[\mu(m^*/m_0)^{3/2}]$, where $\mu$ is the electronic drift mobility in the BST film. In BaTiO$_3$ and SrTiO$_3$ single crystals, $m^* \approx 5m_0$,[11,12] whereas $\mu$ varies over a large range and depends on the resistivity of the sample.[11,16,17,19] Hence, we set $m^* = 5m_0$ and determine $\mu$ from the preexponential factor of the fit. The estimated $\mu = 0.001$ cm²/V s, as shown in Fig. 3(b). This estimated mobility is about ten times smaller than those observed in insulating SrTiO$_3$ (Ref. 16) and BaTiO$_3$ (Ref. 17) single crystals. In insulating crystalline titanates, the mobility is attributed to a trap limited mechanism.[19] If we assume similar trap limited mobility in thin polycrystalline BST films, then the above-stated difference in $\mu$ can be attributed to variation in trap energy levels and densities.

Finally, the self-consistency of the modified Schottky equation [Eq. (2)] is examined by comparing the barrier height ($\phi_b$) estimated from the voltage-dependent data obtained from the temperature-dependent data. The voltage de-

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