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Conduction mechanisms in $BaTiO_3$ thin films

P. Li and T.-M. Lu
Department of Physics and Center for Integrated Electronics, Rensselaer Polytechnic Institute, Troy, New York 12180

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We report the observation of two types of $BaTiO_3$ thin films, one exhibiting the Poole-Prenkel transport mechanism and the other the field-enhanced Schottky mechanism. A factor-of-2 difference in the slope of the $\log_{10}(I/V)$-vs-$V^{1/2}$ curves has been measured for these two types of films. Also, we have unambiguously determined that the static dielectric constant should be used to describe the carrier transport in these films.

The study of carrier transport in insulating films is important both from the fundamental and the practical points of view. Although the conduction mechanisms in insulating films have been studied very broadly,[1,2] the subject is still controversial and very often confusing. Many experimental results show that thin dielectric films subjected to an external high electric field displayed a linear relationship in the $\log_{10}(I/V)$-vs-$V^{1/2}$ plots, where I is the current passing through the film and V is the voltage applied across the film. This dependence is attributed to either the field-enhanced Schottky (ES) (Ref. 3) or the Poole-Frenkel (PF) mechanism.[4] The former is a Schottky emission process [Fig. 1(a)] across the interface between a semiconductor (metal) and an insulating film as a result of barrier lowering due to the applied field and the image force. The latter is associated with the field-enhanced thermal excitation of charge carriers from traps, sometimes called the "internal Schottky effect" [Fig. 1(b)]. These two transport mechanisms are very similar, except that in the PF mechanism the barrier lowering is twice as large as in the ES mechanism due to the fact that the positively charged trap in the PF mechanism is immobile and the interaction between the electron and the charged trap is twice as large as the image force in the ES mechanism. This phenomenon leads to the doubling of the slope, which is given by $(q^3/\pi\epsilon)^{1/2}$, in the $\log_{10}(I/V)$-vs-$V^{1/2}$ plot. q is the electronic charge and ϵ is the dielectric constant of the film.

A natural way to distinguish these two mechanisms is the following. By plotting the current-voltage (I-V) curve in the form of $\log_{10}(I/V)$ vs $V^{1/2}$, which should be a straight line, the slope β can be measured. The slope can also be calculated using the dielectric constant measured from an independent measurement. For the two different mechanisms, the slopes are given by the following relations:

$$\beta_{\mathrm{PF}}=(q^3/\pi\epsilon)^{1/2} \quad \text{for the PF mechanism,}$$

$$\beta_{\mathrm{ES}}=(q^3/4\pi\epsilon)^{1/2} \quad \text{for the ES mechanism.}$$

By comparing the slopes determined from an independent measurement of the dielectric constant with the slope measured from I-V characteristics, the mechanism can be determined in principle. But thus far, the factor-of-two difference in the slope of the ES and PF mechanisms has not been demonstrated unambiguously in an experiment. This is because in most experiments the calculated and measured slopes are not very close. Most studies were done on materials of low dielectric constant. Thus the difference caused by the factor of 2 in the two mechanisms is comparable to the experimental uncertainty, making it difficult to draw an unambiguous conclusion. A related issue, which has caused much confusion, is choosing the value of ϵ to be used in describing the conduction mechanisms. The use of both the static[5] and the optical[3,6] dielectric constant have been proposed. Both suggestions are supported by experimental data reported in the literature.[7–10] An effective "dynamic dielectric constant"[11] has also been suggested to describe some experiments. The key issue is how fast a carrier is assumed to move in the dielectric materials. A fast carrier induces only the electronic component of the polarization and the dielectric response should be optical. On the other hand, if the carrier is slow, such as in the polaron model,[5] then the static dielectric constant should be used.

In this study, we have unambiguously differentiated the Poole-Frenkel transport mechanism from the field-enhanced Schottky emission transport mechanisms in insulating films experimentally. Both types of transport mechanism were found in $BaTiO_3$ thin films deposited using the partially ionized beam technique under different deposition conditions. We have also determined that the carriers in the films are polaronlike so that the static dielectric constant is involved in the conduction of the electrical current.

$BaTiO_3$ thin films 610 Å thick were prepared on n-type Si substrates, using the reactive partially ionized beam deposition technique. Details of the technique have been described previously.[12] The Si substrate has a resistivity of 2–4Ω cm. Separate crucibles were employed for the Ti and the Ba evaporations. The evaporation was performed in an oxygen ambient with a partial pressure of 10^{-2} Pa. Oxygen gas and Ti vapor were partially ionized during evaporation using electron impact ionization to give 3% of ions in the evaporated beam. The percentage was calculated from the knowledge of the deposition rate and the current collected by the substrate. The films were deposited under two different conditions. It has been shown that thin-film properties can be modified very dramatically using the partially ionized beam technique.[13] Type-I films were deposited with the bias of 1.2 kV applied between the substrate and the Ti crucible so that the films were growing under a constant bombardment of the ions (3%). Type-II films were deposited with the substrate floating electrically. All films were deposited at room temperature and have an amorphous structure. As discussed in an early report,[12] however, the films grown under a constant bombardment of ions can have very different physical properties from the floating one. First of all, the chemical reaction between the partially ionized oxygen gas and metal atoms is related to the energy of the oxygen ions.[14] If the oxygen ions have sufficient energy, a more complete reaction between the oxygen and the metal atoms can be achieved. Type-I films were deposited under the bombardment of energetic oxygen and Ti ions and these ions can promote the Ba-Ti-O reaction to form $BaTiO_3$ thin films. Second, the involvement of energetic ions during the deposition can increase the surface mobility[15] and enhance the bond formation between surface atoms and the film underneath.[16] Therefore, the type-I films should have much fewer charged traps or dangling bonds than type-II films due to the more complete oxygen-metal reaction and enhanced bond formation.

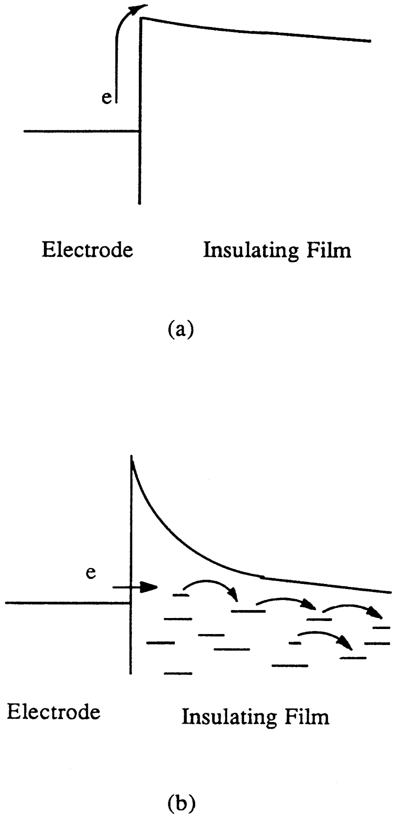

FIG. 1. A schematic diagram displaying (a) the enhanced Schottky (ES) emission transport mechanism and (b) the Poole-Frenkel (PF) transport mechanism.

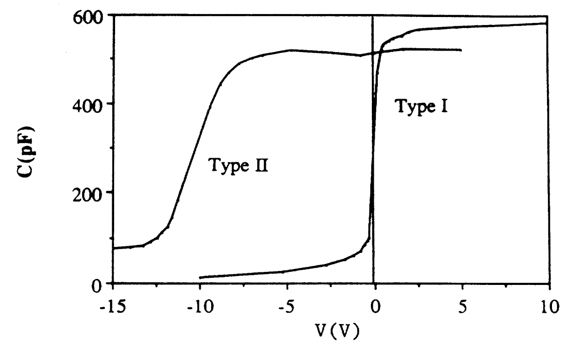

FIG. 2. We plot the measured *C-V* characteristics of the $BaTiO_3$ films on *n*-type Si substrates. Al dots were used as the top electrodes. The area of the capacitor is defined by the top electrode. For the type-I film the flat-band voltage is about 0.3 V and dielectric constant is ~16. For the type-II film the flat-band voltage is larger than 10 V and the dielectric constant is ~13.

The deposited films were annealed at 250 °C for half an hour in vacuum. Circular Al dots with a diameter of 0.6 mm were then deposited on the insulating films to fabricate a metal-insulator-semiconductor (MIS) capacitor for electrical measurements. The back side of the Si substrate was also covered with Al to ensure a good electrical contact. Both capacitance-voltage (*C-V*) and current-voltage (*I-V*) characteristics were measured. The capacitance was measured at 1 MHz. The optical indices of refraction of the films were determined to be 1.85 and 1.84 for type-I and type-II films using the ellipsometry technique with a wavelength of 6328 Å.

Figures 2 and 3 show the measured *C-V* and *I-V* characteristics of both type-I and type-II films. The current in Fig. 2 is plotted as a function of $V^{1/2}$. The capacitance was obtained from the *C-V* characteristics in

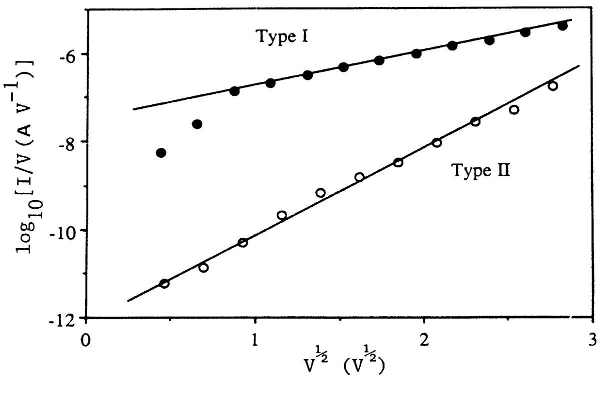

FIG. 3. We plot the measured *I-V* characteristics of the $BaTiO_3$ films on *n*-type Si substrates. The leakage current was measured in the accumulation region. The solid circles denote the type-I film and the open circles denote the type-II film.

the region of accumulation, in that the MIS capacitor was under a positive bias and the total capacitance of the sample is from the contribution of the $BaTiO_3$ films. From the capacitance and the film thickness, the static dielectric constants of the films were determined to be 16 ± 0.8 and 14 ± 1.0 for type-I and type-II films, respectively, using a parallel plate capacitor model. The calculated slopes for the different transport mechanisms are listed in Table I. Notice the large difference between the optical dielectric constant (which is the square of the index of refraction) and the dielectric constant measured at 1 MHz, which, for our purpose, can be considered to be approximately the "static" dielectric constant.

With the above information, many important conclusions can be drawn from the I-V plots shown in Fig. 3. First of all, the $\log_{10}(I/V)$-vs-$V^{1/2}$ plots show a straight-line behavior over a wide range of voltage. It is an indication of either the ES or the PF transport mechanism. Second, the difference in the slope is approximately 2. Third, for the type-I film the measured slope (0.76) obtained from Fig. 3 is not consistent with the calculations if the value of the optical dielectric constant is used, neither for the ES model, for which $(q^3/4\pi\epsilon)^{1/2}=1.94$, nor for the PF model, for which $(q^3/\pi\epsilon)^{1/2}=3.88$. As shown in Table I, the measured slope for type-I films is close to the calculated slope using the ES model while the measured slope for type-II films is close to the value calculated using the PF model. The static dielectric constants used for calculating slopes were measured independently using the C-V technique described above.

From these results, we conclude that the carrier velocity is slow (polaronlike) so that the static dielectric constant should be used to describe the carrier transport through the insulator. The factor-of-2 difference in the slope of the two types of insulators is a display of the two types of conduction mechanisms, namely the ES mechanism and the PF mechanism. The keys to the success of the present experiment and the unambiguous interpretation of the results are (a) the dielectric constant of $BaTiO_3$ films is high and there is a large difference between the static and optical dielectric constants in $BaTiO_3$ films, and (b) the static dielectric constant of the two types of films is about the same and the thickness of the films is the same.

Jonscher and Hill[17] pointed out that the conduction mechanisms in insulating films is intrinsically related to the density of the charged defects in the films. If a film contains a very high density of positively charged traps, a PF mechanism should dominate, otherwise an ES mechanism is possible. Also, a pure ES conduction mechanism, in principle, can only exist in contact with no significant intrinsic barrier, namely, a neutral contact. Otherwise the dependence of $\log_{10}(I/V)$ on V will have a different form.[3] Here the intrinsic barrier refers to the barrier formed either due to the difference in the Fermi levels or due to the existence of surface states and a high charged-trap density in the film and at the interface. Figure 4 is the energy-band diagram of the Si-$BaTiO_3$ contact. The band gap of the $BaTiO_3$ film is about 3.9 eV (Ref. 18) and the affinity is about 2.52 eV.[19] As shown in Fig. 4, the Fermi levels are almost aligned. Hence the energy barrier due to the difference in the Fermi levels is excluded. On the other hand, as pointed out by Shockley,[20] the energy level of surface states in ionic solids is very close to the band edges. Therefore the occupancy of these electronic surface states is almost the same as that of the bands themselves. In this case the surface states should not induce a significant energy barrier at the interface. Amorphous $BaTiO_3$ is closer to an ionic solid. Hence the surface states are likely to play a minor role in this case. The contact between the $BaTiO_3$ film and n-type Si is therefore close to a neutral contact. Hence if a film contains very few charged traps, the ES conduction mechanism can be observed.

It is well known that the total charge density in an insulating film can be measured by the C-V characteristics. Compared with the ideal case (an insulating film without any charged traps), the C-V curve for an insulating film with a certain amount of charged traps will show a voltage shift, known as the flat-band voltage, which is given by[21]

$$V_{FB}=\phi_{ms}-Q_t/C_s .$$

Here, ϕ_{ms} is the work-function difference between the

TABLE I. A summary of the measured slopes of $\log_{10}(I/V)$-vs-$V^{1/2}$ and the calculated slopes by using different transport mechanisms. The dielectric constants used in the calculations were calculated from the C-V characteristics. β, The slopes measured from the I-V characteristics (Fig. 2); β_{ES}, the slopes calculated from the measured dielectric constant using the ES model; β_{PF}, the slopes calculated from the measured dielectric constant using the PF model.

	β	β_{ES}	β_{PF}
Type I	0.76	0.68	1.36
Type II	1.81	0.73	1.46

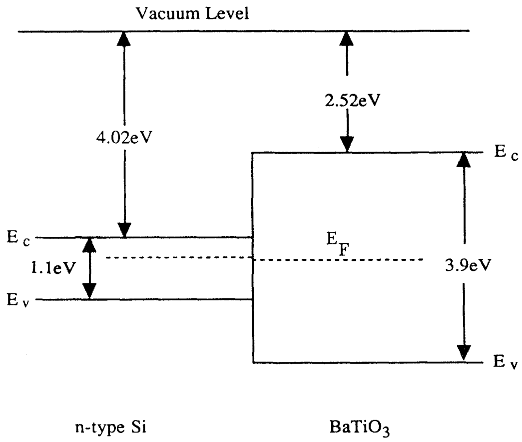

FIG. 4. A schematic diagram showing the energy-band structure at the $BaTiO_3$ (n-type Si) interface. The resistivity of the Si substrate is 2–4Ω cm.

metal of the top electrode and the semiconductor (Si) substrate, C_s is the capacitance per unit ares, and Q_t is the total charge density in the insulating film. It is clear that the magnitude of $V_{\rm FB}$ is proportional to the density of charged traps in the insulating films and the direction of the shift is related to the sign of the charge. For the PF mechanism, traps should be positively charged. This would correspond to a large negative flat-band voltage. For the ES mechanism, the density of charged traps should be low to avoid the formation of an intrinsic barrier at the interface. Hence, $V_{\rm FB}$ should be very small.

Based on the above considerations, we see that there is a correlation, at least qualitatively, between the conduction mechanisms and the measured C-V characteristics. As shown in Fig. 2, there is an obvious large negative flat-band voltage shift (>10 V) in the type-II film. The density of total positively charged traps at the interface and in the insulating film can be calculated from the flat-band voltage using the above equation and is found to be higher than $10^{13}/\text{cm}^2$. These positively charged traps provide a natural means for the electrons to travel through the insulating film via the "internal Schottky" emission process. On the other hand, the flat-band voltage of the type-I films is unusually small (<0.3 V). The density of the total charged trap is two orders of magnitude smaller than that of the type-II film. With the band structure shown in Fig. 4, an ES mechanism of conduction is therefore very likely.

In the above analysis, only the well-known one-dimensional theories for the conduction of carriers in insulators are considered. Numerous modifications to the original theories have been proposed in the literature.[22,23] However, we believe that inclusion of the more sophisticated analysis should not qualitatively affect the main conclusions of the present work.

In summary the conduction mechanisms in $BaTiO_3$ thin films were studied. We found that the carriers in the films are polaronlike so that the static dielectric constant is involved in the conduction. We have unambiguously differentiated experimentally the Poole-Frenkel transport mechanism from the field-enhanced Schottky emission transport mechanism in insulating films. A correlation has been established between the conduction mechanisms and the measured C-V characteristics.

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[1] H. J. Wintle, IEEE Trans. Electrical Insulat. **25**, 27 (1990).

[2] K. C. Kao and W. Hwang, *Electrical Transport in Solids* (Pergamon, London, 1981).

[3] K. C. Kao and W. Hwang, in *Electrical Transport in Solids* (Ref. 2), p. 91.

[4] J. Frenkel, Tech. Phys. USSR **5**, 685 (1938); Phys. Rev. **54**, 647 (1938).

[5] N. F. Mott, Philos. Mag. **24**, 911 (1971).

[6] J. H. Simmons, Phys. Rev. **155**, 657 (1967).

[7] C. A. Mead, Phys. Rev. **128**, 2088 (1962).

[8] S. Banerjee, B. Shen, I. Chen, J. Bohlman, G. Brown, and R. Doering, J. Appl. Phys. **65**, 1140 (1989).

[9] J. C. Schug, A. C. Lilly, Jr., and D. A. Lowitz, Phys. Rev. B **1**, 4811 (1970).

[10] J. Antula, J. Appl. Phys. **43**, 4663 (1972).

[11] S. M. Sze, J. Appl. Phys. **38**, 2951 (1967).

[12] P. Li, and T.-M. Lu, Appl. Phys. Lett. **57**, 2336 (1990).

[13] A. S. Yapsir, L. You, T.-M. Lu, and M. Madden, J. Mater. Res. **4**, 343 (1989).

[14] S. M. Rossnagel and J. J. Cuomo, MRS Bull. **12**, 48 (1987).

[15] T. Takagi, *Ionized Cluster Beam Deposition and Epitaxy* (Noyes Publication, Park Ridge, NJ, 1988), p. 76.

[16] Jean-Claude Dran, in *Materials Modification by High-fluence Ion* Beam, Vol. 155 of *NATO Advanced Study Institute Series E: Applied Science,* edited by R. Kelly and M. Fernenda da Silva (Martinus Nijhoff Publishers, Boston, 1989), p. 357.

[17] A. K. Jonscher and R. M. Hill, in *Physics of Thin Films,* edited by Georg Hass (Academic, New York, 1975), Vol. 8, p. 222.

[18] K. Sreenivas and Abhai Mansingh, J. Appl. Phys. **62**, 4475 (1987).

[19] L. Hafid, G. Godefroy, A. El Idrissi, and F. Michel-Calendini, Solid State Commun. **66**, 841 (1988).

[20] W. Shockley, Phys. Rev. **56**, 317 (1939).

[21] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981), p. 395.

[22] J. L. Hartke, J. Appl. Phys. **39**, 4871 (1968).

[23] J. Godlewski and J. Kalinowski, Jpn. J. Appl. Phys. **28**, 24 (1989).