Analysis of leakage current conduction phenomenon in thin $\text{SrBi}_2\text{Ta}_2\text{O}_9$ films grown by excimer laser ablation

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The dc conduction behavior of thin films of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) has been investigated on the basis of space-charge limited current theory. The theory was generalized to account for the traps, which were inevitably present in this case. The relative percentage of trapped injected charge and the free injected charge was seen to follow a dynamical equilibrium instead of the true thermal equilibrium as the temperature of the sample was raised during the measurement. The onset voltage of the trap filled region (V_{TFL}) showed a decreasing trend with the increase of temperature. This reduction of V_{TFL} was ascribed to the appearance of some excess charge in the conduction band. It was seen that the thermodynamically stable distribution of charges among the energy levels could not be taken to explain such a situation. A dynamic model was proposed to explain this kind of a nonequilibrium distribution of trapped and free charges.

I. INTRODUCTION

The area of ferroelectric materials has shown significant progress towards technological as well as academic advancement.¹ The property of permanent but switchable charge storage makes ferroelectrics very welcome for memory applications.^{2–4} On the other hand, the understanding of their basic properties was also found to be essential to tailor the properties of the active material up to the device quality.

Properties such as the polarization fatigue and conduction behavior are of more importance from the device point of view, since they are the limiting factors for the lifetime of the memory that is stored in the device. The memory is stored in the form of charges. To hold the charges indefinitely, the sample should be highly insulating. On the other hand, the switchability of the dipoles also degrades as the ferroelectric sample passes through many numbers of read-write cycles.^{5,6} Recently, the bismuth layered ferroelectric materials were found to be very promising candidates from the fatigue point of view. These bismuth layered structured compounds exhibit insignificant polarization degradation up to 10^{12} read/write cycles, due to their internal structure.⁷ There have been quite a few attempts to understand the mechanism of polarization fatigue in ferroelectric thin films and it was predicted that the fatigue is intimately related to the trapping of charge carriers in the interfaces.^{8,9} On the other hand, there are very few reports on the conduction behavior of thin films of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT), which is also believed to be responsible for the polarization degradation of the memory devices. It was therefore essential to gain insight into the charge transport mechanism under a dc electric field. The operating voltage range up to 5 V across a thin-film sample produces an enormous electric field inside of it (~ 1

MV/m). So, the high field conduction of insulating thin film is of more interest compared to that in bulk. There are several mechanisms by which the charges can be transported inside an insulator at high fields.^{10–12} It would also be limited by the presence of traps, which are inevitably present inside any real sample.^{13,14} In the actual situation, the distribution of traps inside the sample might be different from the predicted (equilibrium) FD distribution. In the real case, this would be a rate limited dynamic distribution, which after a sufficiently long time, would lead to an equilibrium process. In this article, we have presented the results of dc current conduction measurements on samples of SBT that were prepared by a laser ablation process.

II. EXPERIMENT

Polycrystalline SBT thin films were grown using a KrF excimer laser ablation technique (Lambda Physik 248 nm). A dense target with single phase of SBT ceramic was used as a target. The films were deposited on platinum coated silicon wafers. The substrate temperature during deposition was maintained at 400 °C. The base pressure was initially brought down to 2×10^{-5} Torr and prior to deposition, high purity oxygen gas was introduced into the chamber to increase the pressure to 100 mTorr. The fluence of the laser was kept at 4 J/cm². The as-grown film was subjected to annealing at different temperatures from 650 °C–750 °C for 30 min. The films were structurally characterized in terms of x-ray diffraction (XRD) (Scintag, XDS 2000), and the composition of the films was determined by energy dispersive x-ray analysis (EDAX) (Oxford Instruments). Thin gold dots of 500 μm diameter were deposited by evaporation to form the top electrodes on the films. After forming the top electrodes, the electrical characterization was done in two-probe configuration. Polarization hysteresis properties were studied using a RT-66A ferroelectric test system (with a test pulse width of 8 ms). Capacitance–voltage ($C-V$) characteristics were stud-

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FIG. 1. XRD patterns of SBT thin films (a) as-deposited at 450 °C, (b) annealed at 650 °C, (c) annealed at 700 °C, and (d) annealed at 750 °C for 30 min.

ied using a Keithley 3330 LCZ meter (coupled with a Keithley 230 voltage source) at frequencies 1 to 100 kHz with oscillation amplitude of 50 mV. The leakage current behavior of the SBT thin films was analyzed using a Keithley 236 source measure unit over a voltage range of 0–10 V with a step size and delay time of 0.1 Vs and 0.1–10 s, respectively. All measurements were carried out over a temperature range of 30 °C–250 °C.

III. RESULTS AND DISCUSSION

A. Structure

Figure 1 shows the XRD patterns of thin SBT films annealed at different temperatures. It was seen that the phase started forming at temperatures above 500 °C, but with an orientation along the “c” direction, which turned into a polycrystalline phase after the heat treatment at 750 °C. The grain size was also calculated using the Scherrer’s equation and was found to be in the range of 50 nm. The average grain size was the same along all directions. The atomic force microscopy (AFM) studies also revealed similar grain sizes (~ 60 nm) [Fig. 2(a)]. The structure along the thickness was studied by scanning electron microscope (SEM), which showed a columnar shape of the grains [Fig. 2(b)]. The composition of the films was analyzed using EDAX, which indicated a Sr/Bi/Ta ratio of 0.9/2.5/2.0. The excess bismuth was intentionally incorporated in the target, to facilitate grain growth.¹⁵

B. Polarization hysteresis

The existence of the ferroelectric nature in the SBT thin film was confirmed from the polarization hysteresis, which is displayed in Fig. 3. The remnant polarization was found to be around $10 \mu\text{C}/\text{cm}^2$ whether the coercive field was about 50 kV/cm. These values were in good agreement with the reported values.^{16,17} The hysteresis behavior was also reflected in the $C-V$ plot of the sample, which has been shown

FIG. 2. (a) AFM micrograph of the surface of an annealed SBT thin film. (b) SEM micrograph of the cross section of the SBT thin film.

as the inset of Fig. 3. The asymmetry of the $C-V$ loop was thought to be due to the effect of two different electrodes used for measurement. The deposition conditions while the formation of these two interfaces were also quite different, and therefore, it was likely that the film electrode interfaces would contribute differently to the clamping of domains there.

C. dc electrical properties

The dc leakage behavior of the film has been shown in Fig. 4. The current–voltage ($I-V$) curves were obtained from the measurement over a wide range of temperatures. During the measurement, the voltage sweep was used with a delay time (time delay between the change of voltage and the acquisition of data) of 0.1 s. The current was seen to begin with a linear dependence with voltage, as was evident from its slope in the log–log plot. After a voltage of 5 V and above, the slope of the $I-V$ curves increased up to a value about 10–16 and then again came down to a saturating region where the slope had a value of 2.0. The sudden increase of current in the $I-V$ plot was obtained repetitively, which

FIG. 3. Polarization–hysteresis loop for SBT thin film, annealed at 750 °C for 30 min. The inset shows the C – V curve for the same sample.

ruled out the possibility of breakdown phenomenon to be the reason for the sudden increase of current above 5 V. The current in the linear region was found to fit with the Arrhenius equation:

$$I \sim \exp(-\Delta E / \kappa T). \quad (1)$$

We have calculated the activation energy associated with this type of temperature dependence (shown in Fig. 5), and it was found to be 0.74 eV. This order of magnitude of the activation energy could be associated either to the Schottky barrier at the electrode, or the hopping of oxygen vacancies through the layered perovskite lattice. To check for the Schottky emission theory, we have plotted $\ln J$ as a function of $E^{1/2}$ which has been shown in Fig. 6. It is known that the Schottky current, which is an electrode-limited process, should depend upon the applied field as:

$$I \propto T^2 \exp(-(\phi_0 - \beta E^{1/2}) / \kappa T), \quad (2)$$

where “ ϕ_0 ” is the work function difference between the metal and the insulator, “ β ” is a constant given by

FIG. 4. Current vs voltage behavior of SBT sample.

FIG. 5. Arrhenius plot of low field conductivity for SBT thin films.

$$\beta = \left(\frac{e^3}{\pi \epsilon_0 K} \right)^{1/2}. \quad (3)$$

“ K ” denotes the high frequency dielectric constant of the sample.

The expression for the current should give rise to a linear graph if $\ln I$ is plotted against $E^{1/2}$. The slope of the straight line would be the equal to β , and the calculated dielectric constant from the β value should match well with the high frequency dielectric constant.

For our case, it was seen that, the $\ln J$ vs $E^{1/2}$ curves were far from linear in nature (Fig. 6). As the voltage was increased, the curves almost merged with each other until a temperature of 160 °C. At temperatures higher than 160 °C, the curves became distinctly different from each other. The irregular nature of the curves ruled out the possibility of any Schottky-type conduction.

The temperature dependence of the I – V curve was also compared with that of Schottky-type conduction. It was evident from Eq. (2) that, the exponent should decrease with electric field, at all temperatures. The plot of $\ln(I/T^2)$ vs $1000/kT$ is shown in Fig. 7, which showed an increase of the activation energy with voltage. These two verifications in the

FIG. 6. $\ln J$ vs $E^{0.5}$ plot at various temperatures.

FIG. 7. $\ln(J/T^2)$ vs $1000/T$ plot at different voltages.

present results disqualify the Schottky-type conduction and, hence, the possibility of Schottky emission controlled conduction was ruled out.

The space-charge conduction was explained better with the observed $I-V$ characteristics, with some incorporated corrections. A pure space-charge effect should exhibit a square law dependence on the electric field, which would appear as a straight line with a slope of 2 in a log-log plot. This behavior would be modified in the presence of the bulk generated charges in the sample, as they might be the thermally excited valence-band electrons, or already existing electrons to compensate for the inevitable presence of oxygen vacancies as well. These charges would completely screen the effect of the excess injected charges from the electrode (space-charge conduction arises due to excess charge injection from the electrode into the sample). As long as the number of injected charges does not exceed the number of charge carriers already existing in the sample, the effect of space charge would not be observed. Instead, the bulk generated charge carriers would give rise to a linear $I-V$ characteristics. In our case, the activation energy calculated in the linear region of the $I-V$ plot would appear to correspond to the oxygen vacancy motion. This would occur only if the contact were of an ohmic nature, a characteristic that is completely different from the Schottky effect in thin film. In the case of a Schottky contact, the maximum voltage drop would be across the contact region itself, particularly at low fields, since the contact resistance would be much higher compared to that of the bulk resistance, and, hence, the bulk characteristics (the linear current voltage relation) would be absent. At higher voltages, the contact resistance might come down below the bulk resistance, while the current would be bulk limited, the effect of the electrode would not be observed.

However, for space-charge controlled current, the linear region would extend up to a certain voltage, called as the crossover voltage, and beyond which the current would vary with the voltage as a power law:

$$I \propto V^2, \quad (4)$$

which would continue until the current is close to the saturation current, i.e., the maximum current that the electrode

FIG. 8. Space-charge limited $I-V$ characteristics.

could supply. However, in real samples, there would be several trap sites, which would capture the electrons that had been injected inside the sample, and would prevent them from showing the space-charge effect. There would be two types of traps, the ones above the Fermi level are the shallow traps, and the others below the Fermi level being the deep traps. During trapping, both deep and shallow traps would get filled. However, the shallow traps would always remain partially empty, since, the Fermi-Dirac distribution function (the probability to occupy an energy level) has a value less than unity above the Fermi level. On the other hand, these deep traps would get completely filled, at a voltage called trap filled limit. (V_{TFL}). Beyond V_{TFL} all the excess charges would be injected into the conduction band, and the current would approach the trap free square law [as described in Eq. (4)]. That is the reason why the current should increase with voltage after V_{TFL} . For a set of traps distributed in energy, the increase of current would be less abrupt, and would follow

$$I \sim V^\alpha, \quad (5)$$

until it shows a trap free square region. For our measurements, it was found that the current showed an increase with a power law with an exponent ~ 16 , and after this region, there was a saturation-like region which had a slope of 2.26. These three regions were shown in Fig. 8. The three regions formed a triangle called the Lampert triangle.¹⁸

It could be mentioned here that, in the present case, the films were comprised of columnar grains, in which case, one would expect a space-charge limited conduction. Indeed, it was observed by Scott *et al.*¹⁹ in the case of columnar ultrafine-grain (Ba,Sr)TiO₃ thin films that the space-charge contribution was dominant in the leakage mechanism.

D. Trap filled voltage

In Figs. 9(a) and 9(b), the $I-V$ curves are again shown separately over two temperature regions, one, from room temperature to 150 °C, and the other from 160 °C to 240 °C. It was seen that the trap filled voltage exhibited an increasing

FIG. 9. (a) I - V plot at a temperature range of 60 °C to 160 °C. (b) I - V plot at a temperature range of 160 °C to 220 °C.

trend with temperature, in the first region, but above 160 °C, there was a decreasing trend observed, which continued up to 250 °C. Beyond 250 °C, it was not possible to carry out further experiments due to the electrode damage. It is known in space-charge theory that trap filled voltage is a voltage where the Fermi level would increase well above all deep trap levels. Above the trap filled limit, all those trap levels would remain filled at a given temperature. If the temperature was increased, few of the filled traps would re-emit some electrons from the trap sites, and again those sites would become empty. In other words, the ratio of the free electrons to the trapped electrons would increase with temperature. As a result, one would have to apply a higher voltage to inject further electrons in the sample, so that all the trap levels get filled with electrons. This would be the possible cause for the increment of V_{TFL} with temperature.

This increment was seen to hold good up to a certain temperature. The value of the trap filled voltage was found to increase according to Lampert's space-charge law.²⁰ However, above a certain temperature, the trend was completely opposite, as mentioned in the previous paragraph. The reason for this definitely does not follow the space-charge theory,

given by Lampert, which mainly considered conduction by electronic charges. It was assumed that the space charges would be represented by an equilibrium distribution which would be identical to the Fermi-Dirac distribution function, at all temperatures. To achieve equilibrium, a certain time is required. The charges, immediately after being injected into the sample, have to equilibrate with the surrounding, to reach the time independent distribution of electrons among various energy levels. This has to occur throughout the entire sample. For that, the electrons have to migrate uniformly through the sample, so that they could seek the equilibrium (trap) sites. This means that the space-charge transient would govern the phenomenon of the trap distribution if observed in a short time scale. It is known that the space-charge transient in thin films could be of a time scale of several seconds depending upon the sample.²⁰ The electron distribution would therefore be limited by the competition between the rate of trapping of electrons and the rate of detrapping the electrons.

The trapping rate would be represented by

$$T_{E_c \rightarrow E_t} = N(E_c) \sigma(E_t) N(E_t), \quad (6)$$

where, " T " represents the rate of transition between the energy states mentioned in the suffices, " N " represents the density of unoccupied energy states at energy " E ", and " $\sigma(E_t)$ " is the capture cross section of the traps.

The detrapping of electrons would be given by

$$T_{E_t \rightarrow E_c} = \nu \times N(E_t) \exp(-\Delta E / \kappa T) N(E_c), \quad (7)$$

where the energy difference has been denoted by " ΔE " and the attempt frequency to escape is " ν ".

At a lower temperature, there would be very few electrons in the upper energy state (from where, it is captured to the trap sites), and the trapping rate also would not change much with temperature. Therefore, the entire process would be limited by the detrapping only. But at a higher temperature, there would be a significant amount of electrons in the conduction band (due to thermal generations and so on) which in turn would increase the rate of trapping, causing a greater number of trapped electrons. There would be some contribution from the detrapping of electrons also, but the increased trapping rate might overshadow the detrapping rate at a higher temperature. Therefore, one would expect that, the number of electrons required to fill all the traps would be less at a higher temperature, than it was at a lower temperature. This might bring down the trap filled voltage closer to the actual value. This should saturate at the equilibrium value of V_{TFL} . The variation of V_{TFL} has been plotted in Fig. 10. It was seen that the reduction of V_{TFL} above 200 °C indeed exhibited a saturating trend.

There could be another explanation of the time dependence of the space-charge build up inside the sample. The mobility of the electrons is normally very high in the insulators, since they are light and do not undergo much interelectronic scattering. Therefore, the space charge would take very little time to be established at every point in the sample. The space-charge transient due to electrons would not be observed in the sample in any practical time scale (100 ms to 100 s, the typical delay time used for I - V measurements).

FIG. 10. Trap filled voltage as a function of temperature.

But there are reports of the space-charge transients in insulating samples even in this time scale.²¹ This was attributed to the movement of oxygen vacancies, which are quite slower compared to electrons. The existence of the oxygen vacancies was already proved in the preceding section. It could, therefore, be assumed that both electrons and oxygen vacancies dominated the space-charge phenomenon. At lower temperatures, oxygen vacancies somehow did not respond to higher fields (the nonlinear space-charge region), and the highly mobile electrons were the majority charge carriers of the current. Due to their higher mobilities, they almost instantaneously redistributed themselves within the sample according to the space-charge law, and therefore, the expected increase of V_{TFL} with temperature was noticed. However, at high temperatures, even the oxygen vacancies played a significant role in the space-charge conduction. Since, oxygen vacancy motion is a slower process, it required significant time to respond, and this might be the reason why the linear to nonlinear region transition voltage (or the trap filled voltage) decreased with temperature, or with the increase of delay time.

In Fig. 11, the time dependence of the space charge was reflected in the $I-V$ curves measured with different delay times. It was seen that the initial region of the $I-V$ curves showed a slower than linear dependence on voltage. The $I-V$ measurements with a lesser delay time (~ 0.1 s) showed a current proportional to $V^{0.54}$. On the other hand, for a delay time of 10 s, the voltage dependence was: $I \sim V^{0.92}$. This implied that there was a transient response which interfered with the results of $I-V$ measurement. This transient would have diminished above a time scale of 10 s at room temperature, so that the true leakage current was observed. It was also seen that the V_{TFL} was also decreased as the delay time was increased. This indicated that the shorter delay time would lead to an incomplete trapping of electrons and, therefore, it would need a higher voltage for filling the deep traps.

IV. CONCLUSIONS

In summary, the films of SBT were grown by a pulsed laser ablation technique on platinum coated silicon sub-

FIG. 11. $I-V$ plot at different delay times, corresponding slopes in the linear region are indicated.

strates. The films exhibited good ferroelectric properties with a remnant and saturation polarization of 10 and 18 $\mu\text{C}/\text{cm}^2$, respectively. The dc leakage current in the SBT thin films was analyzed on the basis of space-charge limited current theory. The linear region in the $I-V$ plot was attributed to oxygen vacancy motion, which is very natural in oxides thin films. In our films, the onset (V_{TFL}) of the TFL region in the $I-V$ curve showed an increasing and decreasing trend with temperature. This unusual behavior of V_{TFL} was explained by considering the dynamical equilibrium between the thermally generated and injected charge carriers.

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