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Trap characterization for $Bi_4Ti_3O_{12}$ thin films by thermally stimulated currents

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Abstract. Thermally stimulated current (TSC) measurements performed in the 100 K–400 K temperature range on $Bi_4Ti_3O_{12}$ (BiT) thin films annealed at 550 °C and 700 °C had revealed two trapping levels having activation energies of 0.55 eV and 0.6 eV. The total trap concentration was estimated at $10^{15}\,cm^{-3}$ for the samples annealed at 550 °C and $3 \times 10^{15}\,cm^{-3}$ for a 700 °C annealing and the trap capture cross-section was estimated about $10^{-18}\,cm^2$. From the temperature dependence of the dark current in the temperature range 20 °C–120 °C the conduction mechanism activation energy was found to be about 0.956–0.978 eV. The electrical conductivity depends not only on the sample annealing temperature but also whether the measurement is performed in vacuum or air. The results on the dark conductivity are discussed considering the influence of oxygen atoms and oxygen vacancies.

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The interest shown in the last decade for ferroelectric thin film capacitors used in non-volatile memory devices [1, 2] had renewed the research effort in the field of ferroelectric thin films. The primary goal of this effort is to clarify some problems connected with the fatigue processes [3–5], the transport phenomena in ferroelectrics [6], and the influence of traps on the ferroelectric polarization [7].

Usually, the ferroelectric films are considered isolators and the semiconductor properties are almost ignored. Few works are so far devoted to study the electronic structure of ferroelectric thin films [8–10]. The perovskite ferroelectrics are generally speaking wide-band-gap semiconductors, having the band gap in the range of 3–4 eV. Data like carrier concentration and mobility, affinity, trap levels properties, life time, which one need to build a real device model are very seldom.

Some recent papers had reported, from photoconductivity measurements, the presence of some trapping states in $SrBi_2Ta_2O_9$ (SBT), $SrBi_2Ta_2O_9$ (SBN), and $Bi_4Ti_3O_{12}$ materials (thin films or bulk). From impedance spectroscopy an ionic transport mechanism involving oxygen vacancies and having an activation energy around 1 eV was reported [11]

Regarding the trap investigation it can be said that direct investigation methods, like thermally stimulated currents (TSC), were less used. Some TSC studies were performed on $PbTiO_3$ thin films [12] or $BaTiO_3$ ceramics [13]. The measurements were performed on different temperature ranges, from 100 K up to 700 K, and they revealed the existence of a multitude of trapping levels, their presence and concentration depending on the sample history or on the measurement conditions. The activation energy of these traps, determined from TSC spectra or from photoconductivity measurements, covers a broad range from 0.2 eV up to 2.75 eV, but the nature of the defects associated with them is still not clear [14, 15].

The present papers is proposing to investigate the temperature dependence of the dark conductivity for $Bi_4Ti_3O_{12}$ thin films, in a temperature domain close to the room temperature, considering different annealing temperatures and different measurement conditions (air or vacuum). The aim of this study is to determine which is the dominant transport mechanism at room temperature. Also, the TSC method was applied in order to determine the parameters of the traps that are active near room temperature. The experimental data were analyzed and the final results were interpreted considering the role of oxygen vacancies in transport mechanism and the possibility of oxygen-related defects to act as trapping centers.

1 Experimental

$Bi_4Ti_3O_{12}$ thin films were deposited on Pt/Si substrates using the chemical solution deposition (CSD) method described elsewhere [16] and were crystallized by a 30-min thermal annealing in air at 550 °C and 700 °C. The two sets of samples will be referred as BTO1 (samples annealed at 550 °C) and BTO2 (samples annealed at 700 °C). After annealing, 1.2×1.2 mm top semitransparent gold electrodes were obtained by vacuum evaporation and standard photolithographic techniques. The film thickness was estimated to about 1 μm for all samples.

Dark conductivity and TSC measurements were performed in air and in a vacuum better than 10^{-4} Torr, mounting the samples in a cryostat provided with a CaF window which allows the sample illumination with ultraviolet (UV) or visible (VIS) light. The sample can be cooled-down to 100 K and then heated up to 400 K at a constant rate ($\beta = 0.1\,\mathrm{K/s}$). Basically a TSC measurement consists of the following steps:

(i) the sample is mounted in the cryostat and is cooled down in dark conditions to the desired temperature. Considering the high resistivity of the ferroelectric materials, the samples are cooled down in short-circuit conditions to prevent the charge accumulation on the electrodes.

(ii) after the cooling temperature is reached, a constant voltage is applied on the sample (in this case 1 V) and, while the sample is heated-up at a constant rate, the current flowing through the ferroelectric film is recorded. Knowing the sample geometry the temperature dependence of the dark conductivity can be determined.

For a TSC measurement the sample is cooled again at low temperature and is exposed to a light beam, for a given time. The energy of the incident light have to be at least equal to the activation energy of the intrinsic photoconductivity. In this case charge carriers are excited from the valance band (VB) to the conduction band (CB). Because carriers generation is performed at low temperature, some of the carriers are trapped by the trap centers existing in the sample. The trapped carriers will be released when the thermal energy will become equal with the activation energy of the trap level. In this way, a peak will appear in the recorded current every time a trap level is emptied of the trapped carriers. By subtracting from the TSC curve the dark current, the pure contribution of the trapped carriers to the conduction can be extracted.

The measurements were performed using a constant voltage source model Keithley 240, an electrometer model Keithely 642, and an UV lamp model XBO. For TSC measurements the sample was illuminated 1 min with integral light emitted by the UV lamp.

2 Results and discussions

2.1 Thermally stimulated current measurements

The samples were first structurally investigated by X-ray diffraction (XRD) and scanning electron microscopy. Figure 1 shows the XRD pattern for both samples and Fig. 2 shows the SEM micrograph of the BTO film annealed at 700 °C (BTO2).

In order to extract information about trap levels (activation energy, trap density, capture cross-section) and about the evolution of traps with annealing temperature, TSC measurements were performed on both samples. Figure 3 shows the TSC curve obtained for the BTO1 and BTO2 samples. From the TSC spectrum the global density of the trap levels can be estimated using the integral method [17]. Thus, considering that the TSC peak is due only to the charge carriers released from the traps during heating, the total charge can be computed by numeric integration of the current over the

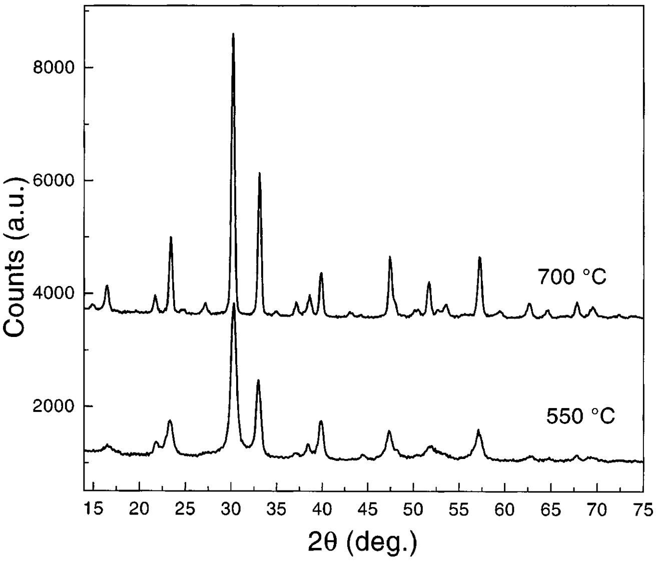

Fig. 1. XRD pattern for $Bi_4Ti_3O_{12}$ thin films annealed at 550 °C (BTO1 sample) and 700 °C (BTO2 sample)

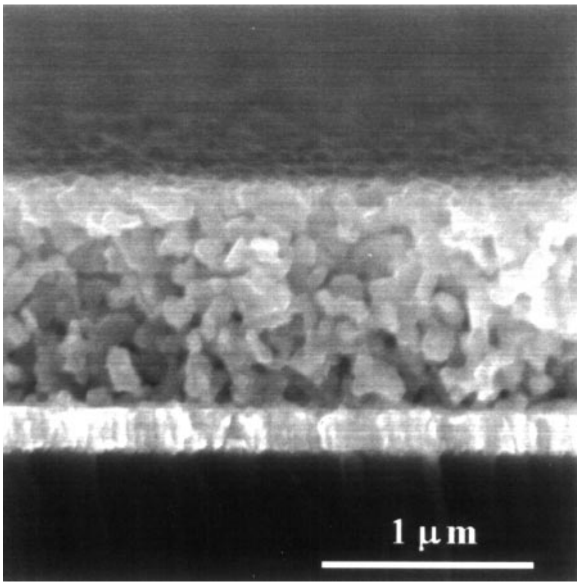

Fig. 2. SEM micrograph for $Bi_4Ti_3O_{12}$ thin film annealed at 700 °C (BTO2)

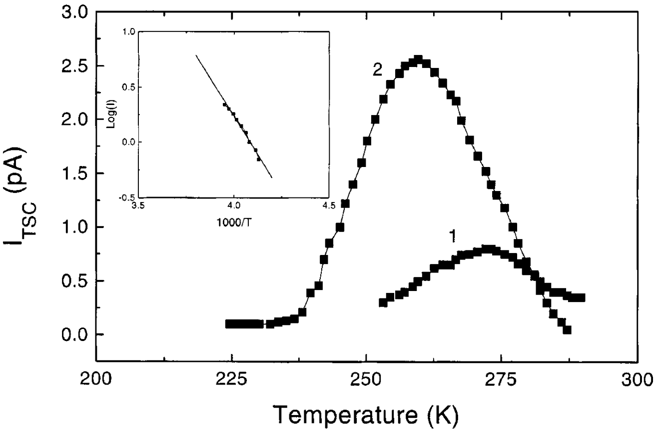

Fig. 3. TSC spectrum for: (1) $Bi_4Ti_3O_{12}$ thin film annealed at 550 °C (BTO1); (2) $Bi_4Ti_3O_{12}$ thin film annealed at 700 °C (BTO2)

temperature range where the peak appears:

$$Q = \int_{T_0}^{T_F} I_{TSC}(T)\frac{dt}{\beta}\,, \tag{1}$$

where Q is the total charge released from the trap levels, T_0 is the temperature of the sample when the heating starts, T_F is the final temperature, and β is the heating rate. The total density of traps can be estimated from the following formula [17]:

$$n_t = \frac{Q}{qVG}\,, \tag{2}$$

where n_t is the total concentration of traps, or more accurate, the total concentration of trapped carriers, q is the elemental charge, V is the sample volume (in this case $V = 1.44 \times 10^{-6}\,\text{cm}^3$), and G is the photoconductivity gain. The value of G was set to 1, considering that all the trapped carriers are released into the conduction band. Using (2) and (3) a value of $9 \times 10^{14}\,\text{cm}^{-3}$ was determined for the trap concentration in the BTO1 samples and $3.1 \times 10^{15}\,\text{cm}^{-3}$ for BTO2.

The activation energy E_t, assuming only a trap level, can be computed from the increasing part of the TSC spectrum. Supposing that at relatively low temperatures, when the trap level begin to discharge, the temperature dependence of the TSC current is exponential and is given by:

$$I_{TSC}(T) = I_0 \exp\left(-\frac{E_t}{kT}\right)\,, \tag{3}$$

the plot $\log(I_{TSC})$ versus $1000/T$ should be a straight line. Indeed, as can be seen from the inset in Fig. 3, a straight line is obtained at lower temperatures in the case of BTO2 samples. From the slope of this line an activation energy E_{t1} of about 0.55 eV was determined.

Taking into account the fact that the current peak from Fig. 3, curve 2, is relatively large and the decreasing part is not exponential, it can be assumed the existence of two levels, instead of one single level, discharging on almost the same temperature range. Thus, a deconvolution has to be performed in order to extract information concerning the two trap levels.

To deconvolute the TSC peak one have to make some assumption. First, the applied voltage is high enough to collect at the electrodes all carriers released during heating. Second, the free carrier concentration is very small, much smaller than the density of the trapped carriers. This fact is confirmed by the experimental data (see the values for the product $n\mu$ and the total trap density N_t). Third, carrier recombination and retrapping is negligible. In these conditions the TSC current is independent on the applied voltage and depends only on the trap parameters and for one peak is given by [18, 19]:

$$i_{TSC}(T) = \frac{1}{2}qVp_t(T)n_t \exp\left(-\int_{T_0}^{T} p_t(T')\frac{dT'}{\beta}\right)\,, \tag{4}$$

where $p_t(T)$ is the probability of a charge carrier to be released from a trap level, having the activation energy E_t at the temperature T. The formula which gives the value of p_t is:

$$p_t(T) = s_t \upsilon_{th}(T) N_c(T) \exp\left(-\frac{E_t}{kT}\right)\,, \tag{5}$$

where s_t is the capture cross-section, υ_{th} is the thermal velocity, and N_c is the state density in the conduction band. υ_{th} and N_c depend only on the effective mass and on temperature and are given by:

$$\upsilon_{th}(T) = \sqrt{\frac{3kT}{m_{ef}}}\,, \tag{6}$$

$$N_c(T) = 2\left(\frac{2\pi m_{ef} kT}{h^2}\right)^{3/2}\,. \tag{7}$$

The deconvolution method supposes that, when more than one trapping level is present, the total TSC current is given by the sum of the individual currents resulting from discharging of individual trap levels and given by the (4):

$$I_{TSC}(T) = \sum_j i_{TSCj}(T) \tag{8}$$

where j is the total number of level observed in the TSC spectrum or supposed to exist. The above sum is fitted with the experimental data to obtain the traps parameters (capture cross-section, activation energy, and trap density) for each level. It is convenient that at least one parameter to be measured using other experimental methods. Usually, the activation energy can be easily determined either using the variation of the heating rate method, the delayed heating method, or the fractional heating method [20].

In our specific case, assuming the existence of two trap levels, the deconvolution method was applied using (4)–(8). The total trap density obtained from the deconvolution is $1.2 \times 10^{17}\,\text{cm}^{-3}$ and is almost two order of magnitude higher than those determined by the integral method ($3.1 \times 10^{15}\,\text{cm}^{-3}$). It means that the applied voltage used for TSC measurements is not enough to collect at the electrodes all the released carriers from the traps. In this case the TSC will be dependent on the applied voltage and on the carrier life time. Formula (4) becomes:

$$i_{TSC}(T) = \frac{A}{d}U\tau\mu q p_t(T) n_t \exp\left(-\int_{T_0}^{T} p_t(T')\frac{dT'}{\beta}\right)\,, \tag{9}$$

where U is the applied voltage, τ is the carrier life time in the conduction band, and μ is the carrier mobility. Using the above formula a better fit between the experimental data and the theory was obtained. Figure 4 presents the deconvolution results for the BTO2 sample.

The total trap density resulting from deconvolution is about $4.8 \times 10^{15}\,\text{cm}^{-3}$ and was obtained assuming a $\tau\mu$ product of $10^{-7}\,\text{cm}^2\text{V}$. Comparing Figs. 3 and 4 it can be assumed that at low annealing temperature the contribution of the trap level with the activation energy of 0.6 eV in the TSC spectra is dominant but increasing the annealing temperature, the contribution of the trap level with the activation energy of 0.55 eV increases faster, becoming dominant at higher annealing temperature. To be note that an activation energy of about 0.58 eV was reported from TSC measurements performed on $Bi_{12}TiO_{20}$ crystals [21]. It is noted that the corresponding peak is non-symmetric, presenting a shoulder on its low temperature side.

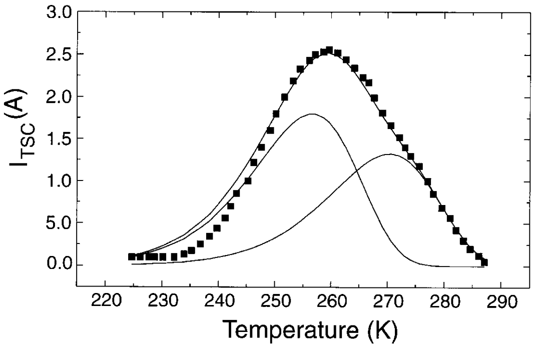

Fig. 4. Experimental TSC spectrum obtained for the $Bi_4Ti_3O_{12}$ thin films annealed at 700 °C and the theoretical TSC spectrum obtained using (8). The fit was obtained using the deconvolution method with the following trap parameters: $E_{t1} = 0.55$ eV; $E_{t2} = 0.60$ eV; $s_{t1} = 1.75 \times 10^{-18}$ cm^2; $s_{t2} = 3.5 \times 10^{-18}$ cm^2; $n_{t1} = 2.8 \times 10^{15}$ cm^{-3}; $n_{t2} = 2 \times 10^{15}$ cm^{-3}. The effective mass was considered to be 0.1 from the free electron mass

About the nature of these traps it cannot be said very much. Probably they are connected with the presence of some structural defects (vacancies, interstitials) in the bulk of the film or near electrodes.

2.2 Dark conductivity measurements

Figure 5 shows the temperature dependence of the dark conductivity for the BTO1 sample, determined under vacuum conditions. For the 20 °C–100 °C temperature the dark conductivity depends exponential on temperature, so we can consider [22]:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{10}$$

where E_a is the activation energy, k is the Boltzman's constant, T is the absolute temperature and σ_0 is the electrical conductivity when $T \to \infty$.

The activation energy of the conduction mechanism E_a was computed using the Arrhenius plot and a value of 0.978 eV was obtained. This value is far away from the mid-gap energy, which is around 2 eV in the case of $Bi_4Ti_3O_{12}$, thus it can be assumed that the observed exponential is not due to the intrinsic conduction. From the same Arrhenius plot the parameter σ_0 can be estimated as $\sigma_0 = 172\ \Omega^{-1}\text{cm}^{-1}$.

The room-temperature conductivity was estimated to be about $10^{-14}\ \Omega^{-1}\text{cm}^{-1}$ and is considerably different comparing with the conductivity value determined in air from the $I-V$ characteristic. As can be seen from Fig. 6 the $I-V$ characteristic at low voltages is linear, the conductivity being $10^{-10}\ \Omega^{-1}\text{cm}^{-1}$. This four order of magnitude difference can be related with a conduction mechanism, other than the bulk conduction. It could be an interface conduction mechanism, maybe related to the grain boundaries conduction, which is enhanced by gas adsorption when the sample is in air. In this case the boundaries conduction could be much higher than the bulk conductivity. In vacuum, a desorption process take place and the bulk conductivity prevails over the conduction at the grain boundaries.

An exponential dependence of the vacuum dark conductivity on temperature was observed for the BTO2 samples too. From the Arrhenius plot a value of 0.956 eV was determined for the activation energy and a value of $1.25\ \Omega^{-1}\text{cm}^{-1}$ was computed for the parameter σ_0. The estimated room-temperature conductivity is about 10^{-16}–$10^{-15}\ \Omega^{-1}\text{cm}^{-1}$. This value is about two orders of magnitude lower than for the samples annealed at 550 °C. No significant differences were observed when the measurements were performed in air. However, the activation energy is higher in this case, the value determined above room temperature being of about 1.1 eV.

Some hypothesis can be made to explain the above presented results. It is very likely that at low annealing temperatures the crystallites are very small, the crystalline structure being not yet very well developed. It can be assumed that the defect concentration is very large, especially at the grain boundaries, and these defects reacts with the various ionic species or with water present in the atmosphere. This leads to a high conductivity at the grain boundaries. In vacuum a desorption process take place leading to a considerably lower dark conductivity. In this case it can be supposed that the bulk conductivity prevails over the conductivity at the grain boundaries. The activation energy for the conduction mechanism based on oxygen vacancies was reported to be around 1 eV in perovskite-type materials [23, 24]. The values determined experimentally in the present study are close this value

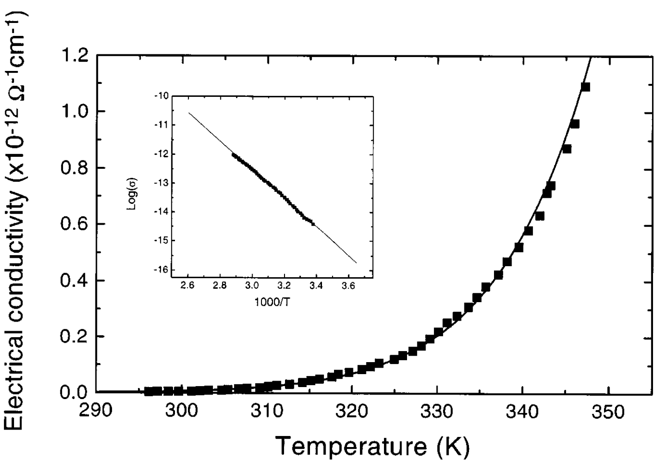

Fig. 5. Temperature dependence of the dark conductivity measured in vacuum for a $Bi_4Ti_3O_{12}$ thin film annealed 30 min at 550 °C

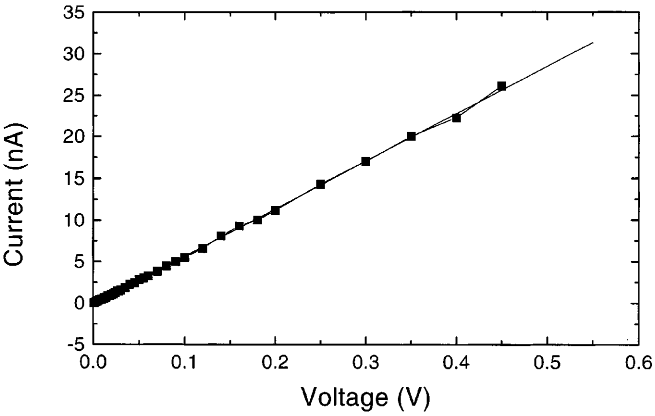

Fig. 6. The $I-V$ characteristic at low applied bias measured in air for the BTO1 sample

(0.956 eV–1.12 eV), so we can suppose that the bulk conductivity could be due to the oxygen vacancies.

At elevated annealing temperatures the crystallites' dimension increases and, due to a better crystallinity, a lower defect concentration and a lower conductivity at the grain boundaries is expected. It is reasonable to assume that in this case the dominant conduction mechanism is a bulk mechanism via oxygen vacancies. The activation energy is again about 1 eV, supporting the above assumption.

From the conductivity value at room temperature the product $n\mu$ can be determined, where n is the free carriers concentration and μ is the carriers mobility. The values are $4 \times 10^4\,(\mathrm{cm\,Vs})^{-1}$ for BTO1 and $7 \times 10^2\,(\mathrm{cm\,Vs})^{-1}$ for BTO2. From the above values one can assume that the free carriers concentration and mobility are very low, sustaining a vacancy or ionic conduction mechanism. This type of conductivity is often found in oxide materials [25].

3 Conclusions

The major conclusions which can be drawn from this study are:

(i) the dark conductivity in the $Bi_4Ti_3O_{12}$ thin films depends on the annealing temperature and is due to the presence of oxygen vacancies for the temperature domain from room temperature up to 120 °C. At low annealing temperatures the surrounding atmosphere influences drastically the dark conductivity due to the ionic species or water vapors adsorbed at the grain boundaries. The activation energy of the conduction mechanism is about 1 eV and the $n\mu$ product is around 10^3–10^4 depending on the annealing temperature. Both values are consistent with the assumption that the dark conductivity is mainly to the thermal activation of oxygen vacancies.

(ii) two trap levels were identified in the $Bi_4Ti_3O_{12}$ thin films annealed at 700 °C using the deconvolution method. The total density of traps was estimated from TSC measurements and was found to be $3.1 \times 10^{15}\,\mathrm{cm}^{-3}$ for 700 °C annealing and $9 \times 10^{14}\,\mathrm{cm}^{-3}$ for 550 °C annealing. The parameters of these traps were determined from the deconvolution method.

Further studies are need to obtain the value of the effective mass and to confirm the low value supposed for the free carrier concentration and charge mobility.

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