CERTAIN PECULIARITIES OF THICKNESS AND TEMPERATURE DEPENDENCES OF ELECTRICAL CONDUCTIVITY IN $Bi_4Ti_3O_{12}$ AMORPHOUS FILMS

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$Bi_4Ti_3O_{12}$ amorphous films have been obtained by dc magnetron sputtering. The electro-physical properties of the films have been investigated in a wide temperature range. In the range of low temperatures (100-T_d) K the charge transfer in $Bi_4Ti_3O_{12}$ amorphous films takes place due to the variable range of hopping. In the range of high temperatures the activation energy gradually varies with a successive change of three different mechanisms of the charge transfer: the hopping electrical conductivity with a constant length of hopping; the activation of holes to the edge of the valance band followed by their motion through hoppings to the mobility edge. The thickness dependence of conductivity is explained by hopping mechanism of the charge carrier transfer and by structural transformations of the amorphous films (polymorphism).

Keywords: $Bi_4T_3O_{12}$ *amorphous films, temperature dependence, electrical conductivity.*

1. Introduction

The increasing interest in studying the complex disordered systems is primarily due to certain peculiarities of their physical properties not found in crystalline states. The ternary compound $Bi_4Ti_3O_{12}$ (BTO) belongs to the compounds with perovskite structure formed by perovskite-like layers obtained on section of cubic perovskite lattice parallel to (001) plane alternating with bismuth-oxygen layers [1]. Besides, significant differences in atomic masses and ionic radii of constructive ions in BTO are responsible for the tendency to structural disorder.

BTO has useful properties for electro-optic, piezoelectric and memory applications [2,3]. For the memory applications, electrical properties on the BTO thin films should be investigated thoroughly [4-7]. In the thin film structure, high electric fields cause non-linear electrical behaviors. The practical application of films with a complex chemical composition is in many respects restricted by poor reproducibility of their electro-physical properties. Their appears to be no definitive report of the measurement and interpretation of the dielectric response function in bulk nanocrystalline ferroelectric BTO; the difficulty relates to the fabrication process by which a stable and reproducible material can be obtained. The Raman spectrum in the nanocrystaline BTO is different from that in the nanocrystaline $BaTiO_3$ Pb_4 TiO_3, etc. [8], which suggests some important values of this material. Thus it is necessary to find a proper technique to synthesize the BTO nanoparticles.

Unlike one-component thin-film substances, a large-scale potential relief leading to the strong dependence of electro-physical properties on the film thickness is realized in the disordered complex compounds [9]. Earlier investigation of the crystal structure showed that $Bi_4Ti_3O_{12}$ is characterized by bismuth oxide $(Bi_2O_2)^{2+}$ layers positioned between the perovskite-like $(Bi_4T_3O_{10})^{2-}$ layers [10]. Cubic Bi_2O_3 is known as a fast-ion oxygen conductor, [12] the high conductivity might happen in the internal $(Bi_2\ O_2)^{2+}$ layer, which has been proven in $Bi_4Ti_3O_{12}$ ceramics, [11] whereas the ion conductivity between the $(Bi_2O_2)^{2+}$ layers is very weak due to low conductivity in the perovskite-like $(Bi_4Ti_3O_{10})^{2-}$ layers. Therefore, the first the dielectric peak in $Bi_4Ti_3O_{12}$ in fact originates from the induced polarization of the ions in the $(Bi_2\ O_2)^{2+}$ layers across the potential barrier of the perovskite-like $(Bi_4Ti_3O_{10})^{2-}$ layers. The ionic polarization has a strong dependence on the external electric field frequency and shows a dispersion in the dielectric response.

The crystal lattice of $Bi_4Ti_3O_{12}$ with the perovskite layered structure shows an increased distortion with decreasing grain size [12,13], the lattice distortion affects the ionic conductivity in the $(Bi_2O_2)^{2+}$ layers, and increases the potential barrier of the perovskite-like layers. As a result of this, the first peak in the curve of temperature dependence of ε (dielectric constant) shifts to a higher temperature with decreasing grain size [13].

Leakage current behaviors in some ferroelectric thin films have been investigated, and various conduction models, including oxygen vacancy diffusion, grain boundary potential barrier height, tunneling space-charge-limited (SCL) emission, Poole-Frenkel (PF) emission, and Schottky emission, have been proposed [14,15]. Moreover, different physical origin, such as electrode kinds, charge injection, film composition, and micro-structures were suggested [16,17]. Therefore, studies of thickness and temperature dependence of electrical conductivity in amorphous $Bi_4Ti_3O_{12}$ film are important for most electrical application.

2. Experimental

The $Bi_4Ti_3O_{12}$ thin films obtained by dc magnetron sputtering were used for investigation [18]. Before sputtering the pressure in the chamber was about 1.2×10 Torr. Then the sputtering was carried out in argon-oxygen atmosphere of 1.2×10^{-2} and partial pressure of Ar 95% and O_2 5 %. The structure of the deposited films was investigated using electron diffractometer EP-100 and electron microscope EM-14. The chemical composition of the films was determined by local *X*-ray spectral method on scanning electron microscope REM-101 M by comparison of spectral line intensity relation for films and standard sample. The glass ceramics plates cooled to 250 K with the chorium-copper-silver contacts were used as substrates. Three layers of contacts provide their strong electrical conductivity, heat conduction and adhesion. The

investigation of the current flow through the contact areas and amorphous films revealed a linear character of the dynamic current-voltage characteristics for the currents of 25 mA confirming the ohmicity of the contacts. The reproducibility of the shape and mutual positions of contacts and amorphous films were achieved using bimetallic masks obtained by photolithographic techniques. The electrical conductivity was measured by the two-probe method. In a previously published series of articles, difference can arise from the use of different electrode materials. A relative error of the electrical conductivity measurements without taking into account a systematic error due to the definition film thickness was ± 1.5%.

The relationship between current and voltage for a space charge limited system is well known (as the Langmuir-Child Law). In vacuum the space charge current J is given by

$$J=(-4/9)\,\varepsilon_0\,(2e/m)^{1/2}Ad^{-2}V^{3/2} \qquad (1)$$

Where ε_o is the permittivity of free space; A - the area of the capacitor cell; d - its thickness; and V - the applied voltage. However, in a solid Eq.(1) is significantly modified. As discussed in detail in, for example, Tredgold's monograph [17-19]

$$J=a\,(V/d)+b\,(V/d)^2 \qquad (2)$$

in solids that have a low trap density and a high dielectric constant.

In Eq. (2) the coefficient a is a constant independent of the electrode materials, but the coefficient b depends strongly on the nature of the cathode material. At very high current densities the dependence upon films thickness becomes d^{-3}, rather than the $bV^{2}d^{-2}$ dependence shown in Eq.(2); but for the low leakage current values appropriate to our films, the inverse square dependence on thickness given in Eq.(2) is correct.

The presence of such a work function mismatch at the electrode interface can in principle result in several different kind of electron emission and leakage current: Schottky emission, Frenkel-Poole emission, and tunneling (field) emission can be identified by their voltage and temperature dependencies, which are, respectively, $T^2\exp(hV^{1/2T-1/2}-eF/kT)$, $V\exp(2hV^{1/2T-1/2}-eF/kT)$, $V^2\exp(-m/V)$. In general it is not easy to distinguish among these three mechanisms and that of space-charge limited currents Eq.(2); one must measure current I versus temperature T and thickness d, in addition to voltage to separate out each contribution. At high fields (10^6 V/cm) and high temperatures (above ambient) the dominant process is expected to be Frenkel-Poole emission. At slightly lower fields and temperatures (300 K and 10^4-10^5 V/cm), Schottky emission should dominate [20,21]. The Schottky emission and space-charge limited current are not independent of each other, as Sze emphasizes explicitly, "For large space charge effect, the tunneling characteristic is found to be very similar to the Schottky-type emission". The space-charge limited current results from carriers injected into the insulator where no compensating charge is present. (A Schottky barrier may our may not exist at the interface.) At high voltages this is almost indistinguishable from Schottky emission, for which a plot of ln (I/T^2) versus $1/T$ yields a straight line with slope given by the effective dielectric constant of the ferroelectric film.

3. Results and discussions

The behavior of the temperature dependence of electrical conductivity of the BTO amorphous film is shown in Fig.1. The activation energy continuously with decreases temperature. It is typical of the variable range of hopping mechanism of the charge transfer.

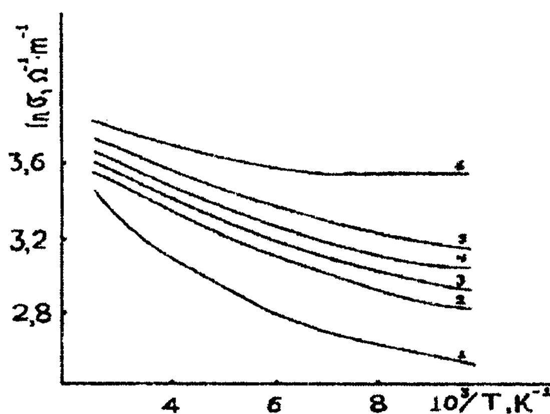

Fig.1. The temperature dependence of electrical conductivity of BTO amorphous films for different thickness d: 1-0.006μm; 2-0.13μm; 3-0.4μm; 4-0.9μm; 5-1.6μm; 6- 2.4μm.

Initial dielectric investigations in single crystal of $Bi_4Ti_3O_{12}$ revealed that there are two dielectric maxima at about 300° and 500°C in the direction of the c axis, besides a dielectric jump at the Curie temperature (676°C) [22]. Later, Ehara could not repeat the peak at 300°C and attributed the difference to the surface charge due to nonohmic contact of electrodes [23]. The peak at 500°C shows a strong dielectric dispersion and disappears as the frequency increase to 5 MHz, the origin considered by Fouscova is related to the intrinsic charge polarization [22]. The temperature dependence of the dielectric constant indicates that there are three peaks in most samples with different grain sizes. The peak at 30°C, as reported by Fouskova and Cross in single crystal $Bi_4Ti_3O_{12}$ [22], disappears from the curves due to the difference in the nature of the electrical contact [23].

As is known, in materials with the Fermi level in the range of the localized states, a low-temperature dc conductivity is established by the carrier hopping through the states in the energy and above the Fermi level and decreases with decreasing temperature [24]. Such a conductivity is characterized by so-called "moving" activation energy and is determined by the distribution of the states (in coordinate-energy space).

Three additional nonlinear conduction theories that may be observed in thin-films materials can be described with

$$J=J_o\exp(\beta E^{1/2}/kT) \quad (3)$$

Included among these conduction theories are Schottky-barrier-controlled conduction, Poole-Frenkel hopping conduction, and Poole-Frenkel hopping conduction with shallow traps. In Eq.(3), and J_0 is a constant and β is a constant that changes value with changes in the conduction mechanism [16,25]. The constant $\beta=\beta_S$ is given by

$$B_s=(e^3/4\ \pi\varepsilon_0 K\infty)^{1/2} \quad (4)$$

For Schottky-barrier-controlled conduction; $K\infty$ is the high frequency dielectric constant.

Poole-Frenkel hopping conduction and Poole-Frenkel hopping conduction with shallow traps are represented by using $\beta=\beta_{PF}=2\beta$ and $\beta=\beta_{PFS}=4\beta_s$ for Poole-Frenkel conduction and Poole-Frenkel conduction with shallow traps, respectively. Since all three of these conduction methods are described by Eq.(3), the dominant conduction mechanism is differentiated by determining the slope of the ln $(J)-V^{1/2}$ curve. The refractive index of the material may be calculated from the slope by using the relation $n=K^{1/2}\infty$; comparison of the calculated refractive index to a measured value of the refractive index reveals which conduction mechanism is operative.

The conclusions of laws for hopping conductivity [26] are strongly simplified in the assumption of the energy independence of localization radius. In this approximation, the conductivity is described in terms of the distribution of the density of the localized states, by possible correlation effects such as the large-scale fluctuations decreasing in some cases the effective dimensionality of the coordinate space, by the interaction of carriers decreasing the density of states near the Fermi level, or by the nearest narrow (defect) bands responsible for decrease of the density of states, on average, through the narrowing energy band of hoppings. Taking into account these effects for the conductivity σ when $g(E)=g_o|E|^n$ (E is the energy from the Fermi level) in the case of the arbitrary dimension δ, we have

$$\sigma=\sigma_0\exp-(T_0/T)^x \quad (5)$$
$$x=n+1/(n+\delta+1)$$

Where σ_o is the constant, T_0 is the value depending on the density of electron states near the Fermi level, δ is the dimensionality of space, n is the index of power dependence of the electron density of states near the Fermi level on the change carrier energy [26]. In the lack of correlation, i,e. at the chaotic distribution of states n=0, δ=3, x=0.25 and the expression (5) transforms to the well-known Mott law [24]. Due to correlations, the temperature dependence becomes stronger leading to the large values of x. The Exp.(5) is usually confirmed experimentally by a satisfactory "linearization" of a low-temperature region the curve of log σ as a function of T^{-x}.

For analysis the Zabrodski method was used [27]. According to this method, the expression (5) is given in the form of the equation system:

$$\log\omega = A - x\log(T),$$
$$\omega=1/T[\partial\log\sigma)/\partial(1/T)]$$

Where A is constant [28]. Then, by the graphical method, the x value is determined using the depending on the density of electron states near the $\log(\omega)=f(\log(T))$ dependence. Figure 2 shows the graphs of $\log(\omega)=f(\log(T))$ corresponding to the temperature dependence of electrical conductivity of BTO amorphous films given in Fig.1.

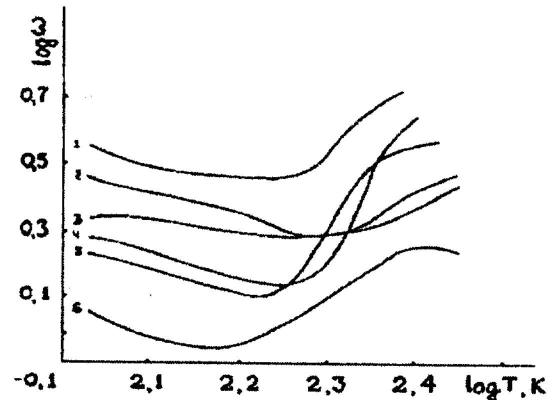

Fig.2. The $\log w=f(\log T)$ dependence of $Bi_4Ti_3O_{13}$ amorphous films with different thickness d; 1-0.006μm; 2-0.13μm; 3-0.4μm; 4-0.9μm; 5-1.6μm; 6-2.4μm.

The linear part of the diagram (Fig.1.) indicates the hopping mechanism of electrical conductivity determining the temperature dependence of the activation energy. The linear regions pronounced form films of large thickness are also observed in the above diagrams at x=(0.26-0.28) ±0.02. With decreasing film thickness the relation (5) does no longer describe the temperature dependence of the activation energy of the electrical conductivity. In the temperature dependence of the electrical conductivity in the range from T_d (T_d is the temperature of the deviation of the $\log(\sigma)\sim T^{-x}$ dependence) to 300 K continuous decrease of activation energy with decreasing temperature takes place. Due to a total reproducibility of the temperature reverse behavior of electrical conductivity, one can assert that there is a lack of irreversible processes of film crystallization in the above temperature region. Therefore to explain, a continuous change of activation energy at $T>T_d$ an additional analysis of possible mechanisms of the current transfer typical of the disordered systems is needed.

The probability of hopping from one localized states to another one is determined according to [29] by the relationship

$$P=V\exp(-2aL-\Delta/KT) \quad (6)$$

where V is the value depending on the phonon spectrum, a determines radius of a localized state, L is the hopping length, Δ is the difference in energies of the two states between which the hopping takes place.

At temperature of $T > T_d$ in the exponent of (2) the summand Δ/KT determining the temperature dependence of the activation energy dominates. At $T>T_d$ the summand Δ/KT becomes negligible and the probability of hopping is independent of temperature. In this case, at temperature close to T_d the hopping length will be constant and the hopping electrical conductivity is determined by the following expression

$$\sigma=\sigma_1 exp(-\Delta W_1/KT) \quad (7)$$

where σ is a constant, ΔW_1 is the activation energy of hopping [28].

Hence, $T > T_d$ just near T_d the linear regions with $x=1$ should be observed. However as seen in Fig.2, such regions near the T_d are lacking for the thin films that can be due to energy position of the active centers [28]. At T_d the sing of thermal elf in films is positive [30] and the conductivity can be realized due to the change of state of holes at the edge of the valence band E_{va}, followed by hopping to the mobility edge [28]. Then,

$$\sigma=\sigma_2 exp(E_F - E_V-\Delta W_1)/KT \quad (8)$$

Where σ_2 is a constant, ΔW_1 is the activation energy of hoppings through the localized states as the holes move from E_v to E_c. In the range of high temperature (T~300 K) a charge transfer is determined by the holes excited to the mobility edge E_c separating the localized states from the nonlocalized ones. In the case

$$\sigma=\sigma_{min}\ exp(E_F-E_C)/KT \quad (9)$$

where σ_{min} is a minimum metallic conductivity [28]. Hence, $T > T_d$ three electrical conductivity mechanism determined by the expressions (7)-(9) are possible, and the smearing of temperature limits of the transition from one charge transfer mechanism to another one leads to a principal change of activation energy.

As the investigation show, electrical conductivity of BTO amorphous films was found not to be saturated up to the thickness of 2.6 μm that is the major peculiarity of such films. A similar result can be explained by the effect of two factors. First, as the film thickness increases, a structural transition from one amorphous state to another (polymorphism) is possible [31]. Secondly, the dependence of electrical conductivity on thickness can be due to a hopping mechanism of the charge transfer when the following relationship is fulfilled:

$$ln\sigma(\infty)/\sigma(d) \approx (L/d)^{1/v} \quad (10)$$

where $\sigma(\infty)$ is the electrical conductivity of infinitely thick films, $\sigma(d)$ is the electrical conductivity of films with the thickness d, L is the hopping length v is three dimensional index of correlation radius [31].

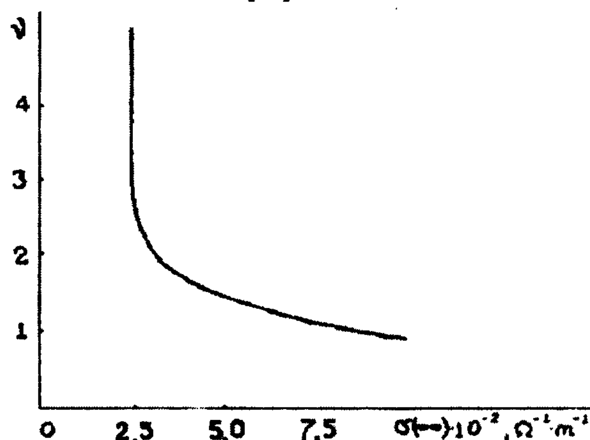

Fig.3. The dependence of the correlation radius index v on $\sigma(\infty)$ of BTO amorphous films

If the polymorphism in films of different thickness can be reduced to minimum by specific technological methods, then the hopping mechanism of the charge transfer is a necessary and a sufficient condition for the presence of the thickness dependence of electrical conductivity obtained from the relationship (10). As the v in (10) is independent of the film composition and numerically is equal to ~ 0.9 [31] one can determine a three dimensional index of correlation radius by studying the dependence $log\ log[\sigma(\infty)/\sigma(d)] \approx f(logd)$. The dependence $v \approx f[\sigma(\infty)]$ is shown in fig. 3. As seen in fig. 3, $v=0.9$ at $\sigma(\infty)\approx 10^3\ \Omega^{-1}m^{-1}$. A similar numerical value of $\sigma(\infty)$ is typical of thickness of ~ 0.6 μm.

Hence, the saturation of hopping conductivity with increase of the thickness should be observed at d~$0.6\mu m$, and the deviation from the dependence (10) can be explained by the short-range order structural variations of films with the change in their thickness.

4. Conclusion

Thus, in the range of low-temperatures (100-T_d) K the charge transfer in BTO amorphous films takes place due to the variable range of hopping. In the range of high temperatures the activation energy gradually varies with successive change of three different mechanisms of the charge transfer: the hopping electrical conductivity with a constant length of hopping; the activation of holes to the edge of the valance band followed by their motion through hoppings to the mobility edge. The dependence of thickness is explained not only by the hopping mechanism of the charge transfer but also by particular shot-range order structural variations.

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AMORF $Bi_4Ti_3O_{12}$ TƏBƏQƏLƏRİNİN ELEKTRİK KEÇİRİCİLİKLƏRİNİN TEMPERATUR VƏ QALINLIQDAN ASILILIĞININ BƏ'Zİ XÜSUSİYYƏTLƏRİ

$Bi_4Ti_3O_{12}$ amorf nazik təbəqəsi sabit cərəyanda maqnetron tovlanması ilə alınmışdır. Onların elektrofiziki xassələri geniş temperatur oblastında tədqiq olunmuşdur. Aşağı temperatur oblastında (100-T_d) K amorf $Bi_4Ti_3O_{12}$ təbəqələrində yükdaşınması sıçrayış mexanizmi ilə baş verir. Yüksək temperatur oblastında aktivləşmə enerjisinin dəyişməsi, yükdaşınmanin üç mexanizminin göstərilən dəyişməsi ilə baş verir: sabit uzunluqlu sıçrayışlı elektrik keçiriciliyi, deşiklərin valent zonasının kənarına doğru aktivləşməsi və onların sıçrayışla keçirici zonanın kənarına keçidi.

Keçiriciliyin qalınlıqdan asılılığı yükdaşınmanın sıçrayış mexanizmi ilə və amorf təbəqələrin struktur dəyişmələri ilə izah olunur.

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НЕКОТОРЫЕ ОСОБЕННОСТИ ЭЛЕКТРИЧЕСКОЙ ПРОВОДИМОСТИ В АМОРФНЫХ ПЛЕНКАХ $Bi_4Ti_3O_{12}$ В ЗАВИСИМОСТИ ОТ ТЕМПЕРАТУРЫ И ТОЛЩИНЫ ПЛЕНКИ

Аморфные пленки $Bi_4Ti_3O_{12}$ были получены магнетронным распылением на постоянном токе. Электрофизические свойства были исследованы в широком температурном интервале. В области низких температур (100-T_d) К перенос заряда в аморфных пленках $Bi_4Ti_3O_{12}$ происходит благодаря прыжкам. В области высоких температур энергия активации значительно изменяется следующими изменениями трех различных механизмов переноса заряда: прыжковая электрическая проводимость с постоянной длиной прыжка; активация дырок на край валентной зоны с последующим их прыжковым переходом на край зоны проводимости. Зависимость проводимости от толщины объясняется прыжковым механизмом переноса заряда и структурными изменениями аморфных пленок (полиморфизм).

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