EFFECT OF THERMAL TREATMENT ON STRUCTURE AND LEAKAGE CURRENT OF $Na_{0.5}Bi_{0.5}TiO_3$ THIN FILMS

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$Na_{0.5}Bi_{0.5}$TiO thin films were grown on heated to 200°C $Pt/TiO_2/SiO_2/Si$ substrates by ex-situ method with high-frequency (13.56 MHz) magnetron deposition. Thermal treatment of the films was carried out at 650°C, 700°C and 800°C. X-ray diffraction investigations showed the films were poly-crystalline and contained additional phase. In the films annealed at 700°C two dominating conduction mechanisms were observed: ohmic at the fields E < 8 kV/cm and Schottky emission in the field range of 30 – 70 kV/cm. It is also observed that the increase of the film annealing temperature to 800°C leads to the increase of leakage currents. It is assumed that high values of the leakage currents were attributed to the presence of both structure defects and additional unknown phase.

Keywords: magnetron deposition, sodium-bismuth titanate, leakage current density, oxygen vacancies.

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1. Introduction

Thin ferroelectric films are increasingly used to create microelectromechanical (MEMS), pyroelectric and other sensor devices, as well as high-speed non-volatile high-capacity random access memory devices – FeRAM (ferroelectric random-access memory). $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) lead-free thin films are considered as promising material for piezoelectric devices [1]. However, the leakage current of deposited films is rather high [2], which hinder their practical application. High values of leakage currents which are comparable with (or bigger then) the switching currents mask the ferroelectric properties of the films. The values of leakage currents and ferroelectric properties of NBT films depend on several factors such as the methods of film formation, the structure of the lower electrode, the crystallization temperature, the concentration of defects [2, 4]. Therefore, the purpose of this work is to study the effect of NBT films heat treatment on the formation of the structure and the leakage current values.

2. Experimental

The ceramics of bismuth sodium titanate was prepared by traditional technology and was used as a target. The heterostructure of the $Pt/TiO_2/SiO_2/Si$ substrate was formed on a flat polished Si(100) crystal silicon wafer. The anti-diffusion SiO_2 layer was obtained by thermal oxidation of the wafers in air at T = 700°C for 8 hours. Adhesive layer of TiO_2 (50 nm thickness) was deposited by the RF magnetron sputtering of a titanium target in an Ar/O_2 (1:1) atmosphere (P = 40 mTorr chamber pressure, substrate temperature 300°C). The Pt layer was deposited on the $TiO_2/SiO_2/Si(100)$ substrate by DC magnetron deposition method in pure Ar (P = 15 mTorr chamber pressure). This layer set the preferential orientation of the film crystallization and was used as an electrode for leakage current measurements. The films NBT (250 nm thickness) were deposited in Ar/O_2 (1:1) mixture atmosphere (P = 7-10 mTorr chamber pressure, substrate temperature 200°C). The NBT films were annealed in air at 650°C, 700°C and 800°C for 1 h. The phase composition of both the target and NBT films was checked by X-ray diffraction (XRD).

Platinum electrodes of 1 mm × 1 mm in size were deposited on the free surface of the NBT films to measure the current-voltage characteristics (I-V). The sample was sequentially connected to a precision serial resistor of 10 MOhm and connected to a highly stable regulated source of DC voltage. The voltage applied to the sample and the current flowing through the sample were measured with a V7-30 voltmeter-electrometer (input resistance more than $2 \cdot 10^{14}$ Ohms). The measuring circuits were carefully screened. Investigations of the electrical conductivity of the NBT films were carried out in the field range 0 − 70 kV/cm.

3. Results and discussion

Fig. 1. shows XRD patterns of both as deposited and annealed at different temperatures NBT thin films. XRD patterns indicate that as deposited NBT thin films exhibit an amorphous phase. The NBT phase formation during annealing starts at 650°C and it is indicated by (100) and (110) peaks. The increase of the annealing temperature to 700°C improves crystallization process. However, XRD patterns indicate presence of some unknown phase along with pure NBT phase.

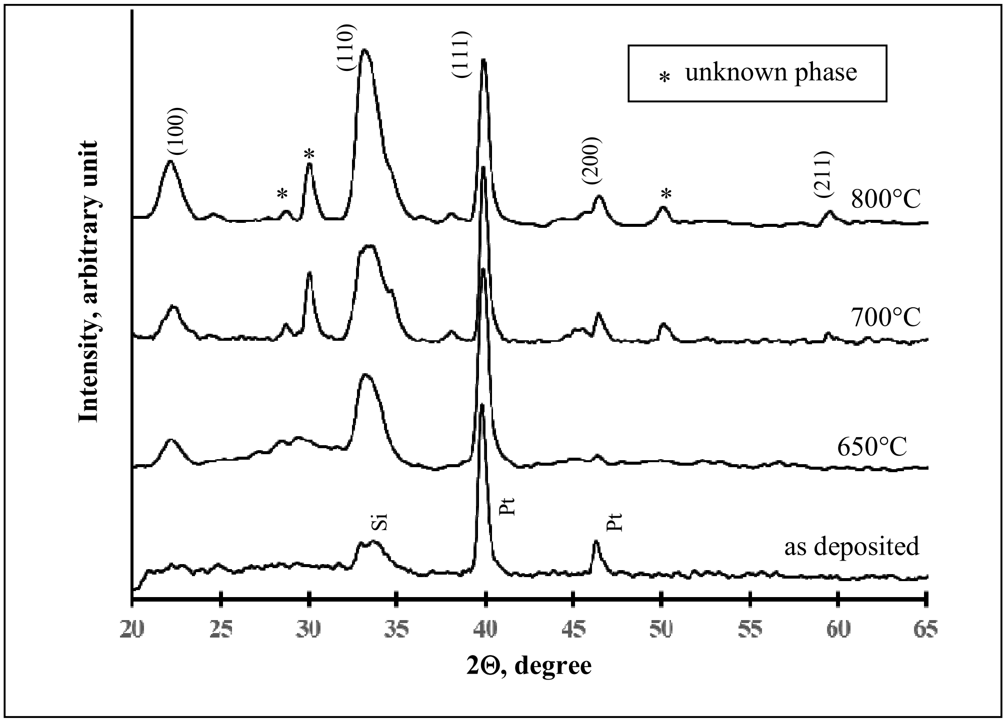
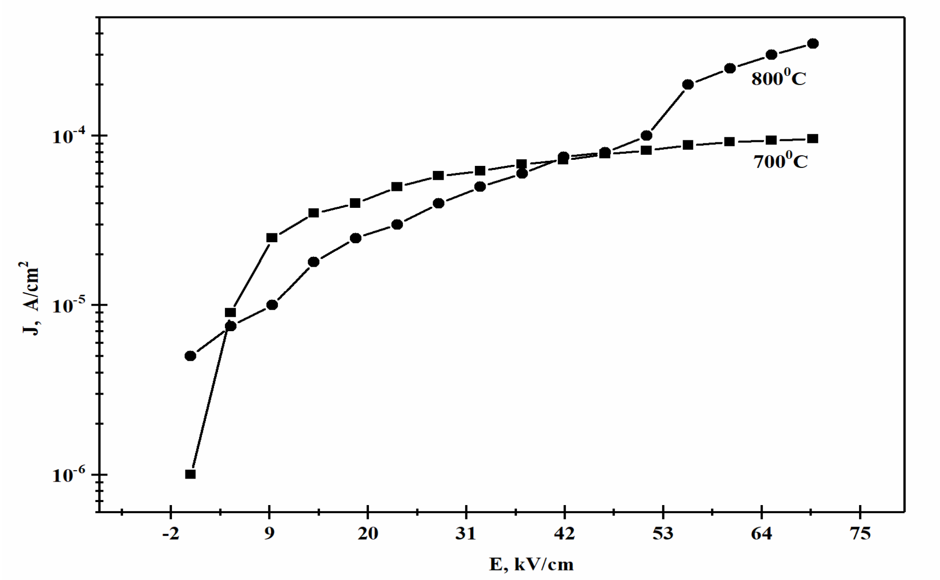


Fig. 1. XRD patterns of as deposited NBT thin films and NBT thin films annealed in air at T = 650°C, 700°C and 800°C.

Perovskite NBT phase can be determined by the presence of peaks at $2\theta = 23°15'$, $2\theta = 33°20'$, and $2\theta = 40°25'$. Additional peaks (not related to the NBT structure) show the presence of additional unknown phase (presumably pyrochlore). Annealing at a higher temperature (800°C) contributes to the formation of the perovskite phase of NBT, but the presence of an unknown phase is still recorded. It is possible that the evaporation of bismuth during heat treatments leads to the partial occupation of the film volume by the parasitic phase. Therefore, NBT thin films annealed at 700°C and 800°C were polycrystalline with mixed grain orientations and contained additional phase.

The leakage current density (J) of NBT thin films annealed at temperature T = 700°C as function of applied electric field (E) is shown in Fig. 2. In the field range 0 − 8 kV/cm the current almost linearly depends on the field strength, so the ohmic conductivity is dominant. It corresponds to the reported in [3] facts that in most cases in the region of small fields (E < 20 kV/cm) the character of conductivity is ohmic. With the further increase of the electric field the leakage current increases slowly and tends to saturation. The electrical conductivity calculated from the initial part of the curve is $\sigma = 1.25 \cdot 10^{-9}$ $Ohm^{-1}cm^{-1}$.

Fig. 2. The leakage current density of NBT thin films preliminary annealed in air at T = 700°C and



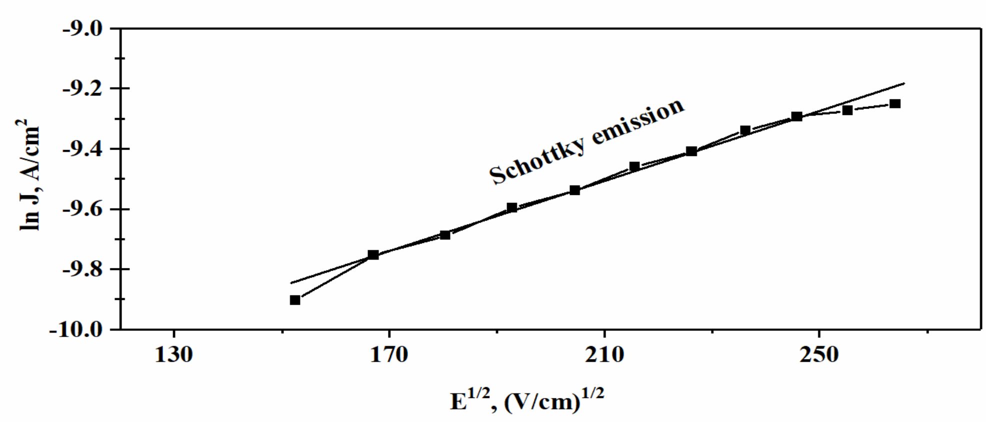
800°C as function of applied electric field.

With increase of the annealing temperature to 800°C sharp increase in J at E > 50 kV/cm is observed (Fig. 2). The absence of J saturation region, which is observed for films annealed at T = 700°C, indicates the avalanche-like leakage current increase process. In some cases, at E > 70 kV/cm, the leakage current rapidly increases up to the electric breakdown.

To determine how various mechanisms of conductivity contribute to the formation of leakage currents, it makes sense to present the experimental data as $\ln J - E^{1/2}$. From the $\ln J - E^{1/2}$ curve of NBT thin film annealed at T = 700°C shown in Fig. 3, the leakage current density linearly relates to the square root of the applied electric field. The linear variations of leakage current densities correspond to the Schottky emission mechanism or to the Poole-Frenkel emission mechanism [3, 4]. In most cases, the Schottky type emission of electrons from the electrodes dominates in the region of small fields. In the region of strong electric fields, the most probable conduction mechanism is the Poole-Frenkel mechanism of charge carrier in oxides [3, 4]. Fig. 3 shows the fitting of experimental results and the $\ln J - E^{1/2}$ curve exhibits the linear relation in the electrical field region 30 − 70 kV/cm, which indicates that Schottky emitted charge carriers [4] mainly contribute to leakage current of the films annealed at T = 700°C.

It should be noted that the structure of the film significantly affects the leakage current density and the shape of the J-E characteristics. It is natural to assume that the mechanisms of conductivity of single-crystal and polycrystalline films are different. In polycrystalline films, all structural defects, especially grain boundaries, affect the charge transfer. Changes in the J-E dependency with the increase of annealing temperature shown in Fig. 2 can be caused by the increase of structure defects after a thermal treatment. In accordance with [2, 4, 5] the conduction in NBT is determined by oxygen vacancies and associated with V_O defects. Therefore, it may be assumed that evaporation of bismuth during the annealing process of NBT thin films leads to the formation of $V_{Bi^{3+'''}}$ vacancies, which stimulate appearance of $V_{O^{2-\bullet\bullet}}$ vacancies. Presence of oxygen vacancies localized at grain boundaries leads to significant increase of leakage current [2, 4].

Fig. 3. ln J-E$^{1/2}$ curve of NBT thin film treated at 700°C.



The differences in leakage current density behavior of the films annealed at 700°C and 800°C can be also attributed to a change of additional unknown phase content.

4. Conclusions

Our study shows that annealing of the NBT thin films at 700°C shows lower levels of leakage currents in comparison with the levels in the films annealed at 800°C. Realization of two conduction mechanisms in films annealed at 700°C can be assumed: ohmic (E < 8 kV/cm) and Schottky emission (field range of 30 – 70 kV/cm). High values of leakage currents can be caused by the presence of an additional phase and structural defects in the films, in particular, $V_{O^{2-\bullet\bullet}}$ vacancies. The increase in the annealing temperature of NBT films does not lead to the decrease of the $V_{O^{2-\bullet\bullet}}$ vacancies number and, as a result, does not lead to J decrease.

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