PREPARATION FEATURES AND ELECTRICAL PROPERTIES OF $Na_{0.5}Bi_{0.5}TiO_3$ THIN FILMS

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Some special features of $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) thin films preparation process and electrical properties of the films are presented. The NBT films were grown on both Pt/sitall and $Pt/TiO_2/SiO_2/Si$ substrates by ex-situ method with high-frequency (13.56 MHz) magnetron deposition. Thermal treatment of the films was carried out in the temperature range 550°C – 700°C in air. Obtained X-ray diffraction data show that annealing at 700°C promotes crystallization of NBT films in ferroelectric perovskite phase with minor inclusions of pyrochlore phase. Dielectric hysteresis (P-E) loops in electric field of 90 kV/cm (50 Hz) and the current density-electric field (J-E) characteristics of the films are investigated. It is found that densities of leakage currents in weak fields depend on the film substrate and are significantly lower for the films deposited on the Pt/sitall structure (~6.9 10^{-10} A/cm^2) in comparison with the films deposited on the $Pt/TiO_2/SiO_2/Si$ structure (~10^{-6} A/cm^2). The main mechanisms of leakage currents in thin NBT ferroelectric films and the role of structural defects in charge transfer process are discussed.

Keywords: sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$), ferroelectric, thin films, leakage current.

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1. Introduction

Improvements in thin ferroelectric films technology have significantly expanded the ways for practical application of ferroelectric materials in microelectronics. Sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is the best known promising lead-free piezoelectric and ferroelectric material for applications in sensors and actuators. It is why efforts of many research groups are focused on studies of NBT thin films properties and on development of the films obtaining technologies. However, existing published data about electrical properties of NBT films are rather contradictory. This is because ferroelectric properties and charge transfer processes in NBT films significantly depend on technological factors and film production methods. Many authors report presence of high leakage currents (~10^{-8}÷10^{-6} A/cm^2), which affect electrical properties of NBT films [1]. The reduction of the leakage currents is the problem that needs to be addressed to achieve reproducible electrical characteristics. It is known that the composition and the pressure of the working gas, the temperature of the substrate during the deposition process, as well as the temperature, the duration, and the atmosphere of the post-annealing processes altogether affect the magnitude of leakage currents. In addition, structure and physical properties of the films depend on the substrate material. Most studies report use of silicon as the substrate for NBT films, which facilitates their integration into modern semiconductor microelectronics. However, chemical reactivity of silicon requires a $Pt/TiO_2/SiO_2/Si$ heterostructure and as a result the structure of the substrate becomes complex, which is not always sensible. On the other hand, microwave technologies successfully use sitall as a substrate material. Sitall substrates demonstrate high values of volume and surface resistivity, low values of dielectric losses, high thermal conductivity. Small values of the linear expansion coefficients allow to expect reduction of substrate mechanical stresses during film formation process when sitall is used as a substrate for a thin film. In this paper we report on structure and electrical properties of NBT thin films deposited on sitall and silicon substrates.

2. Experimental

Polycrystalline NBT films were obtained by ex situ method with RF (RF = 13.56 MHz) magnetron sputtering. Standard polished sitall plates of the ST-32 and Si(100) crystal silicon wafer were used as substrates.

The substrates were preliminarily treated in an ultrasonic bath with acetone, washed in distilled water and subjected to ionic purification in argon atmosphere. A Pt layer was deposited on the substrates at 300°C by the DC magnetron deposition method. This layer set the preferential orientation of the film crystallization and was used as the bottom electrode for further electrical measurements. NBT films (250 nm thick) were deposited in argon atmosphere on the Pt/sitall substrates at 200°C by sputtering a ceramic target of stoichiometric composition. Technological parameters of the deposition: pressure in the chamber – 1 Pa, input RF power density – 3.2 W/cm^2, deposition rate – 3.2 nm/min. Immediately after the deposition process the NBT films were amorphous. To crystallize the films the NBT/Pt/sitall structure was annealed at a temperature of about 550°C – 700°C (for 45 min). The structure was placed in an alundum container with crystalline NBT powder to create saturated vapors of sodium and bismuth during the heat treatment and to prevent intensive evaporation of these volatile components from the surface of the deposited NBT film. The NBT films deposited on the Pt/TiO_2/SiO_2/Si heterostructure were obtained in accordance with the technology described in [2].

The films deposited on the Pt/sitall structure (NBT/sitall) and films deposited on the Pt/TiO_2/SiO_2/Si structure (NBT/Si) were studied. Phase composition and crystal structure parameters of both the films and targets were investigated at room temperature by the XRD method. The film thickness was monitored by optical interference methods using Jenaval and MII-4 microscopes. A grid of silver point electrodes (1mm×1mm single electrode size) was deposited on the free surface of the NBT films and was used to measure electrical parameters. The leakage current – voltage (I-U) characteristics were measured by voltmeter-electrometer V7-30. The remnant polarization (P_r), spontaneous polarization (P_s) and coercive field (E_c) were measured by modified Sawyer–Tower circuit.

3. Results and discussion

Heat treatment of amorphous NBT is accompanied by the formation of an intermediate low-temperature pyrochlore phase [3]. In accordance with X-ray diffraction data, the presence of the 2Θ = 30° reflex on the XRD pattern (Fig. 1a) confirmed the formation of the pyrochlore phase in the NBT/sitall films during annealing at a temperature of about 550°C.

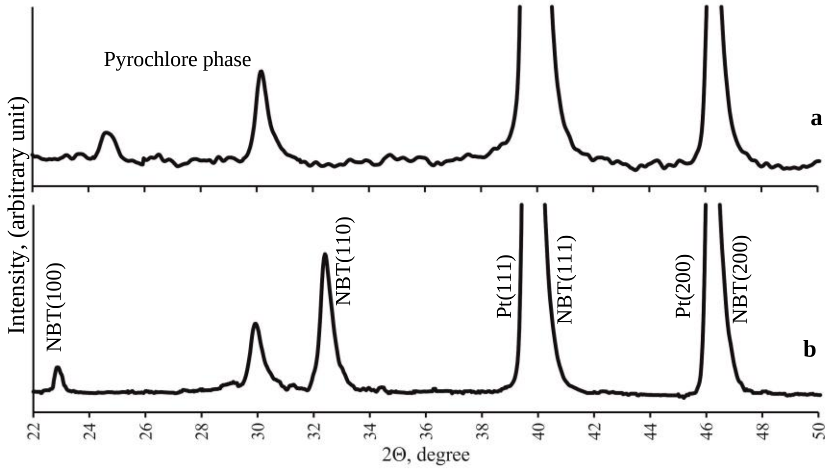

Fig. 1. XRD patterns of NBT/sitall polycrystalline films after annealing at temperatures (a) 550˚C, (b) 700˚C.

The XRD patterns of the NBT/sitall films annealed at 700^{0}C showed the presence of the main attribute reflections of the perovskite phase (2Θ=23°15°(100), 2Θ=33°20'(110), 2Θ=40°25'(111)) and indicated the ferroelectric NBT phase formation (Fig. 1b). At the same time, the reflection in the region 2Θ = 30° showed that residues of the pyrochlore phase were also present in the film material. Thus, after the high temperature annealing the NBT films crystallized into the perovskite phase with inclusions of the pyrochlore phase. It should be noted that the XRD patterns of the NBT/Si films heat treated at 700°C also showed the presence of two phases: the perovskite and, most likely, the pyrochlore phase [2].

Ferroelectric properties of the NBT films were investigated with use of the modified Sawyer–Tower circuit at room temperature. The remnant polarization (P_r), spontaneous polarization (P_s) and coercive field (E_c) values were calculated from the hysteresis loop graphs shown in Fig. 2. It should be noted that the hysteresis loops of the NBT/sitall films were well formed, however, they did not have a clear noticeable saturation region (Fig. 2a). At the same time other works [4] report the loops of the similar shape which is the feature of the ferroelectric NBT films. The P_r, P_s, E_c values measured on the NBT/sitall films were 9 μC/cm², 22 μC/cm², 40 kV/cm, respectively. The dielectric constant ε measured at 1 kHz was ~720. On the other hand, the hysteresis loops of the NBT/Si films were round-shaped (Fig. 2b). This might be caused by a significant contribution of leakage currents, which increase with a growth of applied electric field. In this case it is possible that the saturation section is overlapped by the ellipse of conductivity. The distortions introduced by leakage currents did not allow to calculate values of the spontaneous polarization (P_s) for the NBT/Si films. The remnant polarization P_r = 9 μC/cm² and coercive field E_c = 57 kV/cm were determined at E = 90 kV/cm. Further increase of the applied field led to the film sample breakdown in both cases.

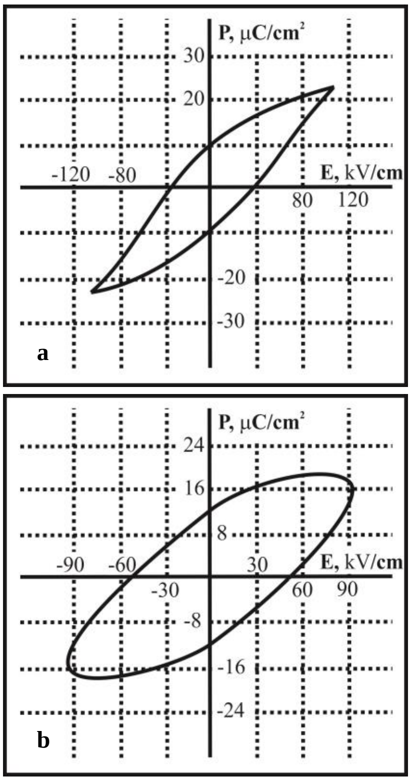

Fig. 2. P-E curve of NBT thin films (a) NBT/sitall, (b) NBT/Si.

That is why it is of interest to study mechanisms of conductivity, which are responsible for leakage currents in NBT films. Figure 3 shows how the leakage current density depends on applied electric field (J-E) in NBT films deposited on different substrates. And it also shows that the values of the leakage current in the NBT/sitall films are significantly lower in comparison to the values in the NBT/Si films over the studied 1–30 kV/cm electric field range.

The NBT/Si films curve on the J-E graph shows that the current values (J) almost linearly depend on the applied field in the region of weak fields (E < 10 kV/cm), so the ohmic conductivity is dominant. An increase of applied electric field leads to slow growth of the leakage current. The NBT/sitall films curve on the J-E graph shows that in the region of weak fields an increase of applied electric field leads to faster growth of the current values (J) in comparison to NBT/Si films dependencies.

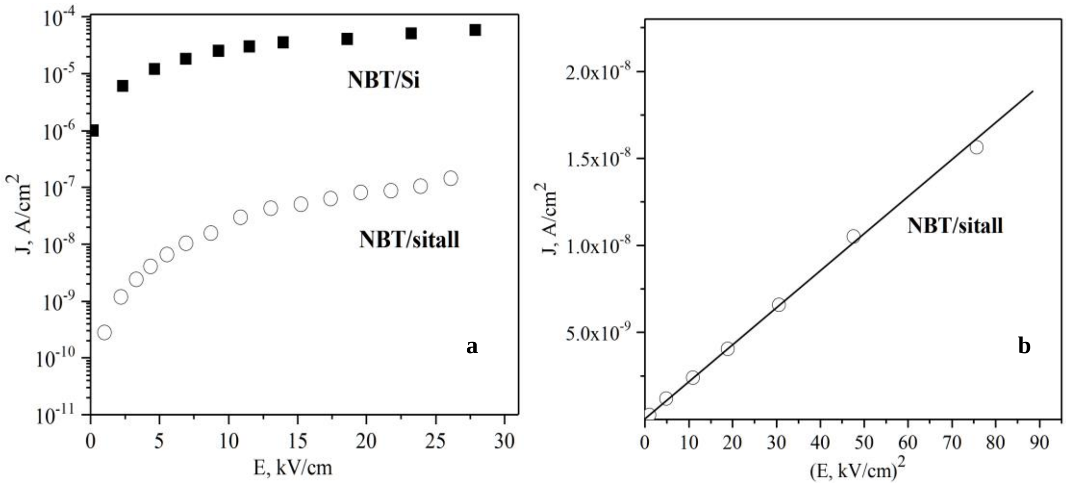

Fig. 3. The leakage current density of thin films NBT
(a) as function of applied electric field E, (b) as function of E^2

It should be noted that leakage currents in thin-film dielectric and semiconductor structures can be associated with the following conduction mechanisms: ohmic conductivity; space-charge-limited conductivity (SCLC); Schottky emission; Poole-Frenkel emission; Fowler-Nordheim tunneling. Hopping conductivity or a combination of different conductivity mechanisms is also possible.

To determine the conductivity mechanism in the investigated samples of NBT films the experimentally measured leakage current data were replotted according to various transportation mechanisms. Thus, the SCLC's are associated with monopolar injection of charge carriers that creates a space charge near the electrode-dielectric barrier. In this case, the current density rises faster than the applied electrical field. The experimental data in this case can be presented as a straight line in the J-E^2 coordinates. Figure 3b shows the J-E^2 dependence for the NBT/sitall films. The linear form of the curve on the J-E^2 graph indicates that the space-charge–limited conductivity dominates in the range of weak fields (E < 10 kV/cm) for the NBT/sitall films.

For fields E > 10 kV/cm the most probable mechanism of conductivity is the Schottky emission for both the NBT/sitall and the NBT/Si films. With the Schottky emission the charge carriers overcome the interface barrier due to thermal activation. Therefore, the current is controlled by the barrier states and it depends on such parameters as temperature, applied field, and barrier height. Figure 4 shows how the experimental current density depends on the applied field (ln(J)-E$^{1/2}$) in the Schottky representation. The ln(J)-E$^{1/2}$ dependence seems like linear, which indicates that the contribution of the Schottky emission charge carriers to the leakage current is predominant.

It should be noted that it is rather difficult to unambiguously determine the nature of the dominant mechanism of charge carrier transport in films. Even though the crystal structure of films is in most cases very similar to the structure of the same bulk material, electrophysical properties of films are different from properties of a bulk material. That is because films do not always have a perfect structure and can be amorphous, polycrystalline, and can contain inclusions of different phases. Electrical conductivity of polycrystalline films is influenced by the presence of grains and grain boundaries, as well as structural defects: point defects, dislocations, and even domain walls, which can act as trapping centers for charge carriers.

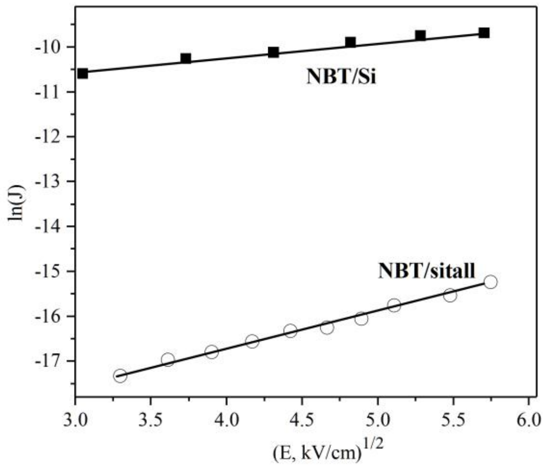

Fig. 4. Schottky representation for thin films NBT/sitall and NBT/Si

If the thermal energy of charge carriers is not enough for a release from the traps and for transition to the conduction band then the hopping conduction mechanism occurs. Jumps of carriers from one defect to another are not random and occur mainly along the direction of the externally applied electrical field. In this case, only some point defects can be involved and the oxygen vacancies V_{O_2}-$^{\bullet\bullet}$ can be such defects. It is known that the process of NBT films annealing is accompanied by both the evaporation of Bi^{3+} and the formation of a $V_{Bi^{3+}}'''$ vacancy, which in turn leads to the formation of oxygen vacancies. The presence of oxygen vacancies suggests possible contribution of the hopping conductivity mechanism to the leakage currents in NBT films [1, 2, 5].

Also considering the mechanism of conductivity in any dielectric it is necessary to consider the ionic type of conductivity. Thus, bulk NBT exhibits high oxygen ion conductivity depending on Na/Bi stoichiometry [6]. Consequently, occurrence of the oxygen ion conductivity in NBT films is also possible. However, mobility of V_{O_2}-$^{\bullet\bullet}$ may be hampered by the formation of defective complexes between $V_{Bi^{3+}}'''$ and V_{O_2}-$^{\bullet\bullet}$. The applied field must be large enough to generate mobile V_{O_2}-$^{\bullet\bullet}$ since additional energy is required to overcome the electrostatic forces between the $V_{Bi^{3+}}'''$ and the V_{O_2}-$^{\bullet\bullet}$. Thus, occurrence of the oxygen ion conductivity is possible at fields significantly higher than $E > 10$ kV/cm, as well as at high temperatures.

In [7] it was determined that the conditions for the formation of the perovskite phase in ferroelectric films are associated with changes in the morphology of the film-substrate boundary. The technological features of the lower Pt electrode deposition process allow to obtain a fine homogeneous polycrystalline structure of the platinum layer on sitall substrates [8]. As a result, during the synthesis process a coarse-grained perovskite structure was obtained on the NBT/sitall films. While in NBT/Si films formation of the perovskite phase occurred through the nucleation of many grains which led to the formation of many grain boundaries. It is known that grain boundaries in polycrystalline films are preferred sites for formation and accumulation of defects, including oxygen vacancies. Oxygen vacancies localized at the grain boundaries can increase leakage currents and decrease polarization of films [5]. Consequently, the significant reduction of the current density in the polycrystalline NBT/sitall films in comparison with the NBT/Si most likely can be associated with changes of the film-substrate boundary morphology which affect the features of the formation of the polycrystalline film structure and the content of defects, including oxygen vacancies V_{O_2}-$^{\bullet\bullet}$.

4. Conclusions

In summary, the electrical properties of polycrystalline NBT films deposited on sitall and silicon substrates were investigated. Observed P-E dielectric hysteresis loops confirmed that the obtained NBT films had ferroelectric properties. It was determined that the coercive field in the NBT/Si films was significantly larger than in the NBT/sitall films. This may be due to the more defects in NBT/Si films. The dependence of the leakage current density on applied electric field was studied for both films. Analyzed behavior of the J-E characteristics allowed to say that in fields E <10 kV/cm the ohmic conductivity mechanism dominated in NBT/Si films and the space-charge-limited conductivity mechanism dominated in NBT/sitall films. For fields E >10 kV/cm the most probable conductivity mechanism is the Schottky emission for both the NBT/sitall and the NBT/Si films. In addition, the presence of the oxygen vacancies $V_O^{2\bullet\bullet}$ allows to suggest that the hopping conduction mechanism may also contribute to the leakage currents in the films. The significant decrease of the current density in the polycrystalline NBT/sitall films in comparison to the NBT/Si most likely can be associated with morphology changes on the film-substrate boundary which lead to reduced number of structural defects, including $V_O^{2\bullet\bullet}$, influencing the leakage currents.

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