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DEPOSITION OF $Na_{0.5}Bi_{0.5}TiO_3$ FILMS BY MAGNETRON SPUTTERING

The polycrystalline films of bismuth sodium titanate $Na_{0.5}Bi_{0.5}TiO_3$ were obtained by radio-frequency magnetron sputtering. Deposition was performed on fused quartz and Si(100) substrates heated to 200ºC in Ar atmosphere. The target was sputtered at 10 mTorr working pressure and with 3 W/cm^2 average RF power. The films were crystallized by subsequent annealing in air at 600ºC and higher temperatures. X-ray patterns indicate that thin films exhibit the amorphous structure even after annealing at 600ºC. A crystalline NBT phase was observed after annealing at 650ºC. X-ray studies of films indicate the formation of bismuth sodium titanate and appearance of an additional phase. It is shown that annealing at 750ºC and higher temperatures decreases the content of NBT phase and increases the content of non-NBT phase (presumably $Bi_2Ti_2O_7$). Optical transmission spectra of NBT films were measured in the wavelength range 280–500 nm. At the absorption coefficient α evaluation, the refractive index dispersion of the substrate and the interference in NBT films were taken into consideration. Band gap E_g was calculated from the Tauc relation. The calculations for the NBT film with the thickness of 290 nm showed that for the direct forbidden transitions E_g=3.16 eV and for indirect allowed transitions E_g=3.07 eV.

Keywords: thin films, magnetron sputtering, bismuth sodium titanate.

Методом високочастотного магнетронного напилення отримані полікристалічні плівки натрій-вісмутового титанату $Na_{0.5}Bi_{0.5}TiO_3$. Осадження здійснювалося в атмосфері Ar на підкладки з плавленого кварцу і Si(100), нагріті до температури 200ºC. Розпилення мішені здійснювалося за тиску робочого газу 10 мТорр, при середній RF потужності 3 Вт/см^2. Подальша кристалізація плівок здійснювалася в повітрі при температурі 600ºC та вище. Рентгенівські дифрактограми показали, що після відпалу при 600ºC плівки мали аморфну структуру. Кристалічна NBT фаза виникала після відпалу при 650ºC. Рентгенівські дослідження плівок показали, що формування фази натрій-вісмутового титанату супроводжується появою додаткової фази. Показано, що відпал при температурах 750ºC та вище зменшує частину NBT фази і збільшує частину не-NBT фази (імовірно $Bi_2Ti_2O_7$). Були виміряні спектри оптичного пропускання плівок NBT в діапазоні довжин хвиль 280-500 нм. При обчисленні коефіцієнта поглинання α враховувалися дисперсія коефіцієнта заломлення підкладки, а також інтерференція у плівках NBT. Ширина забороненої зони E_g обчислювалася за рівнянням Тауца. Розрахунки для плівки NBT товщиною 290 нм показали, що для прямих заборонених переходів E_g=3,16 еВ, а для непрямих дозволених переходів E_g=3,07 еВ.

Ключові слова: тонкі плівки, магнетронне напилення, натрій-вісмутовий титанат.

Методом высокочастотного магнетронного напыления получены поликристаллические пленки натрий-висмутового титаната $Na_{0.5}Bi_{0.5}TiO_3$. Осаждение осуществлялось в атмосфере Ar на подложки из плавленого кварца и Si(100), нагретые до температуры 200ºC. Распыление мишени осуществлялось при давлении рабочего газа 10 мТорр и средней RF мощности 3 Вт/см^2. Последующая кристаллизация пленок осуществлялась в воздухе при температуре 600ºC и выше. Рентгеновские дифрактограммы показали, что после отжига при 600ºC пленки имели аморфную структуру. Кристаллическая NBT фаза появлялась после отжига при 650ºC. Рентгеновские исследования пленок показали, что формирование фазы натрий-висмутового титаната сопровождается появлением дополнительной фазы. Показано, что отжиг при температурах 750ºC и выше уменьшает долю NBT фазы и увеличивает долю не-NBT фазы (предположительно $Bi_2Ti_2O_7$). Были измерены спектры оптического пропускания пленок NBT в диапазоне длин волн 280–500 нм. При вычислении коэффициента поглощения α учитывались дисперсия коэффициента преломления подложки, а также интерференционные явления в пленке NBT. Ширина запрещенной зоны E_g вычислялась из соотношения Тауца. Расчеты для пленки NBT толщиной 290 нм показали, что для прямых запрещенных переходов E_g=3,16 эВ, а для непрямых разрешенных переходов E_g=3,07 эВ.

Ключевые слова: тонкие пленки, магнетронное напыление, натрий-висмутовый титанат.

1. Introduction

High piezoelectric parameters and lead-free composition attract attention to ferroelectric $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) as a perspective material for piezoelectric devices. However, high coercive field and electric conductance [1] prevent using of bismuth sodium titanate piezoceramics in commercial products. Efforts of many research groups are focused on developing of bismuth sodium titanate ceramics sintering technology and special attention is paid to thin films sputtering. It is reported that NBT thin films were prepared by chemical solution de-composition [2], pulse laser deposition [3], radio frequency (RF) magnetron sputtering [4]. Excess surface energy of thin films enables to increase the rate of reaction and to decrease synthesis temperature. The structure and properties of the films are strongly dependent on such characteristics as deposition rate, substrate temperature, substrate-target distance, pressure and sort of the working gas. Using of active oxygen or inert argon as working gas mainly determines chemical composition and structure of the films prepared. Understanding of the processes which accompany the film deposition enables to control the properties of the obtained compound. In this paper we report deposition of the polycrystalline NBT films including details of the ceramics target preparing, sputtering conditions and subsequent annealing. Optical transmission spectra of the deposited films were studied in the range of self-absorption edge.

2. Experimental setup

The polycrystalline films of NBT have been obtained by RF magnetron sputtering method with high-frequency power (13.56 MHz). The inert argon was used as working gas.

The ceramics of bismuth sodium titanate was prepared by traditional technology [5] and was used as the target. The starting components of Bi_2O_3, TiO_2, Na_2CO_3 were weighed in stoichiometric proportions and then powdered in a ball mill. After that the mixture obtained was pressed into tablet and annealed at 800ºC during 15 h in air. Then the tablet was milled, subjected to pressure of 15 MPa during 1 h at 40ºC. Finally the target, prepared as disk of 40 mm diameter and 3 mm thickness, was annealed at 1100ºC during 4 h. The phase composition of the ceramics target was controlled by X-Ray diffraction (the insert to Fig. 1). The films were deposited on heated substrates of fused quartz and crystalline silicon. Heating of the substrate to 200ºC during deposition was carried out by halogen lamp.

The target was sputtered at 10 mTorr working pressure and with 3 W/cm^2 average power. The structures of the targets and films were controlled by X-ray phase analysis; DRON-4M diffractometer operating with copper K_α radiation was used. Optical transmission spectra were studied in a wavelength range 280–500 nm with the help of the spectrophotometer Specord M40.

3. Experimental results

In the absence of oxygen in the plasma, films deposited on the Si substrate are characterized by metallic luster. It could be the result of metal atom transport and absence of gas-transport reactions during sputtering. The X-Ray patterns show that obtained films are condensed in amorphous state.

The deposited films were synthesized by annealing in air for 1 h at temperatures in the range 500–800ºC. It has been observed that NBT phase is formed after annealing at 650ºC and higher temperatures. At the same time, the annealed films become non-transparent and matted.

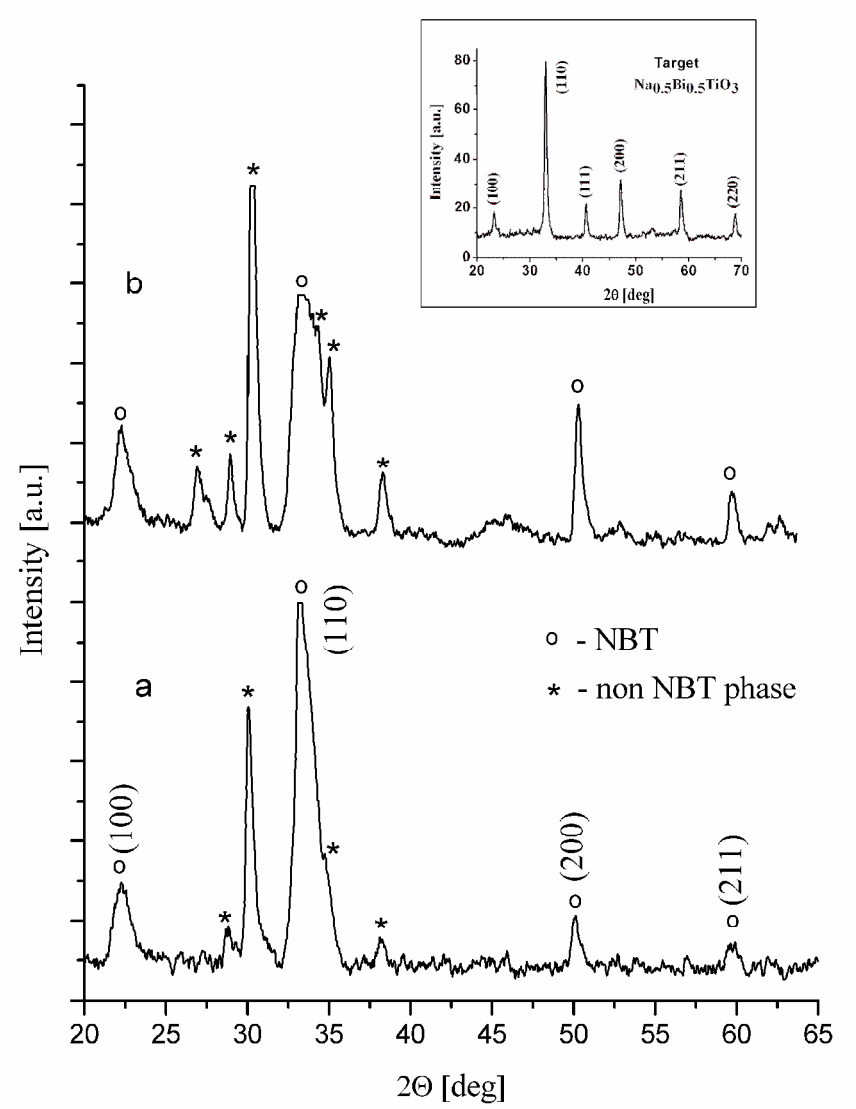

Fig. 1. X-ray diffraction patterns of NBT films (d=240nm) deposited on Si substrate and annealed during 1 h at following temperatures: a – 650ºC, b – 750ºC. X-Ray diffraction pattern for NBT ceramics target is shown in the insert.

According to [6], the structure of bismuth sodium titanate can be identified by the X-Ray reflexes at 2Θ=23º15' corresponding to (100) plane, 2Θ=33º20' – (110) plane, 2Θ=40º25' – (111) plane. The X-ray diffraction patterns of annealed films indicate formation of bismuth sodium titanate and show appearance of some additional non-NBT phase (Fig. 1a). However, the intensity of bismuth sodium titanate reflexes is significantly higher. NBT reflex absence at 40º25' ((111) plane, Fig. 1a, b) could be attributed to certain orientation of crystallites and formation of textured films. Presence of the non-NBT phase demonstrates difficulties of the films synthesis, so some components, sputtered from the targets, do not react to form a bismuth sodium titanate structure. It

shows that synthesis of thin films differs sufficiently from the case of bulk compounds synthesis [7].

As it has been shown in [7], amorphous titanium is a catalytic agent of the synthesis. One can assume that titanium atoms can react with Bi and Na before the appearance of TiO_2 stable oxide. The formation of Ti bonds with Na can be hindered and bismuth-titanium bonds would have advantage in contrast to traditional synthesis process when titanium oxide reacts with bismuth oxide and sodium carbonate. Some authors [6, 8] assume that the accompanying non-NBT phase corresponds to $Bi_2Ti_2O_7$ with pyrochlore structure and give thermodynamic arguments to support this assumption. However, our results show that annealing at 750ºC and higher temperatures decreases the content of NBT phase and, correspondingly, increases the content of non-NBT phase (Fig. 1). Most probably, it is connected with a deviation from Bi stoichiometry due to evaporation of Bi and Bi_2O_3 at temperatures above 700ºC [9]. The excess of unreacted titanium stimulates formation of non-NBT phase and, most likely, changes unit cell parameters of the NBT phase.

Using the film deposition technology described above, we synthesize a set of NBT films with thickness in 230–290 nm range. In order to obtain information on electronic structure and optical parameters valuable for optoelectronic applications, we study optical transmission spectra of the NBT films deposited on fused quartz substrates.

Optical transmission spectra measured in a wavelength range 280–500 nm are given in Fig. 2 for NBT films and for bulk single crystal (d=110 μm).

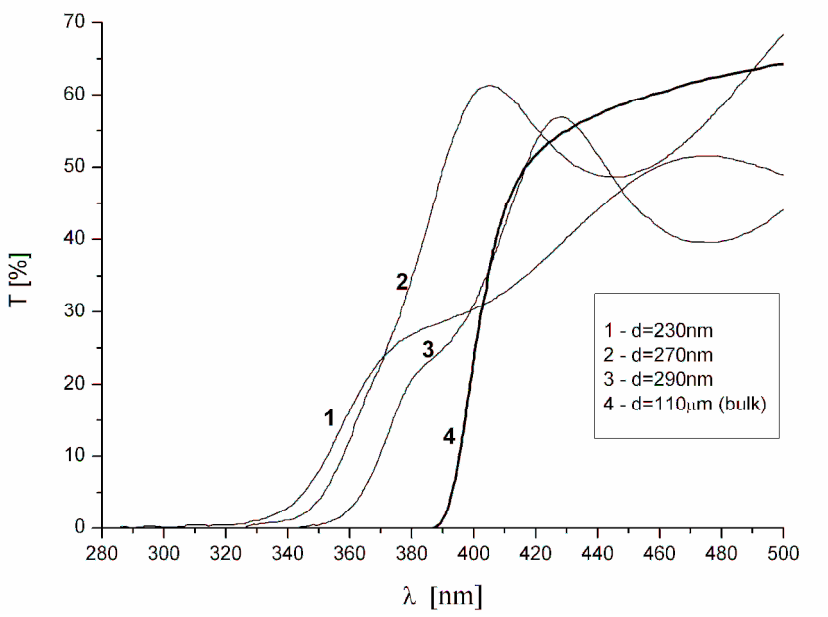

Fig. 2. The optical transmission spectra of NBT films deposited on fused quartz substrate (curves 1-3) and bulk single crystal (curve 4).

To calculate an optical band gap from the transmission spectra, one has to know direct or indirect electronic transitions determine the self-absorption edge [11, 12]. Our evaluation of the absorption coefficient α took into account the dispersion of the substrate refractive index and the interference fringes, which appear in the optical transmission for

the NBT/SiO_2 heterostructure. The band gap energy (E_g) for both NBT thin films (d=290 nm) and bulk single crystal (d=110 μm) was evaluated by the "method of the envelopes" which is explained in details in [10]. E_g was calculated by dint of the expression $(\alpha\hbar\nu)^r=A(\hbar\nu-E_g)$ where r characterizes the transition process, E_g is the optical band gap value, hν is the photon energy and A is a constant. Optical band gap value E_g can be defined by extrapolating the linear part of Tauc plot ($(\alpha\hbar\nu)^r$ versus ($\hbar\nu$)) to the abscissa axis. The r parameter can take the following values: 2/3 – for a direct transition forbidden and 1/2 - for an indirect transition allowed.

The calculations for the NBT film of d=290 nm in thickness showed that the optical band gap energy E_g=3.16 eV when r=2/3, and E_g=3.07 eV when r=1/2. These results are in agreement with the data presented in [10]. The calculated values of energy do not differ a lot and do not allow to make conclusion about nature of the transitions in NBT thin films on the basis of optical transmission spectra analysis. Results of the calculations are shown in the Table 1.

Table 1

Optical band gap in NBT films and bulk single crystal

Thickness d [nm]	*Optical band gap E_g [eV]*
290, r=1/2	3.07
290, r=2/3	3.16
Bulk crystal d=110 μm, r=1/2	3.027
Bulk crystal d=1 mm [12]	3.03

The optical band gap for NBT bulk single crystal d=1 mm is taken from [12] and is given for comparison.

4. Conclusions

The technology used makes possible to prepare the ceramics targets with correct NBT stoichiometric composition. The polycrystalline NBT films were obtained by RF magnetron sputtering method with further annealing at temperatures above 600ºC. The X-ray diffraction patterns of the obtained films showed formation of both NBT phase and additional non-NBT phase. It is shown that varying the annealing temperature significantly influence the ratio of the bismuth sodium titanate and additional non-NBT phases and by this way allow to control the phases ratio. The effect is presumably connected with appearance of unreacted titanium atoms because of evaporation and lack of Bi content. The optical transmission spectra of the NBT films (230–290 nm in thickness) were obtained in the wavelength range 280–500 nm. Calculated E_g values for both indirect allowed transitions and direct forbidden transitions are quite close each other (3.07 eV and 3.16 eV, respectively) and therefore these data do not allow to conclude about the nature of the transition processes in the NBT films.

Acknowledgments

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