Crystallization Behavior and Electrical Properties of BNN Thin Films by IBSD Process

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Abstract

$Ba_2NaNb_5O_{15}$(BNN) thin films have been prepared by the ion beam sputter deposition (IBSD) method on Pt coated Si substrate at temperature as low as 600℃. XRD, SEM were used to investigate the crystallization and microstructure of the films. It was found that the films were crack-free and uniform in microstructure. The electric properties of thin films were carried out by observation of D-E hysteresis loop, dielectric constant and leakage current. It was found the deposition rate strongly influenced the phase formation of the films, where the phase of $BaNb_2O_6$ was always formed when the deposition rate was high. However, the single phase (tungsten bronze structure) BNN thin film was obtained with the deposition rate as low as 22Å/min. The remanent polarization Pr and dielectric constant are about 1~2 μC/cm^2 and 100~200, respectively. It was also founded the electric properties of thin films were influenced by the deposition rate. The Pr and dielectric constant of films increased with the decrease of deposition rate. The effects of annealing temperature and annealing time to the crystallization behavior of films were studied. The crystallization of thin film started at about 600℃. The adequate crystallization was gotten at the temperature of 650℃ when the annealing time is 0.5 hour or at the temperature of 600℃ when the annealing time is long as 6 hours.

Key Words : BNN thin film; IBSD; tetragonal tungsten bronze, deposition rate

1. Introduction

Barium sodium niobate $Ba_2NaNb_5O_{15}$ (BNN) is a ferroelectric solid solution compound with orthorhombic tungsten bronze structure, which belongs to the point group of mm2 at room temperature [1]. The structure and oxygen octahedral are shown in Figure 1. There are three types of sites (A1, A2 and C). The C sites of BNN are empty, A1 sites and A2 sites are filled with Ba^{2+} and Na^{+} ions [2]. BNN has large nonlinear optical coefficients and excellent electro-optic properties. In addition, BNN crystals show remarkable pyroelectric, piezoelectric and ferroelectric properties such as spontaneous polarization of 40μC/cm^2 and dielectric constant of 51 parallel to the c axis [3]. Recently, with the rapid development of techniques for growing thin films, that BNN thin films have been prepared in many methods has been reported, such as sol-gel method, rf magnetron sputtering, and excimer laser ablation, etc.

In this paper, BNN thin films are prepared by IBSD on Pt coated silicon wafers. The effects of some preparation parameters such as deposition rate, annealing temperature and time on crystallization behavior and electronic properties of BNN thin films are discussed.

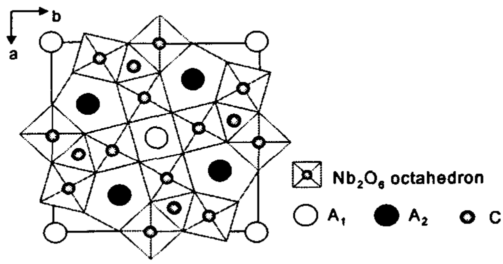


Fig. 1. BNN structure showing the three kinds of sites.

2. Experiment procedure

The composition of selected target is $Ba_{1.8}Na_{0.9}Nb_5O_{14.75}$, which has higher density than stoichiometric $Ba_2NaNb_5O_{15}$ [4]. The ion beam energy was fixed at 1000eV, and deposition rate was controlled by changing the ion current density. The deposition rate varied from 50Å/min to 22Å/min when the ion beam current varied from 40mA to 19mA. Table 1 shows the deposition conditions. The deposition time was varied from 1 hour to 3 hours to get the appropriate film thickness. After deposition, the thin films were annealed at high temperature in O_2 atmosphere for crystallization in a tube furnace. The crystallization behavior of thin films was analyzed by XRD. Surface morphology and profile of thin films were observed using SEM. The ferroelectric behavior, dielectric properties and leakage current characteristics of thin films were studied.

Table 1. Deposition condition for BNN films by ion beam sputtering.

Target	$Ba_{1.8}Na_{0.9}Nb_5O_{14.75}$
Substrate	Pt(100)
Base Pressure	3.0×10^{-6} torr
Working Pressure	5×10^{-4} torr
Discharge Power	410~460V, 0.15~0.4A
Beam Power	1kV, 19~40mA
Accelerator Power	0.1kV, 0.8~2mA
Deposition Temperature	400℃
Deposition time	1~3hours
Ar	2 sccm
O2	2 sccm

3. Results and Discussion

3.1 Deposition rate induced transition

Figure 2 shows XRD patterns of thin films prepared with different deposition rate on Pt(100) coated silicon wafers. After deposition the films were annealed at 700℃ for 30 minutes in O_2. It can be seen that when the deposition rate was high (such as 50Å/min), the signal of tungsten bronze structure (Ref. JCPDF#86-0739) was weak, and major peaks of $BaNb_2O_6$ (Ref. JCPDF#14-0027) were observed. However, when the deposition rate was decreased, the signals of tungsten bronze structure became strong. The peaks of $BaNb_2O_6$ disappeared in the thin film prepared with deposition rate as low as 22Å/min and the tungsten bronze phase was the sole phase. This phenomenon can be explained by this: the $BaNb_2O_6$ is a meta-stable phase, and the tungsten bronze structure is the most stable structure in which the atoms are located in the positions of lowest energy; when the deposition rate is low, the sputtered atoms have enough time to get their lowest-energy positions, and the deposition process was nearer to thermodynamic equilibrium. Therefore, the low deposition rate results in the disappearance of meta-stable phase in thin films. Similar phenomena were observed by Shoichi, Mitsas and Zhitomirsky [5, 6].

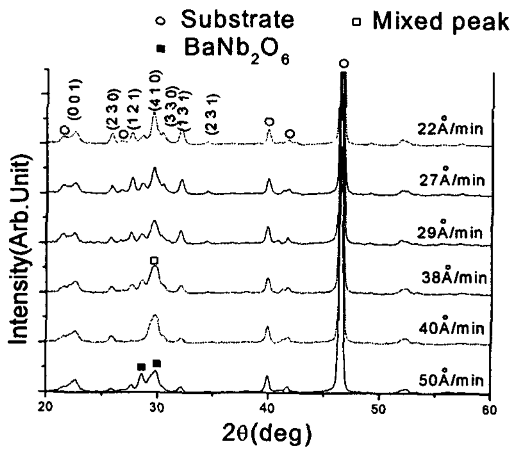


Fig. 2. XRD patterns of BNN thin films prepared with different deposition rates on Pt(100) coated silicon wafers

Figure 3 shows the SEM micrographs of these thin films It can be seen that the surface of the BNN films was uniform, crack free, and no large porosity was found. The photographs of surface of films prepared at high deposition rate shows two kinds of grains. That's because there are two kinds of phases in these films. In the films

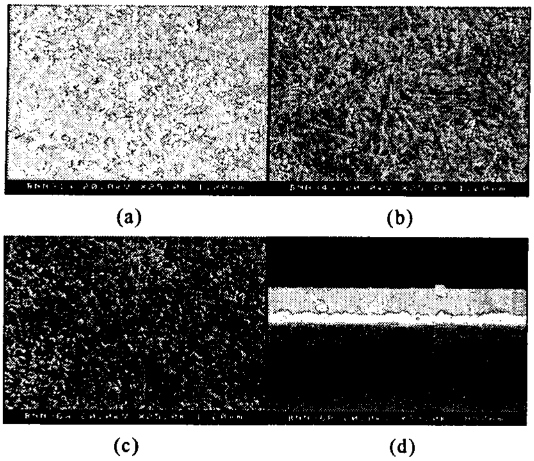


Fig. 3. SEM micrographs of BNN thin films prepared with different deposition rates on Pt(100) wafers: (a) 50Å/min, (b) 38Å/min, (c) 22Å/min, (d)cross structure of film (c).

prepared at deposition rate as low as 22Å/min, only one kinds of grains could be observed, which indicates one kind of phase has disappeared. Referring to the XRD pattern, this phase should be $BaNa_2Nb_6$. The profile of thin film shows the thickness of this film is about 4000Å, and the density is high.

All of the films prepared with different deposition rates show ferrolelectric behavior. Figure 4 show the hysteresis loops of. the films prepared with the deposition rate of 50Å/min and 22Å/min. The remanent polarization Pr of these films are about 1~2μC/cm2, and the coercive electric field Ec are about 40~70KV/cm. These values are high compared to the results reported

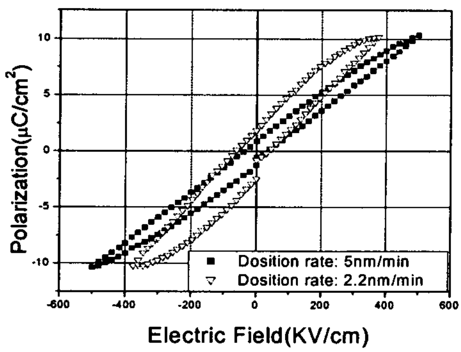


Fig. 4. D-E hysteresis of thin films prepared with different deposition rate on Pt(100) wafers.

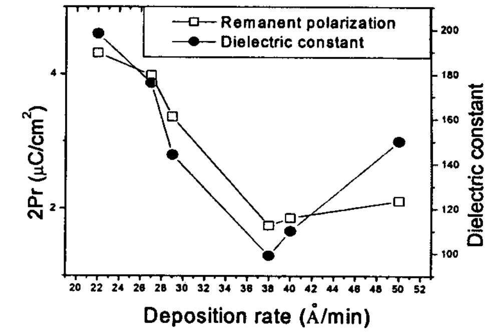


Fig. 5. The remanent polarization and dielectric constant versus deposition rate of thin film prepared with different deposition rate on Pt(100) wafers

in other papers [7]. It is very clear the hysteresis loop of the films prepared with deposition rate of 22Å/min has better shape than that of the films prepared with deposition rate of 50Å/min. The dielectric constants of these films are about 100~200.

Figure 5 shows the remanent polarization and dielectric constants versus deposition rate of thin films on Pt(100) coated silicon wafers. It can be seen that the remanent polarization and dielectric constant of thin films prepared with low deposition rate are higher than that of films preparedwith high deposition rate. It can also be explained by that the amount of ferroelectric phase (tungsten bronze BNN phase) increases with the decrease of the deposition rate.

The leakage current characteristics of BNN thin film, measured with a voltage step of 0.1V, is shown in figure 6. The film was prepared with the deposition rate of 22Å/min on Pt(100). It shows the plot of log$J$ versus square root of electrical field $E^{1/2}$. The current density increases linearly with the external electric field in the region of low electric field that suggests an ohmic conduction. Whenthe electric filed increase above 100KV/cm, the leakage current shows a Schottky emission behavior.

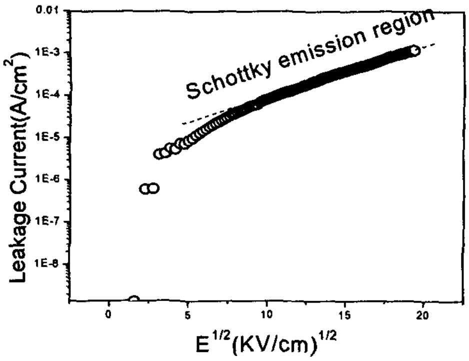
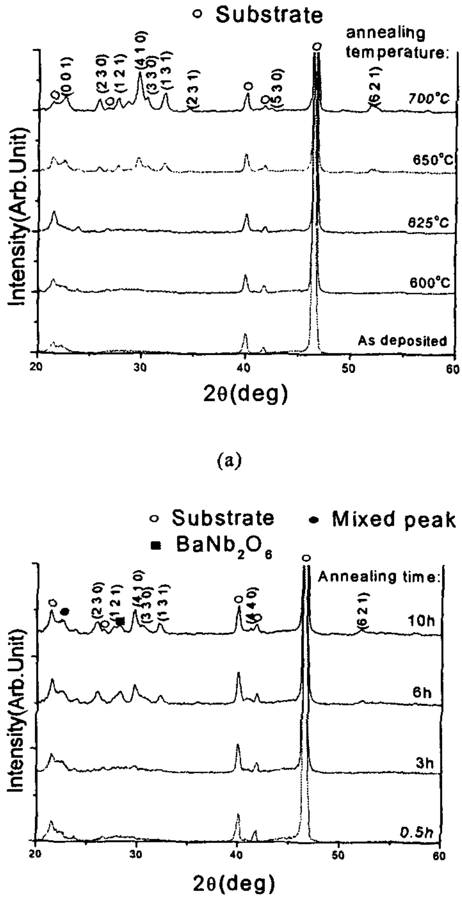


Fig. 6. The current-Voltage characteristic of BNN thin film

3.2 Annealing temperature and time induced transition

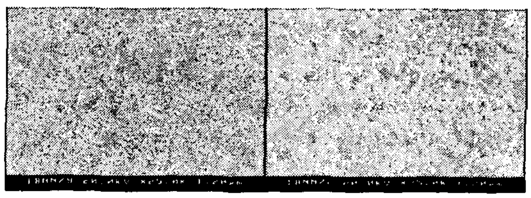
For studying the effect of annealing conditions to the crystallization behavior, the films were annealed at different temperature varied from 550℃ to 700℃ for different hours varying from 0.5 hour to 10hours. Figure 7 (a) shows the XRD patterns of BNN thin films annealed at different temperatures for 0.5 hour. It can be seen that when the annealing temperature was increased to 650℃, the peaks of tungsten bronze BNN phase became strong. Other phase didn't appear during the process of increasing annealing temperature. Figure 7 (b) shows the XRD patterns of thin films annealed at 600→ during different hours. It can be seen that when the film was were annealed for 6 hours both major peaks of tungsten bronze BNN phase and minor peaks of $BaNb_2O_6$ were observed. This $BaNb_2O_6$ phase belongs to monoclinic structure (Ref. JCPDF#86-0739) and it is different from the $BaNb_2O_6$ phase that observed in films prepared with high deposition rate. The presence of $BaNb_2O_6$ phase should be attributed to the low annealing temperature. Even though the annealing time is long enough, the activity energy of atoms is too low to reach the phase transformation completely. From the SEM micrographs (figure 8) of these films, we can find the film annealed at 650℃ is uniform, but there are two kinds of grain in the film annealed at 600℃ for 6 hours. The presence of other grains can be explained by the existence of second phase ($BaNb_2O_6$).



(a)

(b)

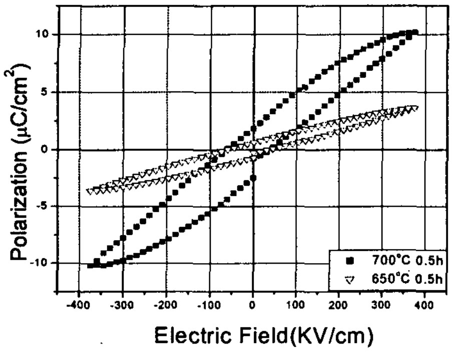
Fig. 7. XRD patterns of BNN film annealed under different conditions: (a) 0.5 hour (b) 600℃



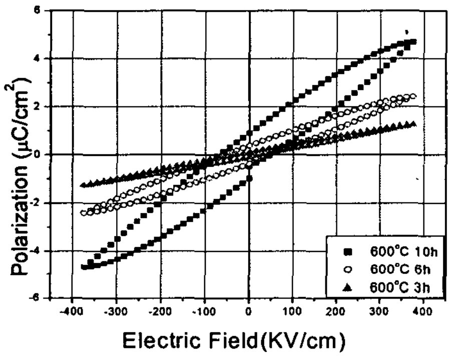
(a) (b)

Fig. 8. SEM micrographs of BNN thin films annealed: (a)650℃, 0.5 h; (b) 600℃,6h.

Figure 9 shows the D-E hysteresis loop of BNN thin films annealed under different condition. It is clear the ferroelctric behavior become better when the annealing temperature increasedor the film annealed for longer time. It indicates the degree of crystallization increase with the increase of annealing temperature or when the annealing time is longer.



(a)



(b)

Fig. 9. D-E hysteresis of BNN thin films prepared with different annealing conditions (a) different temperature, (b) different hours.

4. Conclusion

Crack-free BNN thin films were synthesized on Pt coated silicon substrates in IBSD method. It was found that the deposition rate had a strong effect on the formation of single-phase tungsten bronze structure, where $BaNb_2O_6$ phase was always formed in the films prepared at high deposition rate. When the deposition rate was decreased at 22Å/min the $BaNb_2O_6$ phase disappeared and the tungsten bronze phase was the sole phase. The crystallization started at 600℃, and annealing conditions have distinct effect on the properties of thin films.

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