CRYSTALLIZATION BEHAVIOR AND PHASE RELATIONS OF H-MOD DERIVED THIN FILMS BASED ON BARIUM SODIUM NIOBATES

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$Ba_2NaNb_5O_{15}$, hereafter called BNN, thin film is an attractive candidate for such applications as nonvolatile memory and electro-optic devices. BNN thin films of about 450nm thickness that have different contents of Ba, Na and Nb have been prepared by hybrid metalorganic decomposition, hereafter called H-MOD, process using bare and platinized Si wafers as substrate. XRD and FE-SEM measurements were used to investigate the phase evolution behavior and the microstructure of the films. It was found that Nb content strongly influenced the phase formation of the films, where $BaNb_2O_6$ phase was always formed at the stoichiometric BNN composition. However, the amount of $BaNb_2O_6$ phase decreased with the increase of excess Nb content, and the thin film with single phase orthorhombic tungsten bronze structure was obtained at the temperature as low as 750°C.

INTRODUCTION

Barium sodium niobate $Ba_2NaNb_5O_{15}$ (BNN) has been known as a ferroelectric material with orthorhombic structure, which belongs to the point group mm2 at room temperature [1], and has large nonlinear optical coefficients and excellent electro-optic properties. As a consequence, the material has received much attention for applications in electro-optic devices [2,3]. In addition, BNN crystals show good ferroelectric properties, i.e. spontaneous polarization value of 40μC/cm^2 and dielectric constant value of 51 parallel to the c axis and suffer no optical damage to an intense laser beam which often occurs in $LiNbO_3$ crystal [4,5].

However, industrial applications of BNN have not been realized to date because of the high production cost of single crystals and the poor quality of thin films. The cracking is due to the large thermal expansion of the c-axis at Curie temperature (~570°C) during cooling process [6].

The structure and oxygen octahedron are shown in figure 1. There are three types of sites (A_1, A_2 and C). The C sites of BNN are empty, A_1 sites and A_2 sites are filled with Ba^{2+} and Na^+ ions [7]. BNN thin films have been reported [8,9]. In this paper, BNN thin films were prepared by hybrid metal-organic deposition (H-MOD) process. In this pro-cess, metal alkoxides are combined with metalorganic precursors, which are less sensitive

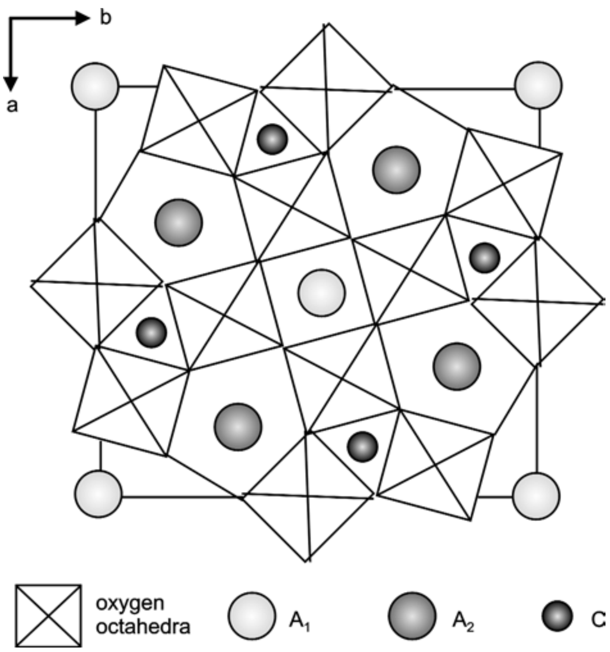

Figure 1. A schematic of BNN structure showing the three different interstitial sites.

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to moisture [10]. It retains MOD's advantages regarding ease of preparation thanks to the moisture insensivity. The stock solution for H-MOD process is more stable than sol-gel process.

In this paper, the effect of composition and annealing temperature on crystallization behavior and microstructure of H-MOD derived BNN thin films is discussed.

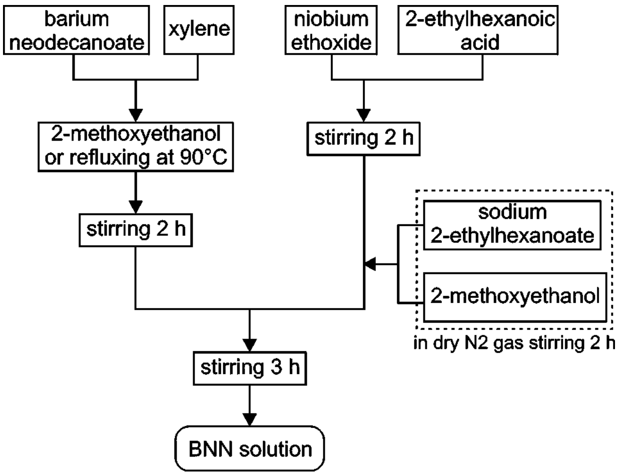


Figure 2. BNN solution preparation by H-MOD process.

EXPERIMENTAL

Figure 2 shows the process flow of preparing a homogeneous precursor solution. Xylene was the preferred solvent since it is known to dissolve most of the metalorganics used in microelectronics. The final concentration of the BNN precursor solution was 0.2M.

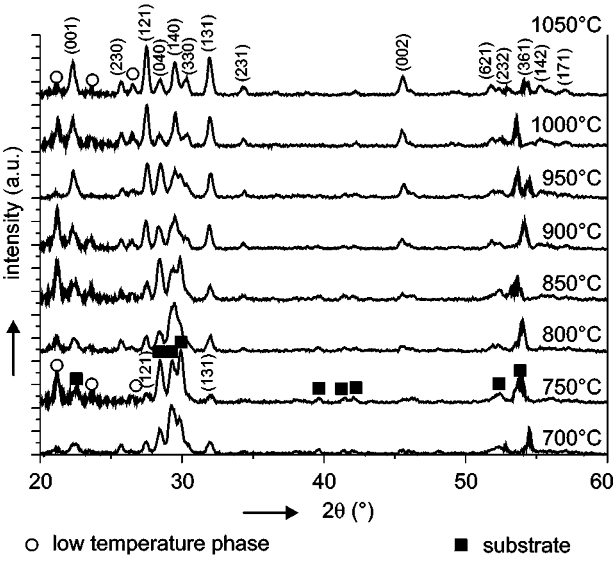


Figure 3. XRD patterns of $Ba_2NaNb_5O_{15}$ thin films annealed at different temperatures on bare Si(100) substrates.

The solution was homogeneous and of light yellow color. BNN thin films were then prepared by spin coating processes where coat-bake steps were repeated until desired film thickness was obtained. Dried films were then annealed in air at elevated temperatures for crystallization. Crystallization behavior was analyzed by XRD (D/MAX-2500, Rigaku, Japan). Surface morphology and cross-section of thin films were observed using SEM (S-4100, Hitachi, Japan). The MFM (metal-film--metal) structure was used to measure the electrical properties. Pt top electrodes with 200 μm diameters was deposited using an ion-beam sputter.

RESULTS AND DISCUSSION

Figure 3 shows XRD patterns for stoichiometric $Ba_2NaNb_5O_{15}$ thin film annealed at different temperatures on Si(100) substrates. Annealing time was fixed to 30 minutes. It could be seen that at low annealing temperatures (such as 750°C), the signals of tungsten bronze structure were very weak, and most of them belonged to $BaNb_2O_6$ phase. However, as an annealing temperature increased, the peaks of $BaNb_2O_6$ decreased,

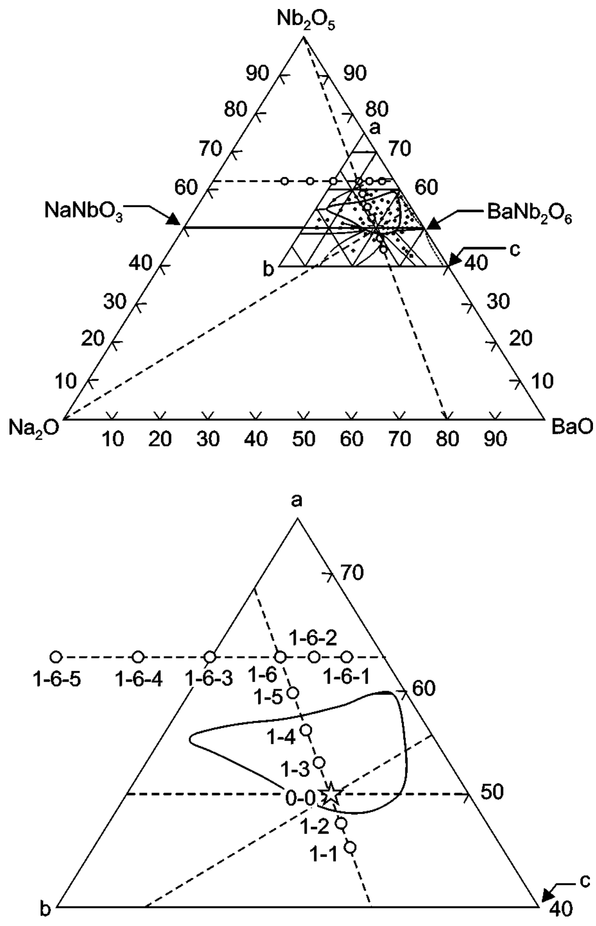


Figure 4. Ternary phase-diagram of $BaO-Na_2O-Nb_2O_5$.

and the signals of tungsten bronze structure became strong. At about 1000°C, The $BaNb_2O_6$ phase disappeared and we were able to obtain single tungsten bronze phase BNN films. $BaNb_2O_6$ phase appeared in BNN crystal during the crystallization process, which was also reported by others [11,12]. It is apparent that the $BaNb_2O_6$ phase is metastable phase when the solution corresponded to the stoichiometric composition. As the film was heated at a higher temperature, the metastable phase transformed to a more stable structure, i.e. tungsten bronze structure. The higher crystallization temperature of the films was attributable to the complex crystal structure as well as the substrate used.

In order to study the effect of composition on crystallization behavior, BNN thin films with different compositions were prepared. The compositions of films are indicated in ternary phase-diagram of BaO-Na_2O-Nb_2O_5 (figure 4), where the star indicates the composition of stoichiometric $Ba_2NaNb_5O_{15}$.

Figure 5 shows the XRD patterns of BNN films with different compositions coated on Pt(100) substrates. The composition varies along the line connecting (1-1) to (1-6) in the diagram, where the ratio of Ba^{2+}/Na^{+} is fixed while the Nb content was changing. Annealing condition was fixed at 750°C for 30 minutes. The XRD patterns showed that the films corresponding to the stoichiometric composition was mainly composed of $BaNb_2O_6$ phase. When the Nb_2O_5 content was increased to approximately 62.5 % (composition number 1-6), $BaNb_2O_6$ phase disappeared, and single phase tungsten bronze structure was obtained. It is noted that the Nb_2O_5 content is 50 % in stoichiometric BNN. The reason why the film needs excess niobium is still not clear. As some papers mentioned above reported, some of the niobium ions did not form NbO_6 octahedra but entered into A sites and covalently bonded to the oxygen ions [13], even at the temperature higher than 1000°C. Therefore, as to our H-MOD derived BNN thin films, it is likely not all of the niobium ions formed NbO_6 octahedra,

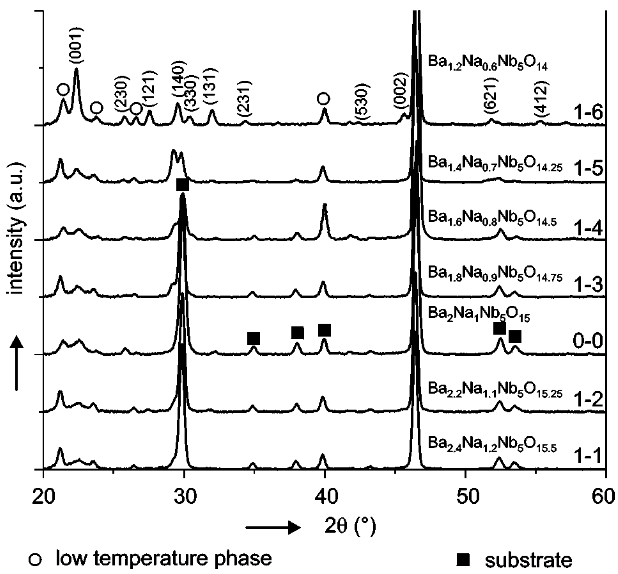
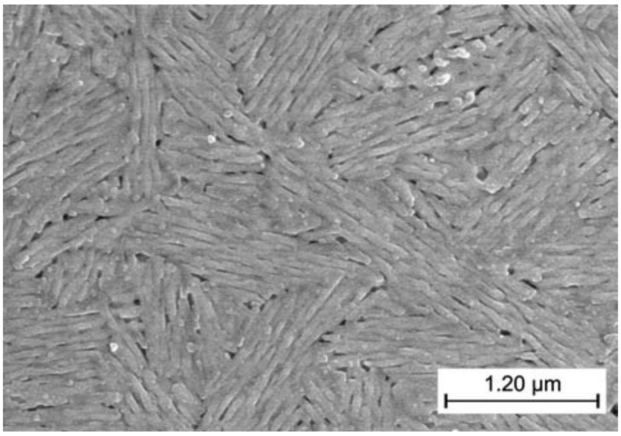
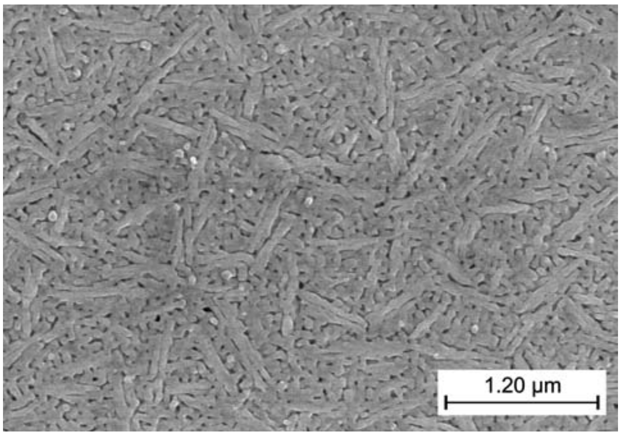


Figure 5. XRD patterns of $Ba_{2(1-x)}Na_{(1-x)}Nb_5O_{(15-5x/2)}$ thin films with different x values prepared on $Pt(100)/TiO_2/Si$ substrates.



a)



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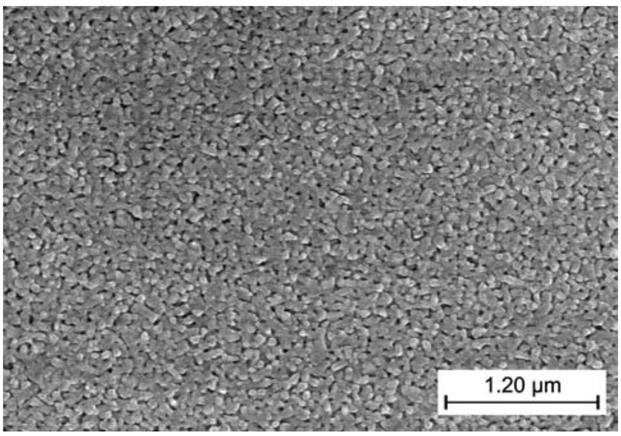
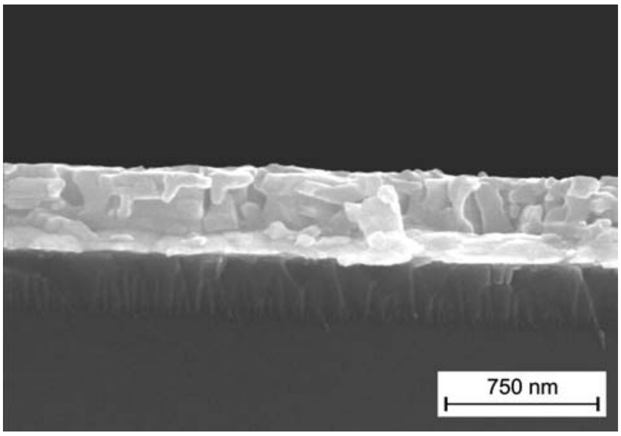
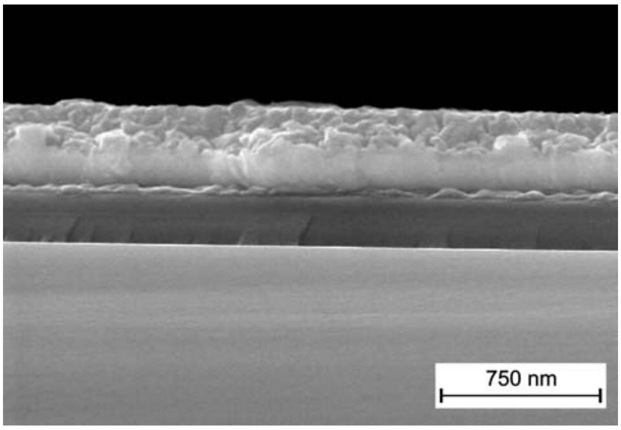


c)

Figure 6. Plane and cross-sectional SEM micrographs $Ba_{2(1-x)}Na_{(1-x)}Nb_5O_{(15-5x/2)}$ thin films on $Pt(100)/TiO_2/Si$ substrates.



d)



e)

Figure 6. *Continue*

thereby causing the deficiency of NbO_6 octahedra, and there are not enough A sites for introducing the Ba^{2+} and Na^{+} into the lattices. This situation made the formation of orthorhombic structure in stoichiometric BNN difficult at low temperatures. Figure 6 shows the SEM micrographs of BNN films with different compositions corresponding to the composition number 0-0,1-4,1-6 in figure 5. From the cross-sectional photograph, the thickness of films was determined to about 450 nm. The surface photographs indicated that the films were crack-free and uniform with very small grains. The BNN film with $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ composition showed random polycrystalline structure. However, in stoichiometric BNN (0-0) film, the grain growth direction was parallel to substrate. This accounted for the fact that stoichiometric BNN showed a very strong peak nearby 2θ = 30° in the corresponding XRD pattern. In photographs of film with $Ba_{1.6}Na_{0.8}Nb_5O_{14.5}$ composition (composition number 1-4), some part of the picture was similar to those in $Ba_2NaNb_5O_{15}$, and the rest was the same as those in $Ba_{1.2}Na_{0.6}Nb_5O_{14}$. Please note that the composition of $Ba_{1.6}Na_{0.8}Nb_5O_{14.5}$ (1-4) is halfway between the two films.

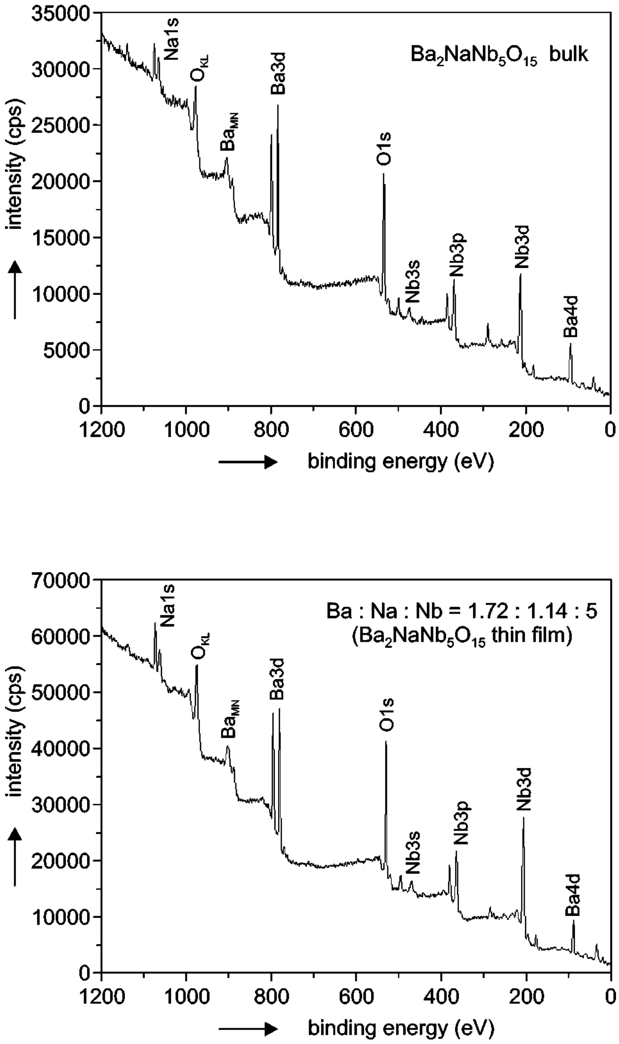


Figure 7. The XPS spectra of BNN bulk and thin films with composition corresponding to $Ba_2NaNb_5O_{15}$.

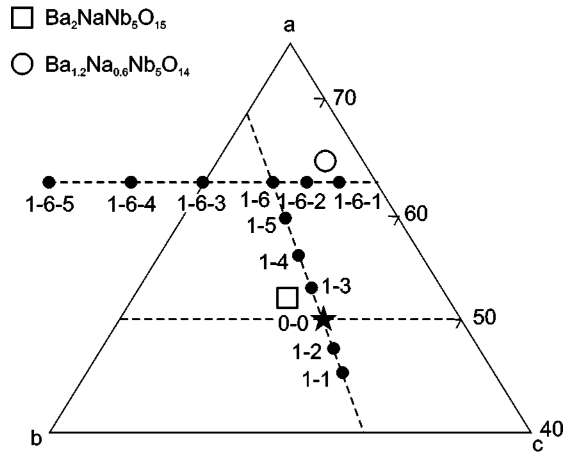


Figure 8. Summary of XPS measurements.

Since there might be the possible loss of elements during the heat-treatment process, the analysis of film composition is important. Figure 7 shows the XPS result from BNN bulk and thin films, in which the BNN bulk sample was used as a reference. The atomic ratio of Ba, Na and Nb in stoichiometric BNN (0-0) thin film was 1.72 : 1.14 : 5, while in $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ thin film it was 1.32 : 0.32 : 5. This and other results were summarized in the ternary phase diagram in figure 8. Considering the measurement errors, these values are near the compositions that we expected. The XRD patterns of BNN films with other compositions were also measured (figure 9). The compositions of films correspond to the line (1-6-1) ~ (1-6-5) as shown in the diagram, where Nb content is fixed, while the Ba^{2+}/Na^{+} ratio is changing. The XRD patterns of these films were all similar. This result supports the fact that the structure of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ is of tungsten bronze structure, since Ba^{2+} ions and Na^{+} ions can partially substitute each other. Figure 10 shows the XRD patterns of BNN films with the composition of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ (1-6) annealed at different temperatures. The result shows the film crystallization started at temperature of about 650°C, which was also supported by SEM observation. The grain size increased with the increase of annealing temperature.

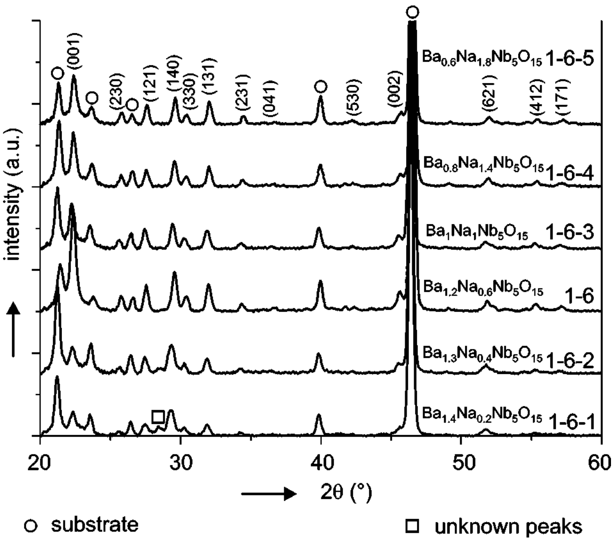


Figure 9. XRD patterns of $Ba_xNa_{(3-2x)}Nb_5O_{14}$ thin films with different x values on Pt(100)/TiO_2/Si substrates.

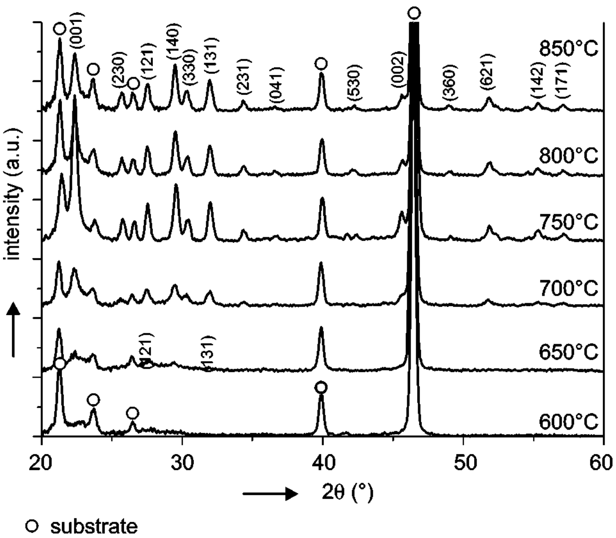


Figure 10. XRD patterns of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ thin films annealed at different temperatures.

CONCLUSIONS

Crack-free BNN thin films of about 450 nm thick were successfully deposited onto either bare Si or Pt/TiO_2/Si substrate utilizing the H-MOD process. Crystallization behavior was studied with respect to film compositions. It was found that the Nb content had a marked effect to the formation of orthorhombic tungsten bronze structure, and the tungsten bronze structure appeared only if excess Nb ions were added to the stock solution.

Acknowledgement

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KRYSTALIZACE A FÁZOVÉ POMĚRY V TENKÝCH VRSTVÁCH NIOBIČNANU BARNATOSODNÉHO PŘIPRAVENÉHO ROZKLADEM METALORGANICKÝCH LÁTEK

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Tenké vrstvy $Ba_2NaNb_5O_{15}$, dále označovaného BNN, jsou vhodným kandidátem pro použití v trvalých pamětových a elektrooptických zařízeních. Vrstvy BNN s tlouštkou kolem 450 nm s různým obsahem Ba, Na a Nb byly připraveny metodou rozkladu hybridních metalorganických látek, dále označovanou H-MOD, s využitím čistých a poplatinovaných Si destiček jako substrátu. Rtg difrakce a FE-SEM byly užity ke zjištění vývoje fázového složení a mikrostruktury vrstev. Bylo zjištěno, že obsah Nb značně ovlivňuje vznik tuhých fází ve vrstvách, přičemž fáze $BaNb_2O_6$ vznikala vždy při složení odpovídající vzorci BNN. Množství $BaNb_2O_6$ se ale snižovalo s rostoucím přebytkem Nb a při teplotě 750°C byla připravena tenká vrstva s čistou fází ortorombického wolframanového bronzu.