MICROSTRUCTURE OF NaNbO₃ THIN FILMS PREPARED BY SOL-GEL METHOD ON ALUMINA AND SILICON SUBSTRATES

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Abstract
Lead-free ferroelectric NaNbO₃ (NN) thin films (~ 200 nm thickness) were prepared using sol-gel method, deposited by spin-coating method on platinized alumina or silicon substrates and sintered at 650°C. X-ray diffraction (XRD) analysis indicated that the NN film on the Pt/SiO₂/Si substrate possessed a single perovskite NaNbO₃ phase, while NN film on the Pt/Al₂O₃ substrate contained a small amount of secondary pyrochlore Na₂Nb₈O₂₁ phase. Scanning electron microscopic (SEM) and atomic force microscopic (AFM) analyses confirmed that roughness Rₚ of the thin NN/Pt/SiO₂/Si film (~ 15.0 nm) was significantly lower than that of the KNN/Pt/Al₂O₃ film (~ 51.5 nm). The particle morphology in the heterogeneous microstructure of NN films was characterised by the bimodal particle size distribution and small spherical nanoparticles on both substrates and larger cuboidal particles on Pt/Al₂O₃ and spherical clusters on Pt/SiO₂/Si were observed. The effect of different substrates on the surface morphology and cross-section of thin films was confirmed.

Keywords: sol-gel, coating, thin films, NaNbO₃ perovskites, microstructure

1 Introduction
Thin films of alkaline niobates as the sodium (NaNbO₃, NN) have been intensively studied due to ecological issues [1,2]. Environmental considerations dictate that the lead-free ferroelectric thin films use in the new generation of functional devices [3,4] in many microelectromechanical systems (MEMS) [5,6]. Physical and chemical methods of preparation of thin films onto different substrates are known: sputtering, pulsed liquid deposition (PLD), physical vapor deposition (PVD) and chemical solution deposition (CSD, sol-gel). The CSD method, based on the sol–gel process, is divided in several steps: solution synthesis, coating on a substrate, pyrolysis and crystallization process [7,8]. During sol-gel process in dependency of interaction type of entrance component (Na₂CO₃) with Nb-complex, solvent (acetic acid) and stabilizer (n-propanol), amorphous film with metastable pyrochlore phase originates already at calcining temperature of 300–400°C, where pyrolysis organic compounds into inorganic oxides Na₂O and Nb₂O₅ occurs [5]. The final perovskite phase forms from the transformation of pyrochlore phase during sintering at 500-700°C. The substrates seems to play an important role affecting the phase formation and growth of the perovskite film on substrate (SrTiO₃, MgAl₂O₄, or Al₂O₃ and Pt/SiO₂/Si) [9,10]. In NN film, the pyrochlore NaNb₂O₈ phase forms at about 620°C and the perovskite NaNbO₃ phase appears at 440°C and is increasing in an amount upon reaching
temperatures of 700-800°C [11,12]. NN films prepared by sol-gel methods on different substrates distinguish from the nucleation and transformation temperature of perovskite phase, particle morphology and size [13,14].

The present paper describes the preparation of NN thin films using the sol-gel synthesis and the spin-coating method. The influence of substrate on the phase composition and microstructure of NN thin films deposited on the Pt/Al₂O₃ and Pt/SiO₂/Si substrates by spin-coating method was investigated.

2 Experimental material and experimental methods

NN thin films were prepared using the sol-gel synthesis according to method in ref. [15,16]. The Na/Nb mole ratio was 1.0 : 1.0. After an Nb-complex addition at the temperature of 80°C, the yellow sol was formed. Basic NN sol was diluted with n-propanol to 1.0M concentration and following deposited on platinized alumina and silicon (Pt/Al₂O₃ or Pt/SiO₂/Si) substrates by spin-coating method. Organic gels were calcined at 400°C/10min and sintered at 650°C/1h in air. The phase composition of NN films was determined by the X-ray diffraction analysis (XRD, Philips X’Pert Pro) using CuKα radiation. The surface and cross-section of microstructures of NN thin films were characterized using a scanning electron microscope (SEM, Jeol-JSM-7000F) and atomic force microscopy (AFM), dimension Icon from Veeco (USA).

3 Results and discussion

The XRD diffractograms of NN thin films deposited on Pt/Al₂O₃ and Pt/SiO₂/Si substrates and prepared at 650°C are shown in Figs. 1 and 2, respectively. XRD diffractograms of NN thin films on both substrates verified the formation of perovskite NaNbO₃ (PDF4 00-014-0603) phase (Fig. 1 and 2) and the additional secondary pyrochlore Na₂Nb₈O₂₁ (PDF4 00-013-0329 + PDF4 00-030-1229) phase in NN/Pt/Al₂O₃ film (Fig. 1). The two peaks at 40° and 46° corresponding to the Pt planes of both substrates, appear for Pt thin films deposited on crystalline Al₂O₃ (Fig. 1) and amorphous SiO₂/Si (Fig. 2) substrates after sintering at 650°C [9]. In the NN film on Pt/SiO₂/Si substrate the XRD peaks exhibit weaker peak intensities. The effect of different substrates on phase formation of thin films was determined from Figs. 1 and 2 and pure perovskite phase in NN film on Pt/SiO₂/Si substrate was revealed, while NN/Pt/Al₂O₃ film contained small amount of secondary pyrochlore Na₂Nb₈O₂₁ phase.

![Fig.1 XRD diffractogram of NN thin film deposited on Pt/Al₂O₃ substrate after sintering at 650°C (× - perovskite NaNbO₃ phase, □ - Na₂Nb₈O₂₁ pyrochlore phase and s - Pt/Al₂O₃ substrate).](image-url)
In Figure 3, the SEM cross-section microstructures of ~200 nm thickness NN thin films deposited on Pt/Al₂O₃ or Pt/SiO₂/Si substrate and sintered at 650°C are shown. The film surface roughness is visible in the cross-section of NN thin film on Pt/Al₂O₃ substrate (Fig. 3a) contrary to much smoother and uniform surface morphology of KNN/Pt/SiO₂/Si film (Fig. 3b) with columnar structure.

![XRD diffractogram of NN thin film deposited on Pt/SiO₂/Si substrate after sintering at 650°C (× - perovskite NaNbO₃ phase and s - Pt/Al₂O₃ substrate).](image)

![SEM cross-sectional micrographs of NN thin film prepared on (a) Pt/Al₂O₃ and (b) Pt/SiO₂/Si substrates after sintering at 650°C.](image)

The SEM surface and the 2D AFM topography micrographs of NN thin films deposited on Pt/Al₂O₃ and Pt/SiO₂/Si substrates prepared at 650°C are shown in Fig. 4 and 5, respectively. The heterogeneous microstructure of the NN film surface on both substrates is characterized by the bimodal particle size distribution. A bigger cuboidal particle clusters (up to 1 μm in length) composed of fine particles with dimension under 80 nm (Fig. 4a) were found in the heterogeneous microstructure of NN/Pt/Al₂O₃ thin film. Besides the SEM surface observation of NN/Pt/SiO₂/Si thin film (Fig. 4b), showed that the bigger clusters of perovskite particles (representing agglomerates of smaller spherical particles of ~50 nm size) are surrounded by the fine cuboidal about 100 nm particles. From the atomic force microscope (AFM) analysis, the surface morphology, the root mean square roughness (R_d), and the average roughness (R_a) were
determined. Figures 5a and 5b show large-scale two-dimensional 2D AFM images of the NN thin film deposited on Pt/Al₂O₃ and Pt/SiO₂/Si substrates. From the AFM measurements, the values of root mean square roughness (Rₛ) and average roughness (Rₐ) over scan areas of 2.5 × 2.5 µm of thin films deposited on both substrates were determined. The effect of substrate on surface topography of NN films is apparent. The surface roughness Rₛ and Rₐ tends to be enhanced in the NN films from 51.5 nm to 39.2 nm for Pt/Al₂O₃ and 15.0 nm to 14.0 nm for Pt/SiO₂/Si substrate. The surface morphology studies are in consistent with the structural and topography results. The roughness Rₛ over scan areas of 2.5×2.5 µm of Pt/Al₂O₃ and Pt/SiO₂/Si substrate was ~5.7 nm and ~1.0 nm, respectively.

Fig.4  SEM surface micrographs of NN thin film prepared on (a) Pt/Al₂O₃ and (b) Pt/SiO₂/Si substrates after sintering at 650°C.

Fig.5 2D AFM surface micrographs of NN thin film prepared on (a) Pt/Al₂O₃ and (b) Pt/SiO₂/Si substrates after sintering at 650°C.

The three-dimensional 3D AFM micrographs of NN films on both substrates (Fig. 6) showed the film roughness and particle shape are comparable with SEM observations of films. NN/Pt/Al₂O₃ film (Fig. 6a) had island-like structure, representing major portion of rough surface with a cuboidal particle clusters and a minor portion of smooth surface with spherical particles. On the other hand the ridge-like structure of NN/Pt/SiO₂/Si film (Fig. 6b) contains major portion of smooth surface (a bigger clusters of perovskite particles) and minor portion of rough surface (cuboidal particles). The effect of Pt/SiO₂/Si substrate causes stronger decrease in rough surface...
portion between smooth surface than one on Pt/Al\(_2\)O\(_3\) substrates. The mechanism of the microstructure formation with morphologically varied perovskite particles in sodium niobate thin film prepared from the same sol on different substrates depends on the structure of the Pt film deposited on crystalline Al\(_2\)O\(_3\) (rough surface) and amorphous SiO\(_2\) (smooth surface).

**Fig.6** 3D AFM surface micrographs of NN thin film prepared on (a) Pt/Al\(_2\)O\(_3\) and (b) Pt/SiO\(_2\)/Si substrates after sintering at 650°C.

**4 Conclusions**

Lead-free NaNbO\(_3\) thin films of about 200 nm thickness were prepared by sol-gel method, deposited by spin-coating method on Pt/Al\(_2\)O\(_3\) and Pt/SiO\(_2\)/Si substrates and sintered at 650°C. Effect of different substrates on the phase formation in thin films was determined and the pure perovskite NaNbO\(_3\) phase in NN film on Pt/SiO\(_2\)/Si substrate were revealed. From the XRD diffractograms resulted that the NN film on Pt/Al\(_2\)O\(_3\) substrate contained a small amount of the additional secondary pyrochlore Na\(_2\)Nb\(_8\)O\(_{21}\) phase.

In the microstructures of thin films, the effect of substrate on particle shapes and sizes was clearly observed. The particle morphology in the heterogenous microstructure of NN films on both substrates was characterized by the bimodal particle size distribution and small spherical nanoparticles and larger cuboidal particles were observed. Pt film on Al\(_2\)O\(_3\) and SiO\(_2\)/Si substrates causes creation of NN cuboidal and spherical clusters, respectively. The results of AFM analyses confirmed that the roughness R\(_q\) of NN film on Pt/SiO\(_2\)/Si substrate (~ 15.0 nm) was significantly lower than one (~ 51.5 nm) of film deposited on Pt/Al\(_2\)O\(_3\) substrate. The effect of Pt/SiO\(_2\)/Si substrate causes stronger decrease in rough surface portion between smooth surface than one on Pt/Al\(_2\)O\(_3\) substrates.

**References**


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