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Preparation and characterization of highly (222)-oriented bismuth magnesium niobate thin film by sol-gel method

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ABSTRACT

Highly (222)-oriented $Bi_{1.5}MgNb_{1.5}O_7$ thin films have successfully been prepared on SiO_2/HR-Si substrates by sol-gel method with rapid thermal annealing (RTA). The films were characterized using X-ray diffraction, high-resolution transmission electron microscope and atomic force microscope. The results revealed that the thus-derived films possessed a cubic pyrochlore structure with regular and smooth surface, and exhibited superior dielectric constant of about 170. The growth of (222)-oriented BMN thin film can be explained as a self-assembly process, and the mechanism of self-assembly process was elaborated. The formation of the large dielectric constant of the film was mainly assigned to the highly (222) orientation and large in-plane tensile strain.

1. Introduction

Bismuth based cubic pyrochlore thin films have received extensively attention for their versatile potential applications, such as integrated decoupling capacitors, nonlinear optical devices and microwave agile devices in communication systems [1–3]. The $Bi_{1.5}MgNb_{1.5}O_7$ (BMN) thin film, as a typical cubic pyrochlore, earns special interest recently due to their excellent dielectric properties, i.e. high dielectric constant, low loss, large dielectric nonlinearity [4,5]. To utilize the prominent characteristics of BMN in thin film devices, a lot of attempts have been made to produce BMN thin films [4–7]. Furthermore, previous works have demonstrated that the (222)-oriented BMN thin films have superior dielectric properties compared with the randomly oriented ones [6,7]. This result suggests that it is desirable to fabricate (222)-oriented BMN thin films in such way to optimize the dielectric properties.

The sol-gel technique, compared with other thin film deposition methods, has advantages of low cost and precise composition control, which is especially necessary for BMN thin films for the high volatility of Bi [8]. As composition is the key factor that determines crystal structure and dielectric properties of BMN thin films, the sol-gel process is expected to provide the attractive advantage of control to realize orientation structure of the films. Moreover, the total growth processes of BMN films (including nucleation, crystal growth, coarsening) prepared by the sol-gel method and other physical deposition methods are different. Therefore, the preparation and characterization of the (222)-oriented BMN film derived by sol-gel method have technical and theoretical significance.

In this article, highly (222)-oriented $Bi_{1.5}MgNb_{1.5}O_7$ thin film was successfully prepared using sol-gel method with rapid thermal annealing. The structures, surface morphologies and dielectric properties of the film were investigated. A growth mechanism of self-assembly process of the (222)-oriented BMN thin film was proposed. The processing-orientation-property relationship in the (222)-oriented BMN film was discussed.

2. Experimental procedure

Analytically pure (AR) $Bi(NO_3)_3 \cdot 5H_2O$ (99.00%), $Mg(NO_3)_2 \cdot 6H_2O$ (99.99%) and Nb_2O_5 (99.99%) were used as the raw materials. The precursor solution was synthesized similarly to the previous researches on Bismuth based thin films in a manner [3]. Meanwhile, an appropriate amount of monoethanolamine was dissolved in anhydrous ethanol as the stabilizer and diluent. The final concentration of the solution was adjusted to 0.12 Min BMN stoichiometry. The precursor solution was deposited on the on

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SiO_2/high resistivity Si (HR-Si) substrate by spin coating followed the rapid thermal annealing (RTA) process at 750 °C for 60 s for each layer. The Coating-RTA procedure was repeated until the desired thickness was reached. Final crystallization of the RTA-processed films was carried out at 750 °C for 30 min.

The thickness of the final crystallized film was about 300 nm, which was determined by profile-system (KLA-Tencor, D-100). The crystalline structure of thin films was characterized using X-ray diffraction (Rigaku D/MAX-B). The high-resolution transmission electron microscope (HRTEM, JEOL model 2100F) and the fast Fourier transform (FFT) techniques were also adopted to study the crystallization and the microstructure. The surface morphology of the film was performed by atom force microscope (AFM, Model easy Scan 2, Nanosurf AG). For the dielectric measurements, Au interdigital electrodes (IDEs), 200 nm thick, was prepared on BMN/SiO_2/HR-Si by standard photolithography and the lift-off process. The interdigital electrodes (IDEs) patterns consisted of 20 fingers were separated by a 20 μm gap, and each finger had a width of a 20 μm and active length (length for which the fingers overlap) of 800 μm. The relative dielectric constants of the BMN films were measured using multi-layered substrate analysis with conformal mapping method [9].

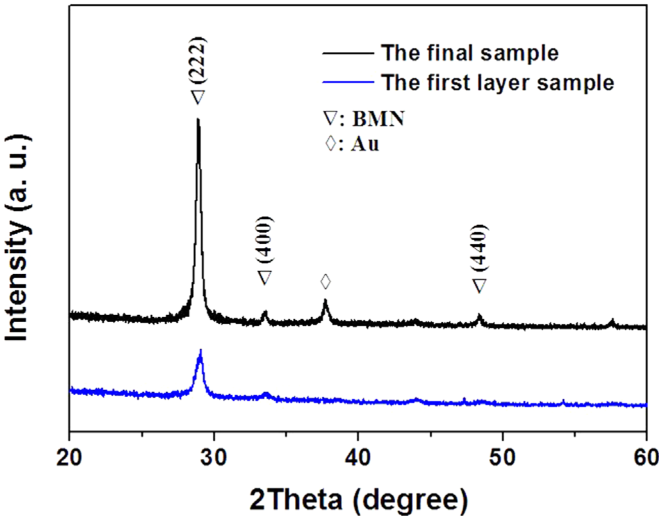

Fig. 1. XRD patterns of the first layer and final crystallized BMN thin films.

3. Results and discussion

Fig. 1 shows the XRD patterns of the first layer of the BMN thin film and final crystallized BMN thin film.

It is evident that all films are crystallized in cubic pyrochlore phase and present a (222) preferred orientation. And with the repetitions of coating-RTA procedure, the character peak (222) of the films strengthened, indicating the enhancement of the crystallinity and orientation degree. Since the SiO_2 is amorphous, there is no epitaxial relationship between BMN and the substrate. However, the thin film is not randomly oriented. The growth process of (222)-oriented BMN film derived from sol-gel method can be explained as a self-assembly process.

A schematic sketch of the growth mechanism of self-assembly process is shown in Fig. 2.

After the first layer of BMN sol-gel film is coated and preheated on bare SiO_2/HR-Substrate, the nucleis are formed and gradually grow into crystals. Since the SiO_2 is an amorphous material, the crystals should be randomly oriented. However, because the (222) plane of BMN film has a lower surface energy than the other planes, the crystals will grow preferentially along the ⟨222⟩ direction [10]. After the second layer of BMN sol-gel film is coated and preheated, the new crystals can be formed using the former layer as a growth template. And with the increase of the film thickness, the growth of BMN film may be governed by two mechanisms: quasi epitaxial growth imposed by the former BMN (222) template and self-assembled growth driven by minimization of the surface energy. Finally, the post-annealed process is used to promote the crystallinity of the BMN film.

Fig. 3 shows the TEM microstructures and AFM surface morphologies of the final crystallized BMN thin film.

The TEM image reveals that the film is composed of fine and uniform particles, with an average grain size of approximately

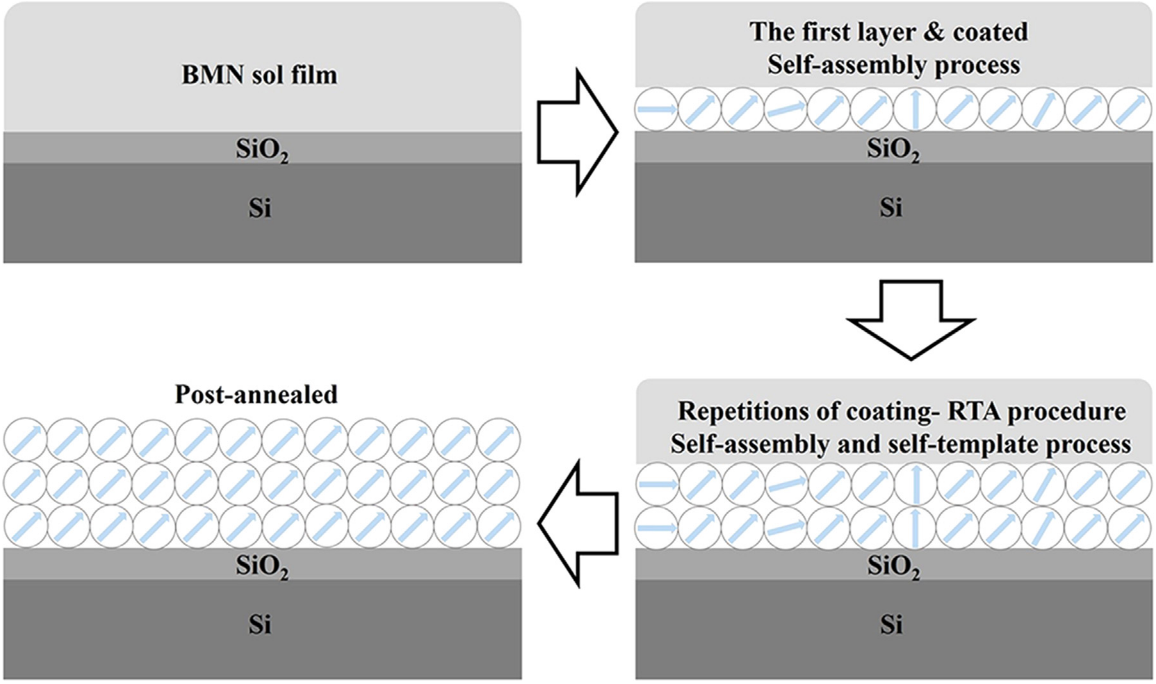

Fig. 2. Schematic sketch of the growth mechanism of self-assembly process.