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Fabrication and Structural Properties of Sol–Gel Derived SBN Films

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Abstract

Structural changes in sol–gel derived $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN) films have been studied as functions of annealing temperature, annealing atmosphere, and film thickness. The tetragonal tungsten bronze (TTB) structure SBN was obtained at annealing temperatures above 700°C. Post-annealing in air, oxygen, or argon ambient showed no apparent different effects on the structural properties of the films. Preferred and better oriented (001) SBN layers, however, were found to improve with film thickness. Enlarged grain size and a much reduced surface roughness have also been observed in thicker films. In the present studies, we have fabricated crack-free SBN films of up to 2·3 μm thick with good mean crystallinity. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: strontium barium niobates, films, sol–gel processes, X-ray methods.

1 Introduction

Strontium barium niobates is known to have a large electro-optics coefficient of $2{\cdot}7\times10^{-10}$ m/V.[1] When fabricated into films, it can be very useful in integrated electro-optic devices such as electro-optic waveguide modulators and Bragg deflectors. Various preparation processes for high quality SBN films of a few micrometers thick are therefore of great interest and have been reported previously.[2–6] In this paper, we will report the effects of annealing temperature, annealing atmosphere and film thickness on the crystalline orientation, grain size and surface morphology of the sol–gel derived SBN films. Under proper processing conditions, high mean structural quality TTB phase SBN films with thickness up to 2·3 μm have been successfully prepared.

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2 Experimental

The precursors used for preparing the sol–gel SBN were strontium alkoxide, barium alkoxide and niobium alkoxide. They were prepared individually by dissolving the corresponding metals or chloride salts in 2-methoxyethanol and then mixed together to form the SBN sol according to the desired stoichiometric ratio of Sr:Ba = 0·6:0.4. The resultant sol was subsequently dip-coated on (100)Si wafers. A more detailed description of the preparation process can be found elsewhere.[7] The crystallographic structures of the films were studied by X-ray diffractometry (XRD) using Cu-K_α radiation. The film thickness was obtained by measuring the cross section of SBN films using a scanning electron microscope. The composition, on the other hand, was determined by energy dispersive X-ray micro-analysis. Surface roughness and grain size were examined in detail by atomic force microscopy (AFM). All AFM images were recorded in air with a nominal applied force of 66 nN. Two lateral scan dimensions, 1×1 and $5\times5\,\mu m^2$, were employed. In each case a grid of 1024×1024 points was used.

3 Results and Discussion

3.1 Annealing temperature

Figure 1 shows the XRD patterns of SBN films annealed at different temperatures for 2 h. The film thickness was kept at about 650 nm. No sharp diffraction peaks corresponding to the crystallization of SBN are observed for samples annealed at 500°C indicating that the films are in a non-crystalline state. At 600°C, peaks corresponding to the crystallized SBN are observed. This is slightly lower than the crystallization temperature of 634°C obtained from DTA data for dried gels.[7] This observation confirms that the presence of the substrates relaxes part of the crystallization criterion by lowering the crystallization temperature. For

higher annealing temperatures, well defined XRD patterns with peaks of different crystal orientations are observed. Careful analyses of the positions of the peaks reveal that the SBN annealed at 600°C are composed of both tetragonal and orthorhombic phases. From studies of the SBN powders,[8] the origin of this orthorhombic phase appears to arise from $SrNb_2O_6$ (SN). As the annealing temperature is further increased to 700°C, the unwanted orthorhombic phase is suppressed and only the ferroelectric TTB phase SBN remains.

3.2 Annealing atmosphere

Some of our samples were annealed under different gas ambient in order to examine the possible effect of atmosphere on the structure of our SBN films. The films were coated on (100)Si substrates to ~650 nm thick and annealed at 700°C for 2 h. XRD patterns of these films are similar to those shown in Fig. 1(c). In contrast to the report for $Pb(Zr_xTi_{1-x})O_3$ (PZT) where samples annealed under argon atmosphere had a high degree of oxygen deficiency resulting in structural distortion,[9] our results show no evidence of any distortion due to annealing atmosphere. Indeed, our XRD data suggest that all samples are crystallized in the ferroelectric tetragonal phase. The XRD peak intensity ratio (001)/(121) in films annealed in oxygen is 2·2 while for films annealed in argon and air, the ratios are only 1·4. Apparently enhanced (001) orientation is obtained in films annealed in oxygen ambient.

3.3 Film thickness

SBN films were prepared by multiple dip-coating of the sol on (100)Si substrates. In order to study the effect of film thickness on the structural quality, films with different number of dip-coated layers were fabricated. Figure 2 shows the XRD patterns of the SBN films with various thicknesses. The intensity of the spectra increases naturally with the film thickness. However, the intensity ratios (001)/(121) and (001)/(131) increase linearly with film thickness. This implies that the (001) SBN oriented growth is preferred.[7] The rocking curves of the (001) peak were also measured. Inset shows the dependence of the full width half maximum (FWHM) of the rocking curves on the film thickness. It is seen that the FWHM of the rocking curves decreases with increasing film thickness. These results clearly suggest the fact that enhanced (001) SBN orientation is obtained by increasing the number of dip-coated layers.

The improved mean crystallinity, however, may be simply due to the prolonged annealing. Each separate dip-coated layer has its own specific thermal history. For example, the bottom layer is

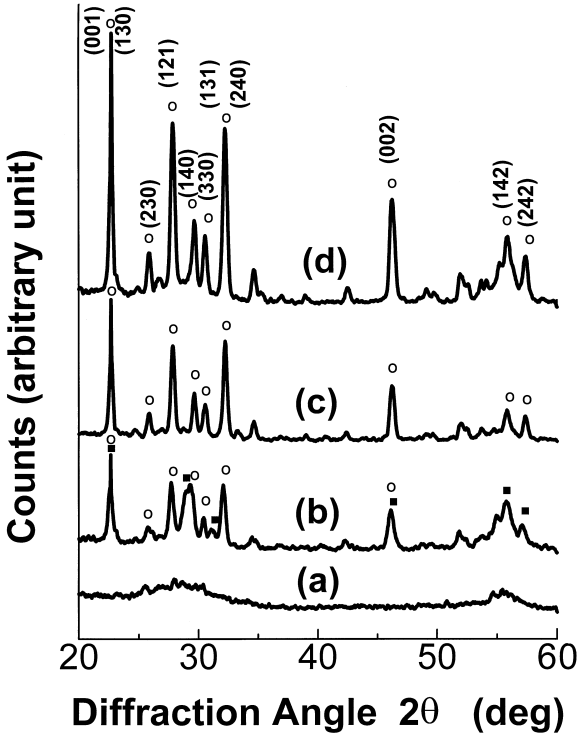

Fig. 1. XRD patterns of SBN films deposited on (100)Si substrates and annealed at different temperatures: (a) 500°C; (b) 600°C; (c) 700°C, and (d) 800°C. (■) Orthorhombic phase and (○) tetragonal phase.

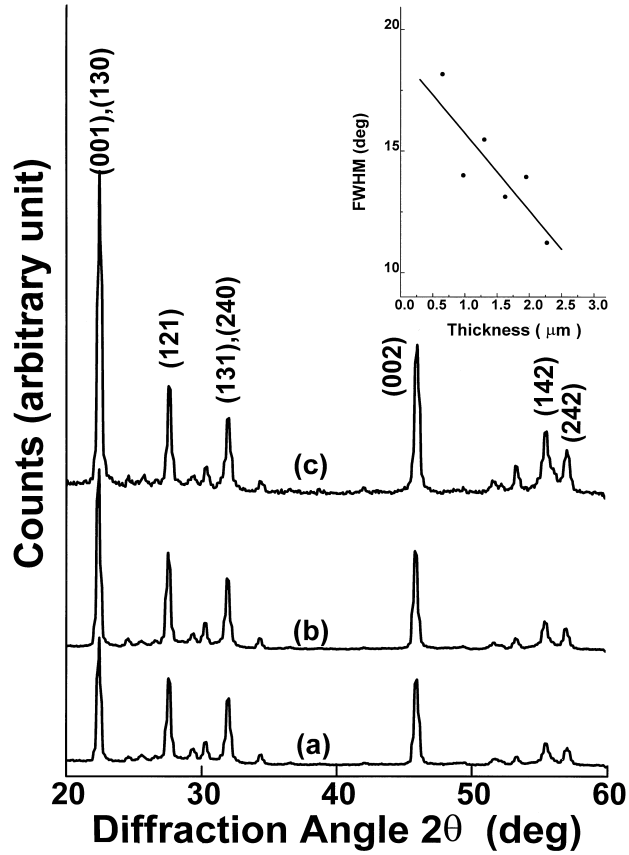

Fig. 2. XRD patterns of SBN films deposited on (100)Si substrates and annealed at 700°C. The thickness was (a) 0·65 μm; (b) 1·3 μm, and (c) 2·3 μm. Inset is the full width half maximum of the rocking curves of SBN films with different thickness.

annealed for 20 and 70 h for the 0·65 μm and 2·3 μm films, respectively. In order to unravel this ambiguity, two films of 0·65 μm thick (10 dip-coated layers) were prepared. Each dip-coated layer was annealed at 700°C for 2 h (sample A) or 6 h (sample B). XRD patterns of these films are similar to those shown in Fig. 2(a). The intensity ratios (001)/(121) and (001)/(131) for both films have no apparent difference. Furthermore the FWHM of the rocking curves for the (001) peak remain the same for both samples. These results suggest that the structural properties of the dip-coated films are fixed within the first 2 h and do not change later on. We therefore conclude that the improved mean crystallinity of the film is not due to prolonged annealing. In fact, in this layer by layer growth process, each of the dip-coated layer would act as a self-template layer for the next coating. The structural properties of the film therefore progressively improved from bottom to top. As the films comprise stack of many dip-coated layers, these XRD results reflect the mean properties of the films only. Accordingly, our multi-coated films show an improved mean crystallinity.

In addition to the crystalline orientation, we have also studied the surface roughness and grain size of our SBN films. The AFM images of the 1·0 and 2·3 μm thick films on the 5×5 μm^2 scale are shown in Fig. 3(a) and (b), respectively. The surfaces of the films (with thickness up to 2·3 μm) are, in general, dense and crack free. This observation is consistent with the SEM measurement.[7] Surface profiles, however, reveal root-mean square roughness values of 55 and 15 nm for the 1 and 2·3 μm films, respectively. These roughness values are comparable to those observed in PZT films grown by other methods.[11] Displayed in Fig. 4 are the topography of the SBN films on the 1×1 μm^2 scale. The thinner films show an irregular grain growth with severe grain agglomeration. As film thickness increases, the film surfaces show an improved top layer quality with enlarged and more uniformly distributed grain size of ~100 nm. The shape of the grain is more spherical with no sign of grain agglomeration. This causes the microstructure of the thicker films to become more homogeneous with higher packing density and smaller surface roughness. We believe that the addition of dip-coated layers helps to fill the large pores and depressions. This consequently leads to a more tightly packed crystalline structure, and an improved grain growth. The reduction of surface roughness and the narrower grain size distribution are therefore primarily due to continual multiple coating. From our results, it is evident that thicker sol–gel derived SBN films show a better mean structural quality.

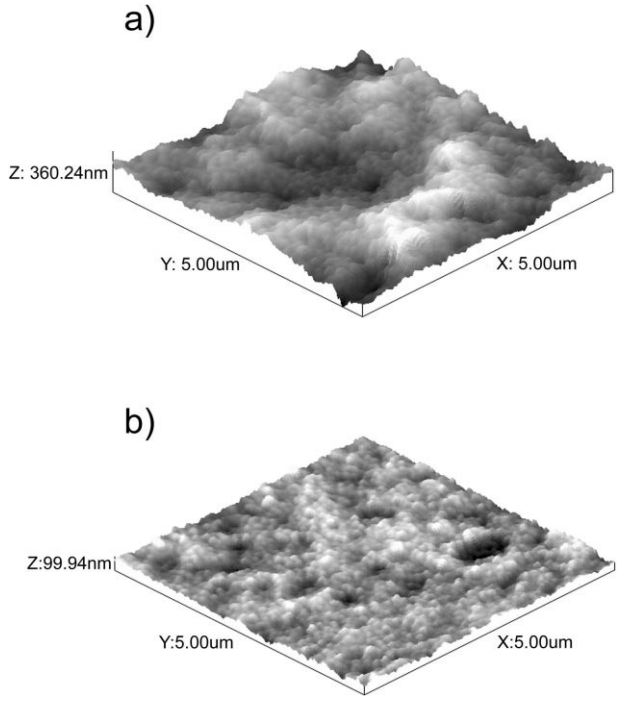

Fig. 3. AFM images of the (a) 1 μm, and (b) 2·3 μm thick films for the 5×5 μm^2 scans.

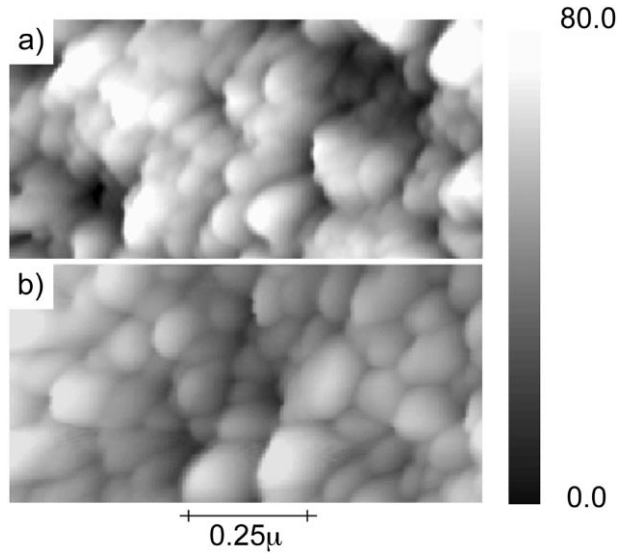

Fig. 4. Section of AFM images of the (a) 1 μm, and (b) 2·3 μm thick films for the 1×1 μm^2 scans.

4 Conclusion

Structural properties of sol–gel derived SBN has been studied as a function of annealing temperature. SBN films of TTB structure are obtained at annealing temperatures above 700°C. Both the effects of annealing atmosphere and film thickness on the structural properties of the sol–gel derived SBN films have been studied. No structural distortion was observed at different annealing

atmospheres. However, the (001) orientation is enhanced by annealing the films in oxygen ambient. The layer by layer growth process, on the other hand, produces a progressively improved crystalline structure from bottom to top. In fact, preferred and better oriented (001) SBN layers have been obtained in thicker films. In addition, enlarged grains with improved homogeneity and a much reduced surface roughness have also been observed. In this study, we have obtained good mean structural quality SBN films of up to 2·3 μm thick. Our results suggest that the fabrication of good structural quality SBN films of a few micrometers thick for use in integrated electro-optics devices is possible by the sol–gel method.

Acknowledgement

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