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Impedance spectroscopy and relaxation phenomena of (Na,K) excess $Na_{0.5}K_{0.5}NbO_3$ thin films grown by chemical solution deposition

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ABSTRACT

$Na_{0.5}K_{0.5}NbO_3$ (NKN) and 10 mol% (Na,K) excess $Na_{0.5}K_{0.5}NbO_3$ (NKN10) thin films on Pt/Ti/SiO_2/Si substrate were prepared by chemical solution deposition. Crystallization of NKN10 thin films was confirmed by X-ray diffraction. The (Na,K) excess $Na_{0.5}K_{0.5}NbO_3$ thin film shows a ferroelectric P-E hysteresis loop. Dielectric properties and impedance spectroscopy of thin films were investigated in the frequency range from 0.1 Hz to 100 kHz and the temperature range of 25 ~ 500 °C. By analyzing the complex impedance relaxation with Cole-Cole plots, we found impedance relaxations for the thin film. The contribution of electrical conduction is discussed in relation to grain, grain boundary, and interface effects.

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1. Introduction

Much attention has been paid to ferroelectric ceramics and thin films for electro-optic, piezoelectric and ferroelectric memory (FRAM) devices [1–5]. A typical material for these applications is Pb(Zr,Ti)O_3 (PZT), which still has, however, problems related to lead oxide toxicity in the environment. Recently, lead-free ferroelectrics have been extensively investigated as the most promising candidate materials for piezoelectric and FRAM applications. One of these, $Na_{0.5}K_{0.5}NbO_3$ (NKN) has been studied extensively because it has good piezoelectric and ferroelectric properties [6–9]. Electrical properties of NKN ceramics and thin films, including dielectric, polarization-electric field (P-E), and leakage current characteristics, have been investigated over the past several years [10,11]. The properties of ceramics and thin films remarkably depend on the growth conditions, annealing temperature and composition. Growth of NKN thin films is particularly difficult due to volatilization of (Na,K) ions. To make a practical device, it is necessary to prepare NKN thin films with high quality.

Complex impedance spectroscopy is the most commonly used experimental technique to analyze the dynamics of ionic movement in solid. Specifically, the electrical contribution from grain, grain boundary, and interface effects can be evaluated by complex impedance measurements. The purposes of this work are: (a) to prepare high quality $Na_{0.5}K_{0.5}NbO_3$ thin films, (b) to investigate the effect of (Na,K) excess in these films and (c) to determine the impedance relaxation and the various contributions to electrical conductivity in these films by analyzing impedance Cole-Cole plots.

2. Experimental work

For the preparation of NKN and (Na,K) excess NKN thin films, sodium acetate [CH_3COONa], potassium acetate [CH3COOK], and niobium pentaethoxide [$Nb(OCH_2CH_3)_5$] were used as starting materials. 2-methoxyethanol [$CH_3OCH_2CH_2OH$] was used as a solvent, while acetylacetone [$CH_3COCH_2COCH_3$] was used as a chelating agent. To compensate for the loss of Na and K ions during thermal annealing, 10 mol% (Na,K) was added to the NKN precursor solutions. The concentration of the final solution was adjusted to 0.1 mol/L. The precursor solutions were spin-coated on Pt(111)/Ti/SiO_2/Si(100) substrates at a rate of 2500 rpm for 20 s. The film was dried at 150 °C for 5 min on a hot plate. Subsequently, the dried gel film was calcined at 350 °C for 5 min and then heated at 500 °C for 5 min in an oxygen atmosphere using a tube furnace. These steps were repeated 20 times for coating and calcination. Finally, the NKN film was annealed at 700 °C for 30 min in an oxygen atmosphere, and the thickness of the thin film was estimated to be 250 nm by measuring the cross section of scanning electron microscopy. The phase and structure of the films were identified by X-ray diffraction (XRD) using a thin film diffractometer (Philips, XPERT PW1710) operated at 40 kV and 30 mA with Cu Kα radiation of 1.54056 Å wavelength with a scanning speed of 0.05°/s and a step of 0.05°. Surface morphology of the film was characterized by scanning probe microscope (SPM) (Digital Instruments, Multimode) in tapping

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mode. Au reflex coated Si_3N_4 cantilever (Veeco, DNP-S10) with an elastic constant of 0.58 N/m and an integrated tip of about 10 nm in diameter. For electrical contacts, Pt top electrodes 2.5×10^{-4} cm^2 in area were deposited on the film through a shadow mask by dc sputtering. Ferroelectric properties were investigated using a ferroelectric tester (Radiant Technologies, RT66a). Dielectric properties and impedance relaxation were investigated over the frequency range of 0.1 Hz ~ 100 kHz and the temperature range of 25 ~ 500 °C by a LCR meter (Hioki 3522) with heating rate of 0.5 °C/min.

3. Results and Discussion

3.1. Preparation, dielectric and ferroelectric properties of NKN and (Na,K) excess NKN thin films

Fig. 1 shows X-ray diffraction patterns of the NKN and NKN10 thin films annealed at 700 °C for 30 min. NKN thin films exhibited unknown-secondary phases, which is caused by the volatilization of (Na,K) ions [7,12]. For the NKN and NKN10 thin films, corresponding XRD peaks of pure NKN can be indexed on the basis of the orthorhombic structure. The total lack of a large (001) peak for the NKN films made from the stoichiometric solution indicates that the films have totally different compositions and structures. However, the NKN10 thin film exhibited (00l) and (011) peaks consistent with the NKN single phase, indicating that the NKN10 thin films with excess (Na,K) are well crystallized. Thus, excess Na and K must be added to the initial solutions to mitigate volatilization of these ions from the films during processing. The lattice constants of the NKN10 thin film were calculated from these peaks as a = 2.286 Å and c = 3.945 Å, which are similar to those of bulk NKN [13].

Fig. 2 shows the AFM surface morphologies of the NKN10 thin films annealed at 700 °C. As shown, the surfaces are uniform. Grains of the NKN10 thin film developed at an annealing temperature of 700 °C for 30 min.

Fig. 3 shows the P-E hysteresis loops of the NKN10 thin films at room temperature. Previous work found that the P-E hysteresis loop of NKN thin films exhibited a leaky shape, however, that of NKN10 thin film exhibited typical ferroelectric P-E hysteresis loops. At an applied voltage of 280 kV/cm, the remanent polarization ($2P_r$) and the coercive field ($2E_c$) of the NKN10 thin film were 12.8 μC/cm^2 and 113 kV/cm, respectively.

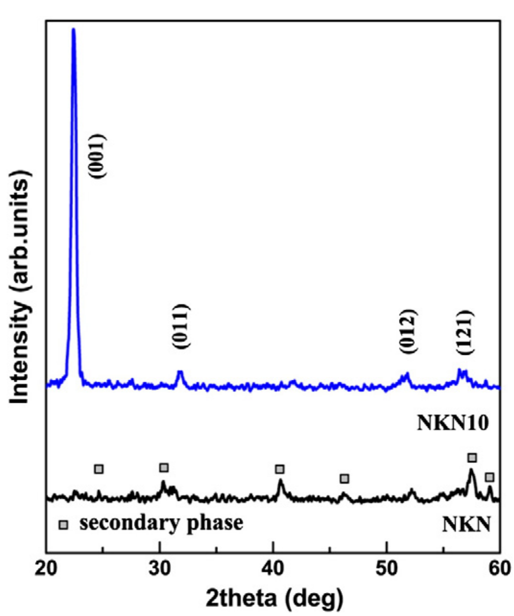

Fig. 1. X-ray diffraction patterns of NKN and NKN10 thin films.

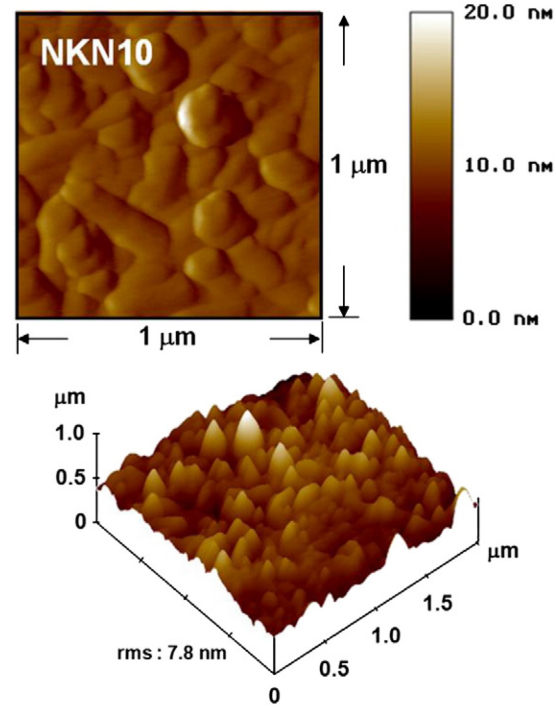

Fig. 2. Surface morphology of the NKN10 thin films annealed at 700 °C for 30 min. For each figure, the width is about 1 μm.

Fig. 4 shows the dielectric constants as a function of temperature at several frequencies. The Curie temperatures of NKN10 thin film was observed to be about 363 °C, based on the peak of the dielectric constant, which were slightly lower than that of bulk NKN, which is 420 °C [11]. The difference in Curie temperatures originates from the compositional difference between the thin film and ceramics. As the temperature increases, the dielectric constant of NKN10 thin film rises and a dielectric anomaly can be also observed, which is similar to that of previous results for bulk NKN ceramics [11].

3.2. Impedance spectroscopy and electrical conductivity of NKN10 thin films

The experimentally measured parallel values of resistance and capacitance were converted to their equivalent quantities and are

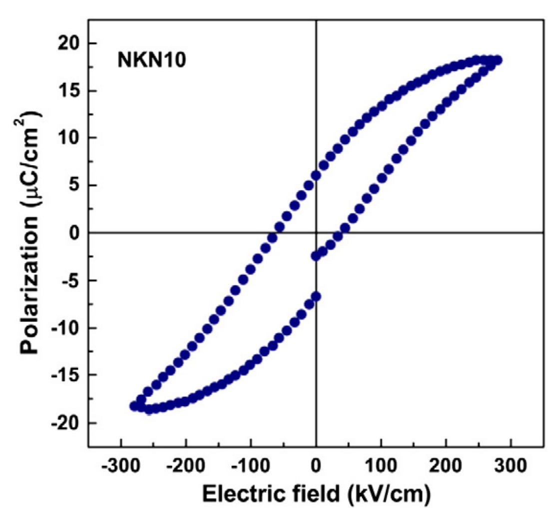

Fig. 3. Ferroelectric P-E hysteresis loop of NKN10 thin films at an applied field of 280 kV/cm.

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