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Frequency and temperature dependence of dielectric and electrical properties of radio-frequency sputtered lead-free $K_{0.48}Na_{0.52}NbO_3$ thin films

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ABSTRACT

Lead-free $K_{0.48}Na_{0.52}NbO_3$ (KNN) ferroelectric thin films were prepared using the radio-frequency magnetron sputtering method. The crystallized KNN phase was confirmed using X-ray diffraction. The KNN thin film exhibited a well-saturated ferroelectric polarization-electric field hysteresis loop with high remanent polarization. The dielectric and electrical properties of the KNN thin film were investigated over a wide range of frequencies from 10 Hz to 1 MHz, and over a wide range of temperatures from 25 °C to 500 °C. The complex impedance relaxations are shown in an impedance Cole–Cole plot. With increasing temperature, the AC conductivity increased, which obeys the power law, $\sigma(\omega)=\sigma_0+A\omega^s$. The activation energy for the conduction process is calculated to be 0.57 eV from the slope of the AC conductivity at the low frequency.

1. Introduction

Much attention has been paid to ferroelectric thin films for device applications. One of the typical materials is lead zirconate titanate (PZT) [1,2], but that is problematic because of the toxicity of lead oxide in the environment. Recently, lead-free ferroelectric has been extensively investigated for piezoelectric device and ferroelectric random access memory (FRAM) applications [3–5]. $K_{0.5}Na_{0.5}NbO_3$ (KNN) based ceramics and thin films have been studied extensively because of their good piezoelectric and ferroelectric properties [6–11]. Previously, KNN films on several substrates were prepared by radio-frequency (RF) magnetron sputtering and pulsed laser deposition (PLD). This work focused on its tunability, optical and communication application [6–8]. They only mentioned the ferroelectric hysteresis loops as candidates for investigation of the possibility of use in FRAM devices. Thus, there has been limited reporting in detail on the dielectric and electrical properties of KNN films.

However, it is difficult to obtain a high-quality KNN film [12–14], so the ferroelectric and electrical properties of KNN film are not yet fully understood. To make practical use of lead-free ferroelectrics and piezoelectrics, it is necessary to investigate the growing characteristics and ferroelectric properties. In this work, we prepared a high-quality KNN film using the RF sputtering method and investigated the dielectric and electrical properties. In order to investigate the electrical properties of KNN thin film, the dielectric constant and electrical conductivity were investigated over wide ranges of frequency and temperature. The contribution of the electrical conductivity is evaluated using complex impedance analyses.

2. Experimental work

The KNN thin films were grown on $Pt/Ti/SiO_2/Si$ substrates using the RF magnetron sputtering method. Prior to the deposition process, the chamber was evacuated to a base pressure of 1.0×10^{-6} Torr and then filled with gas mixture of oxygen and argon to a total pressure of 60 mTorr. The KNN thin films were deposited at 600 °C for 4 h and annealed at 700 °C for 60 min in an oxygen atmosphere. X-ray diffraction (XRD) studies confirmed the formation of a single-phase crystal structure. To study the electrical properties, 2.5×10^{-4} cm^2 area Pt top electrodes were deposited on the film through a shadow mask using DC sputtering. The ferroelectric polarization-electric field (*P-E*) hysteresis loops were measured using a ferroelectric tester (RT66A, Radiant Technologies). The dielectric and electrical properties of the thin film were investigated over the frequency range from 10 Hz to 1 MHz and over the temperature range from 25 to 500 °C using an impedance analyzer with a heating rate of 0.5 °C/min. The composition of the KNN film in this work confirmed by electron probe microanalysis (EPMA) is estimated to be as $K_{0.48}Na_{0.52}NbO_3$.

3. Results and discussion

3.1. Dielectric and ferroelectric properties of KNN film

Fig. 1 shows the ferroelectric *P-E* hysteresis loops and X-ray pattern of the KNN thin film at room temperature. The XRD peaks of the KNN films can be indexed on the basis of the orthorhombic

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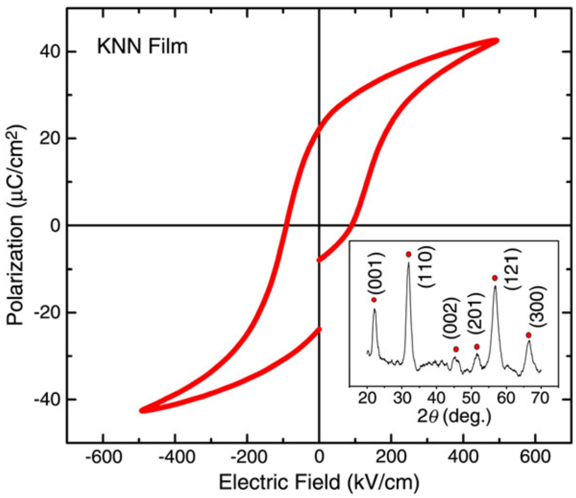

Fig. 1. Ferroelectric *P-E* hysteresis loops and XRD patterns (inset) of the KNN films.

structure [7]. The post-annealed film with (001) and (110) XRD peaks has a pure perovskite phase with orthorhombic symmetry, and no secondary impurities can be found. The XRD patterns of KNN film are consistent with bulk KNN ceramics of previously known XRD pattern, which indicates that the KNN thin films are well crystallized. Some results have reported ferroelectric *P-E* loops with leaky shapes [15,16], but in this work, the ferroelectric *P-E* hysteresis loops were well-saturated. For an applied field of 500 kV/cm, the remanent polarization (P_r) and the coercive field (E_c) for a 300 nm thickness KNN thin film were 22.5 μC/cm^2 and 90 kV/cm, respectively.

The dielectric response may be described in terms of the complex dielectric constant: $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. The real part of the dielectric constant, $\varepsilon'(\omega)$, describes the "elastic" loss-free reaction of the material to an externally applied AC electric field, while the imaginary part, $\varepsilon''(\omega)$, is associated with the conductivity; $\sigma(\omega) = \varepsilon_0\omega\varepsilon'' = \varepsilon_0\omega\varepsilon'\tan\delta$.

Fig. 2 shows the temperature dependence of the real and imaginary parts of the dielectric constant, ε' and ε'', over the temperature range from 25 to 500 °C. The Curie temperature of the KNN thin film at 100 kHz was observed to be 460 °C, which is slightly higher than that of previously known KNN ceramic with 430 °C [17]. The difference in the Curie temperatures between the KNN thin film and ceramic was caused by compositional fluctuations and film/substrate interfacial effects. The dielectric behavior of KNN film differentiated as a consequence of the Na and K occupation in the crystallographic A site of ABO_3 structure.

As the temperature increases, the dielectric constant at low frequencies rises, and dielectric dispersion can be observed. Since the motion of the impurity ions cause electrical degradation and long-term instability of ferroelectric films, it is important to clarify the low-frequency dielectric dispersion and electrical conduction mechanism [18,19].

With increasing temperature, the imaginary part of the dielectric constant slowly increased and then abruptly increased above 200 °C, which is due to the increasing electrical conductivity. The dielectric behavior of KNN films is similar to that of bulk KNN [17].

3.2. Impedance relaxation of KNN film

The experimentally measured parallel values of resistance and capacitance were converted to their equivalent values and are displayed in the form of complex impedance ($Z^* = Z' - iZ''$) plots [18–21]. The complex impedance can be expressed by introducing a

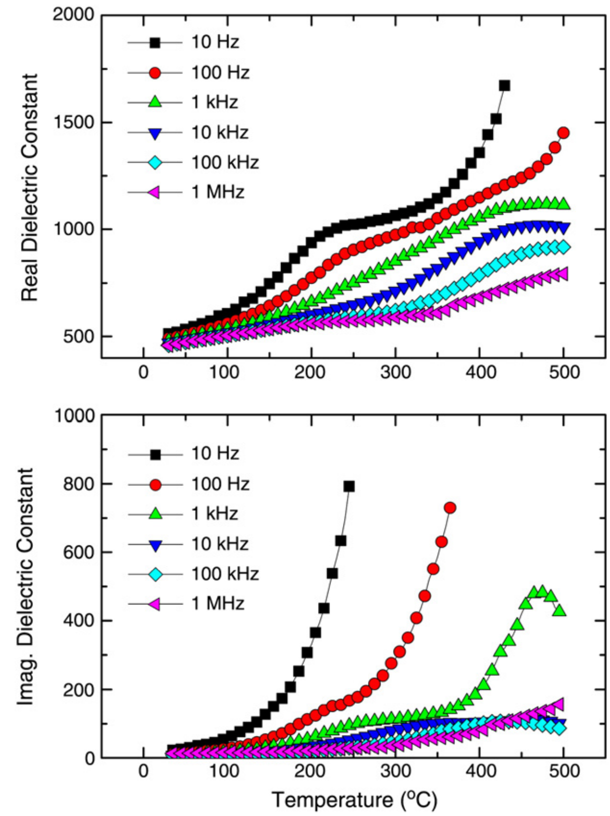

Fig. 2. Temperature dependence of dielectric constant of the KNN films measured at 10 Hz, 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

temperature-dependent factor n into the Debye expression, i.e, the Cole–Cole expression [19,21]:

$$Z^*(\omega) = \frac{Z_0}{1 + (i\omega\tau_0)^n}, \tau_0 = 1/\omega_0 = 1/2\pi f_r \quad (1)$$

where τ_0 is the mean relaxation time, and n where $0<n<1$, indicating polydispersive multi-Debye-type relaxation. If n is 1, then the relaxation can be explained by the Debye-type response [19].

Fig. 3 shows the frequency dependencies of the real part, Z′, and the imaginary part, Z″, of the complex impedance at a temperature of 250 °C. As the frequency increases, the real part, Z′, decreases, while the imaginary part, Z″, shows a peak. The complex impedance plot of the KNN film exhibits one impedance semicircular arc. Thus, one impedance arc of KNN film is representative of the bulk properties of grain (DC resistivity). The centers of the impedance semicircular arc lie below the real axis. Thus, the impedance relaxation can be explained by the Cole–Cole response [18,21]. The electrical contribution of the grain was introduced by an equivalent circuit as shown in the inset of Fig. 3.

Fig. 4 shows the complex impedance plots of KNN films at various temperatures. The KNN films exhibit one impedance semicircular arc over wide frequency and temperature ranges. The semicircular arcs are representative of the grain effect. Thus, the complex impedance plot of the KNN films exhibit one impedance semicircle characteristic of Cole–Cole type relaxation. The semicircular impedance is representative of the bulk properties of grain. In addition, a second small arc in the temperature range from 400 to 450 °C is observed on the lower frequency side, which is caused by electrode-interface effects.

3.3. Conduction behavior of KNN film

Fig. 5 shows the frequency dependencies of the AC conductivity, σ_{ac}, with increasing temperature. With increasing frequency, $\sigma(\omega)$