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Lead-free (K, Na)NbO_3 ferroelectric thin films: Preparation, structure and electrical properties

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ABSTRACT

Lead-free ferroelectric (K, Na)NbO_3 (KNN) thin films were prepared on Pt/Ti/SiO_2/Si substrate by a sol–gel method. Sodium acetate, potassium acetate and niobium pentaethoxide were used as starting metal–organic compounds in KNN precursor solutions. The thermal decomposition of KNN gel was studied by thermal analysis method. Thin films of KNN with a perovskite structure were obtained by pyrolysis at 400 °C and rapid thermal annealing at 500–650 °C. The KNN thin films showed relatively dense and uniform microstructure with grain size of about 100 nm. KNN thin films annealed at 650 °C exhibited a dielectric constant of 258 and loss tangent of 0.05, respectively, at 1 kHz. A ferroelectric hysteresis loop with a remnant polarization and coercive field of 3.54 μC/cm^2 and 160 kV/cm, respectively, was obtained for the KNN thin film.

1. Introduction

Lead-based ferroelectric ceramics such as Pb(Zr, Ti)O_3 have been widely applied in industry as sensor, actuator, and transducer materials due to their excellent piezoelectric and ferroelectric properties [1]. However, as these lead-based ceramics contain a large amount of toxic Pb, the use of these ceramics has caused serious environmental problems. Therefore, it is necessary to develop lead-free piezoelectric ceramics for replacing the lead-containing ceramics in various applications. Among several lead-free piezoelectric materials, $K_{0.5}Na_{0.5}NbO_3$ (KNN) is a promising candidate, as it has a high Curie temperature, good ferroelectric and piezoelectric properties as well as biocompatibility [2]. Therefore, a number of modified KNN ceramics have been extensively studied to improve their electrical properties [3–11]. Compared with bulk materials, ferroelectric and piezoelectric thin films are important for memory and micro-sensor as well as micro-actuator applications [12]. Additionally, studies on ferroelectric thin films may provide possibility for us to further understand the intrinsic properties of the materials, because it is possible to grow textured or epitaxial thin films to control their crystallographic orientations [13].

To obtain KNN thin films of high quality, many preparation techniques such as rf-magnetron sputtering [14,15], pulsed laser deposition (PLD) [16,17], metal–organic chemical vapor deposition (MOCVD) [18] and sol–gel methods [19–21] have been employed. However, the high volatility both of sodium and potassium complicates the fabrication of KNN thin films by physical vapor deposition processes [22,23]. Sol–gel technology offers an alternative to deposition with advantages such as low temperature fabrication, precise control of the chemical composition of the film, and reduced equipment cost, making it promising for producing homogeneous thin films. The crystallographic phase, microstructures and electrical properties of thin films fabricated by sol–gel methods can be affected by the choice and composition of starting materials as well as the processing conditions. For the (K, Na)NbO_3 (KNN) thin films fabricated by sol–gel methods, which reported in literature [24,25], potassium ethoxide and sodium ethoxide were usually used as starting metal alkoxide compounds for the preparation of KNN precursor solutions. It is well known that these metal alkoxides are extremely sensitive to moisture, so it is difficult to achieve precise control of the chemical composition of thin films of KNN. Wang et al. [26] reported a novel method to prepare thick films of KNN with better results that used sodium acetate and potassium acetate as precursors. However, the chemical properties of the precursor gel and the process parameters of thin films preparation were not studied.

In this work, sodium acetate and potassium acetate were used as starting metal–organic compounds for the preparation of KNN precursor solutions. The chemical properties of KNN precursor gel were studied by thermal analysis. The influences of the process parameters on the microstructure, dielectric properties and ferroelectric properties of the resulting thin films of KNN have been investigated.

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2. Experimental details

KNN precursor solutions were prepared by a sol–gel method. Sodium acetate (CH_3COONa), potassium acetate (CH_3COOK) and niobium pentaethoxide ($Nb(OC_2H_5)_5$) were used as starting materials. Equal molar of sodium acetate and potassium acetate were dissolved in a solution of glacial acetic acid solution under continuous stirring at 60 °C. Niobium pentaethoxide was permixed with acetyl acetone (used as a chelating agent) and then mixed with the sodium acetate and potassium acetate solutions under continuous stirring. 2-Methoxyethanol was added to adjust the viscosity of the solution to obtain the concentration of 0.3 M. Thin films of KNN were first deposited on $Pt/Ti/SiO_2/Si$ substrates by a spin-coating technique with a spin rate of 3000 rpm for 30 s. The as-deposited thin films were then pyrolyzed at various temperatures from 350 to 450 °C for 3 min to remove organic species. Following this, the films were annealed at various temperatures from 500 to 650 °C for 5 min in a rapid thermal processing (RTP) furnace (RTP-500, East Star Inc., China) to form a perovskite structure of KNN. The procedure was repeated four times to achieve KNN films with a total thickness of about 120 nm.

Thermo gravimetric analysis (TGA) and dynamic thermal analysis (DTA) of the dried KNN gel sample was conducted using TGA/SDTA 851 with a heating rate of 10 °C/min from room temperature to 800 °C. The phase composition and structure of the KNN thin films were characterized by X-ray diffraction (XRD) (Rigaku D/Max-2400) with Cu Kα radiation. The surface morphologies of the thin films were examined using a field-emission scanning electron microscope (FESEM, JEOL JSM-6700F). The thickness of the thin films was measured by a step profiler (Ambios Inc., XP-2). For the dielectric measurements, top Au dot electrodes with a diameter of 1 mm were sputtered onto the top of the KNN films via a shadow mask to form a metal–insulator–metal (MIM) structure. Measurement of the dielectric properties was performed using an Agilent 4294A Impedance Analyzer. The ferroelectric hysteresis loops of the thin films were evaluated using a ferroelectric Analyzer (aixACCT TF-2000 FE Analyzer).

3. Results and discussion

3.1. TGA and phase structure analysis

Fig. 1 illustrates the thermal decomposition behavior of the dried KNN gel. TGA and DTA analysis were carried out in air at a heating rate of 10 °C/min. A significant weight loss is observed below 300 °C due to the evaporation of residual solvent from the gel. An exothermic peak at 354 °C appears in the DTA curve, corresponding to the decomposition of carboxylate–alkoxide precursors. A step is found in the TGA curve in a temperature range from 510 to 604 °C that is accompanied by two exothermic peaks in the DTA curve. This behavior is caused by crystallization of KNN and the formation of a perovskite phase.

Pyrolysis is a very important step in obtaining high quality thin films by sol–gel methods. The temperature used for pyrolysis is a critical factor, because the structure and properties of thin films, such as crystallinity and surface morphology, can be significantly affected by the volatilization of organic compounds during pyrolysis [27]. XRD characterization of the films prepared at various pyrolysis temperatures are shown in Fig. 2. The intensity of the KNN peaks depends on temperature used for pyrolysis. Weak perovskite phase is observed in the KNN films pyrolyzed at 350 °C and annealed at 650 °C. The intensities of the KNN peaks increase as the pyrolysis temperature increases. However, a secondary phase is observed in the film pyrolyzed at 450 °C that is assigned to the $K_4Nb_6O_{17}$ phase. This is a compound devoid of potassium compared to $KNbO_3$. One possible reason for the formation of this secondary phase is the volatilization of potassium at higher pyrolysis temperatures.

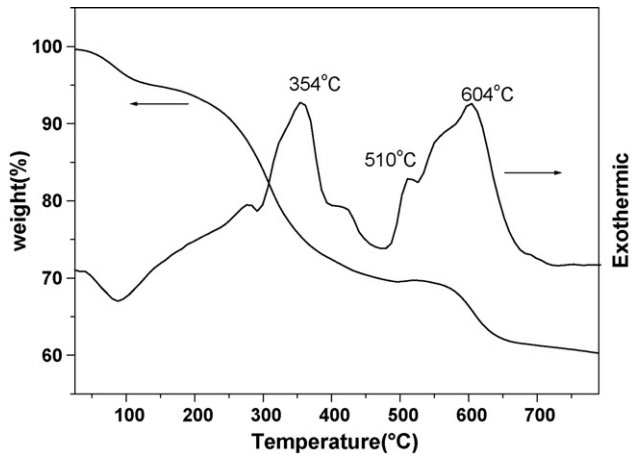

Fig. 1. TGA/DSC curves of KNN precursor.

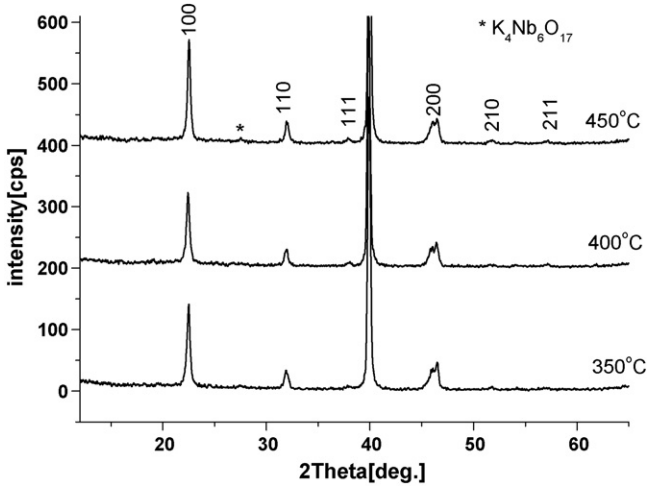

Fig. 2. X-ray diffraction patterns of KNN thin films pyrolyzed at various temperatures for 3 min, and annealed at 650 °C for 5 min.

Fig. 3 shows the XRD profiles of KNN thin films crystallized for 5 min at various annealing temperatures. All of the KNN thin films crystallized with the perovskite phase on the $Pt/Ti/SiO_2/Si$ substrates. The intensity of the KNN peaks increased as the annealing temperature increased, especially for the (1 0 0) and (1 1 0) reflections. The peaks also became narrower with increasing temperature, indicating crystallite growth and/or improved crystallization. The intensity of the (1 0 0) reflection of the KNN thin films was relatively high because the surface energy of the (1 0 0) plane of KNN is relatively low compared with that of the other planes [28]. Thus, KNN thin films exhibit a preferred (1 0 0) orientation. These results agree with those reported by Wang et al. [26].

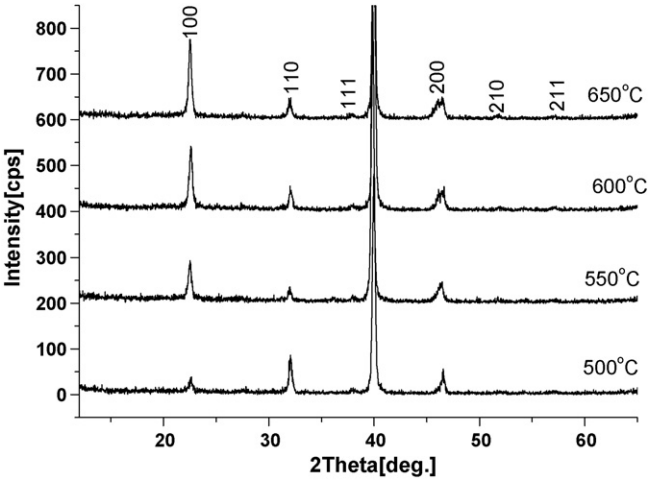

Fig. 3. X-ray diffraction patterns of KNN thin films pyrolyzed at 400 °C for 3 min, annealed at various temperatures for 5 min.

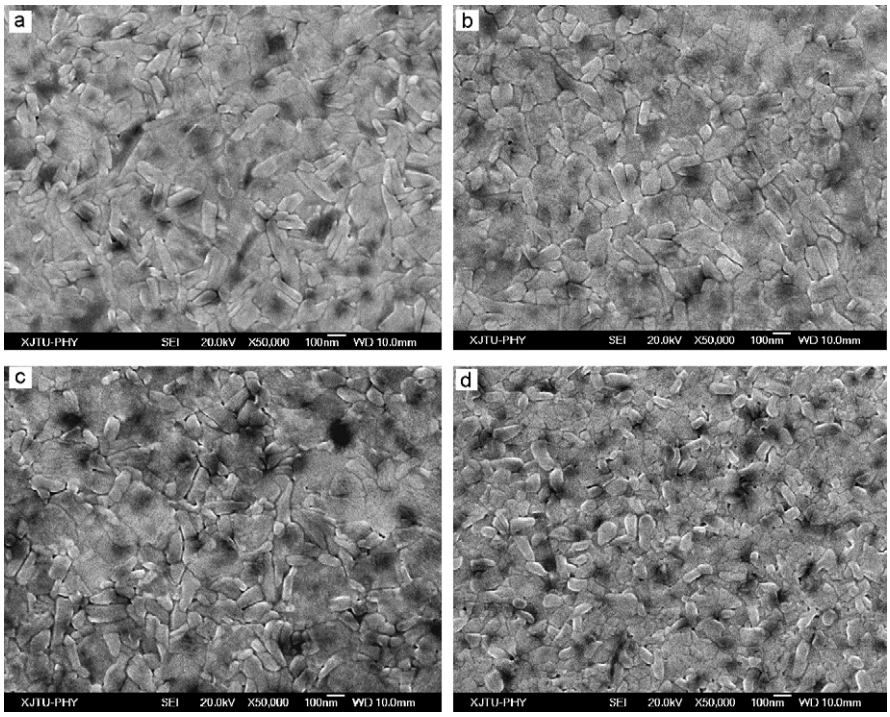

Fig. 4. SEM images of the KNN films pyrolyzed at 400 °C for 3 min and annealed at various temperatures for 5 min: (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C.

3.2. Surface morphology

Fig. 4 shows FESEM images of KNN thin films crystallized for 5 min at various annealing temperatures. It can be seen that the crystal grains are small at low annealing temperatures. As the annealing temperature is increased, the grain size increases. The images also reveal that the KNN thin films are uniform and crack-free.

3.3. Electrical properties

Fig. 5 shows the dielectric properties of KNN thin films pyrolyzed at 400 °C for 3 min and then annealed at 650 °C for 5 min. The dielectric constant and loss tangent are 258 and 0.05, respectively, at 1 kHz. The dielectric constant and loss tangent of the KNN thin films are both lower than those reported in the literature [21,24,25]. However, this result can be explained by different methods used to obtain dielectric measurements. The dielectric constant of the thin films was higher than that of a film grown by MOCVD [18] and was comparable with that of a film grown by PLD under low oxygen pressure [16] using the same measurement method. The higher dielectric constant of the thin films grown by a sol–gel technique was attributed to the preferred (1 0 0) orientation of the KNN.

Fig. 6 shows polarization–electric field (P–E) hysteresis loops for KNN thin films grown on Pt/Ti/SiO_2/Si substrates and annealed at various temperatures. The loops were measured at a frequency of 1 kHz at room temperature. The KNN thin films annealed at 550 and 600 °C showed weak ferroelectricity, which was related to their degree of crystallization. The XRD results revealed that the KNN thin films annealed at 550 and 600 °C showed low crystallization. Meanwhile, high electric fields could not be applied to these KNN thin films due to low breakdown fields. On the other hand, KNN thin films annealed at 650 °C exhibited a typical P–E ferroelectric

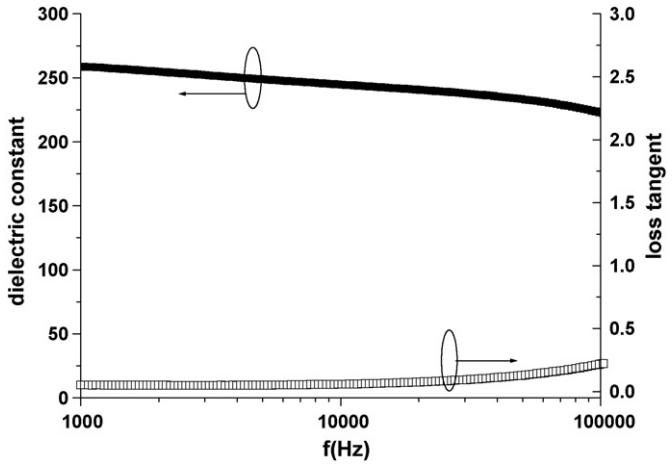

Fig. 5. Dielectric constant and loss tangent as a function of frequency for KNN thin films annealed at 650 °C.

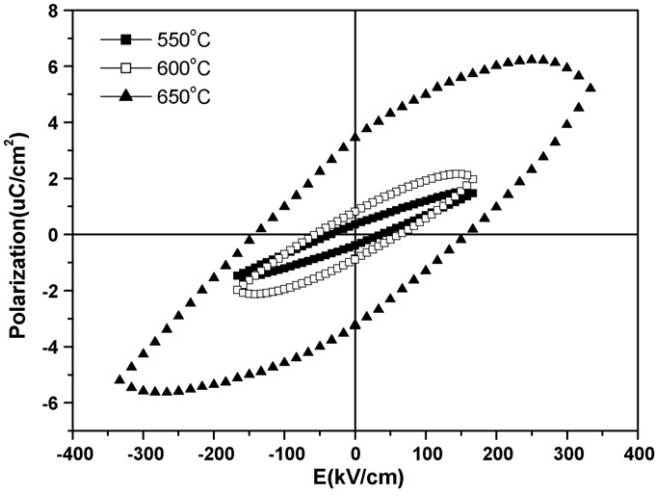

Fig. 6. P–E hysteresis loops of KNN thin films annealed at various temperatures for 5 min on Pt/Ti/SiO_2/Si substrates.

hysteresis loop that was relatively round in shape, indicating that the dielectric loss of the films was high. Calculated values for the remnant polarization (P_r) and coercive field (E_c) of the film were 3.45 μC/cm^2 and 160 kV/cm, respectively, at an applied field of 300 kV/cm. The P_r value was smaller than those of KNN thin films fabricated by CSD [24,25]. For the film annealed at 500–650 °C, SEM images showed the presence of holes on the grain boundaries. These holes may degrade the ferroelectric properties of KNN thin films. Further studies are needed to explore the optimal pyrolysis and annealing conditions required to improve the electrical properties of KNN thin films.

4. Conclusions

Lead-free ferroelectric (K, Na)NbO_3 thin films were prepared on Pt/Ti/SiO_2/Si substrate by a sol–gel method. Sodium acetate, potassium acetate and niobium pentaethoxide were used as starting materials in the KNN precursor solutions. The synthesized KNN precursor solutions were stable and transparent. The optimum pyrolysis and annealing temperatures were 400 °C and about 650 °C, respectively. A single perovskite phase with dense morphology and preferred (1 0 0) orientation was obtained at a relatively low annealing temperature of 650 °C. The dielectric constant and P_r were 258 and 3.54 μC/cm^2, respectively, at 1 kHz. These results show that KNN is a promising material for lead-free piezoelectric thin films.

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