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Preparation and characterization of sodium potassium niobate-silver niobate lead-free films by chemical solution deposition

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Abstract

Lead-free ferroelectric $0.82K_{0.5}Na_{0.5}NbO_3-0.18AgNbO_3$ (KNN – AN) films were successfully synthesized by a chemical solution deposition (CSD) method. In particular, silver acetate was dissolved in 2-methoxyethanol with the aid of nitric acid and molecular sieve was used to remove residual moisture in the precursor solution at room temperature. The effects of the thickness on the structures and electrical properties of the KNN–AN films were systematically investigated. The KNN–AN film with the thickness of 2.53 μm showed good dielectric properties and well saturated polarization-electric field hysteresis loops.

Keywords: KNN – AN films; Chemical solution deposition method; Electrical properties

1. Introduction

Many researchers have paid attention to lead-free materials to replace the lead-based materials for protecting the environment [1–7]. Recently, the KNN based ceramics and films have been widely studied to improve their electrical properties [8–20]. However, the K, Na and Nb are likely to deviate from stoichiometry because of the volatilization of K and Na during the anneal process at high temperature and the vacancies left by the evaporation of K and Na ions will result in poor ferroelectricity and high leakage current of the KNN films [5,8,19]. A lead-free solid solution system of $(1-x)K_{0.5}Na_{0.5}NbO_3-xAgNbO_3$ (KNN – AN, with x=0–0.36) ceramics have been reported, which exhibited a much improved thermal stability and electrical properties [21].

In this work, the Ag^+ ion was introduced into the precursor solution to synthesize the KNN–AN films. The key process in preparing of the KNN–AN precursor solution was using nitric acid to dissolve silver acetate in 2-methoxyethanol. However, the moisture in the nitric acid would hydrolyze the niobium ethoxide and result in precipitation. To solve this problem, the molecular sieve was used to remove residual moisture and the precursor solution was successfully prepared. The optimum electrical properties are found in the ceramics of 0.82KNN–0.18AN [21]. Thus the structural and electrical properties of the 0.82KNN–0.18AN films with different thicknesses had been investigated.

2. Experimental procedure

For the preparation of the 0.82KNN – 0.18AN precursor solution, potassium acetate (CH_3COOK), sodium acetate (CH_3COONa), silver acetate (CH_3COOAg) and niobium ethoxide ($(CH_3CH_2O)_5Nb$) were used as the starting chemicals and 2-methoxyethanol was used as the solvent. The Polyvinylpyrrolidone (PVP) powder with a molecular weight of 360,000 was added to enhance the film thickness and improve electrical properties, and the mole ratio of PVP monomer to KNN–AN was 1:1. In particular, silver acetate was dissolved in 2-methoxyethanol with the aid of nitric acid and molecular sieve was used to remove residual moisture in the precursor solution at room temperature. Fig. 1 shows the flow chart of

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the procedure for preparation of the KNN–AN precursor solution. The final concentration of KNN–AN precursor solution was 0.5 mol/L.

The precursor solution was spin-coated onto Pt/Ti/SiO_2/Si substrate at 4000 rpm for 40 s. The wet film was dried at 100 °C for 2 min on a hotplate. The dried film was pyrolyzed at 330 °C for 5 min and annealed at 650 °C for 10 min in a rapid thermal annealing (RTA) furnace with a heating rate of 50 °C/s. In this experiment, 2 layers, 3 layers and 4 layers of the KNN–AN films were prepared. The 4 layers of KNN film was also prepared with the same method for comparison. The Au circular top electrodes with diameter of 0.5 mm were deposited on the surface of the films to evaluate the electrical properties.

The thermogravimetric analysis-differential scanning calorimetry (TGA–DSC) was carried out by a Ntezsch STA 449 C thermal analysis system. The phase structures of the films was identified by Rigaku D/MAX2400 X-ray diffractometer (XRD) with Cu Kα radiation. The microstructures of the films were observed using FEI Quanta 250 FEG SEM. According to the SEM cross-section images, the film thicknesses were determined. The dielectric properties were measured using an Agilent 4980, and the polarization–electric field (*P*–*E*) hysteresis loops were measured using aixACCT TF Analyzer 2000 system. The current voltage characteristics (current–voltage, *I*–*V*) were examined with a semiconductor characterization system (4200-SCS, Keithley).

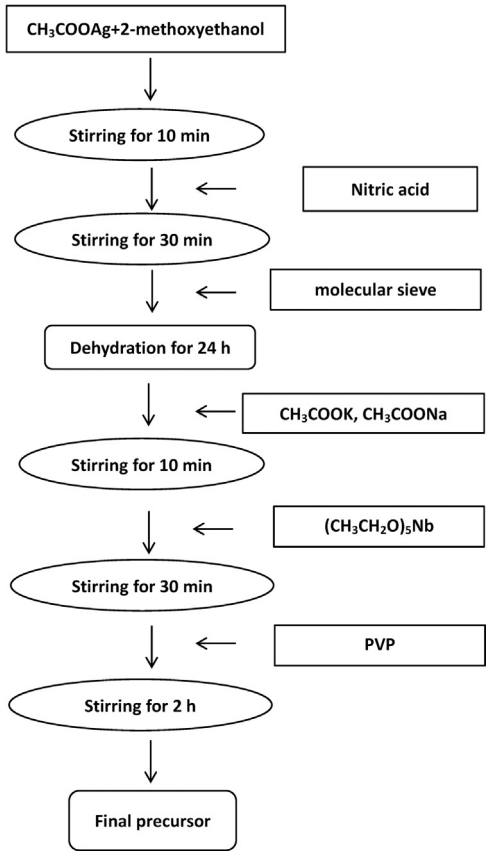

Fig. 1. Flow chart of synthesis of the KNN–AN precursor solution.

3. Results and discussion

Fig. 2 shows the TGA–DSC curves of the dried KNN and KNN–AN gel powders. The precursor solution was dried at 100 °C before the measurement. For the KNN gel powder, the

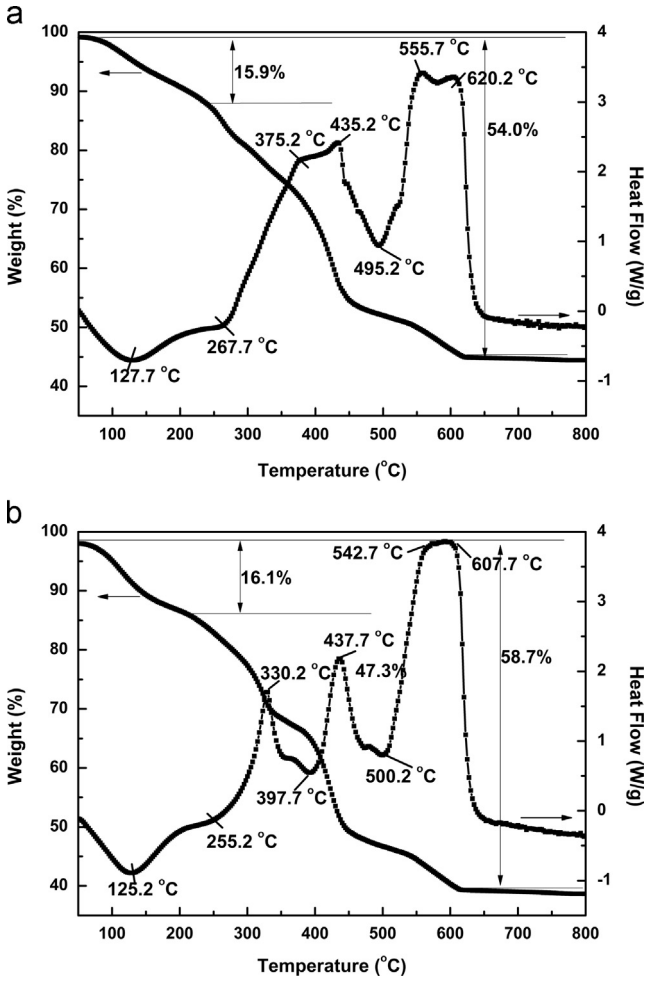

Fig. 2. TGA/DSC curves of (a) KNN and (b) KNN–AN dried gel powders.

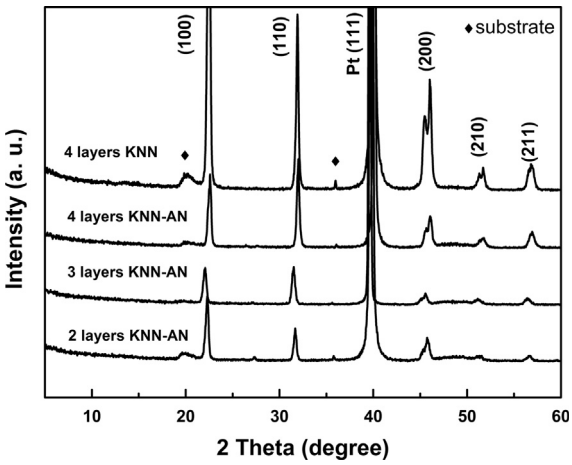

Fig. 3. XRD patterns of the KNN film and the KNN–AN films.