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Optimizing the processing conditions of sodium potassium niobate thin films prepared by sol-gel spin coating technique

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ABSTRACT

In the present study, potassium sodium niobate (KNN) thin films were synthesized by means of sol-gel spin coating method. Along with the synthesis, the effects of annealing temperature and various number of coating layers on both the structural and electrical properties were looked into. The results of the study revealed that the annealing temperature had a great impact on the properties of KNN. In addition, the XRD diffractograms and texture coefficient of the synthesized films confirmed that a highly oriented orthorhombic perovskite structure was obtained at 650 °C, whereas at a relatively higher temperature (700 °C), a spurious phase of $K_4Nb_6O_{17}$ was evolved. In addition, the growth of KNN at 650 °C exhibited a reasonable resistivity value for piezoelectric applications. Looking into the results, it was discovered that the KNN thin films also found to be dependent on a number of coating layers. Field emission scanning electron microscopy (FESEM) showed that KNN with five coating layers was highly crystalline, cracks-free, and had significantly more homogenous surface morphology and the size of grains being uniform, the resistivity of KNN thin films improved with the increasing number of coating layers i.e., up to five.

1. Introduction

As it has been revealed through recent studies, Lead zirconia titanate or PZT has widely been used in various electronic devices such as sensors, actuators and transducers due to the excellent ferroelectric and piezoelectric properties associated with it. Notwithstanding, PZT may potentially ruin the green house effect owing to the existence of the toxic lead, too [1,2]. It was due to such unique strengths and weaknesses of PZT, lead-free piezoelectric materials have widely drawn the attention of researchers in the area of piezoelectricity. For instance, such studies in the areas of environmental and health issues looking into Pb- free based materials have been obvious. It has been clearly spelt out in the restriction of hazardous substances directive (RoHS) that any homogenous component containing more than the weight of 0.1% lead is subject to restriction [3]. As a response, various attempts have over the years been made to circumvent the toxicity of lead. As an example, extensive research has been carried out to identify alternative piezoelectric materials. Such attempts have culminated in identifying potassium sodium niobate (KNN) as one of the most potential materials for new lead-free piezoelectric. As testified in related recent studies, it may exhibit a relatively higher Curie temperature (420 °C), higher dielectric constant (~700), higher remanent polarization (14 μC/cm^2), lower coercive field (~140 kV/cm) and higher piezoelectric constant (~300 pC/N) [4,5]. However, it is worth highlighting that the KNN ceramics, the origin of which can be traced back to the early 1950s were then disregarded owing to some difficulties of processing. It has to be noted that the rapid evaporation of alkaline elements (K^+, Na^+) in the course of thermal treatment may lead to compositional in-homogeneity, resulting in a KNN-based ceramic product with low piezoelectric activity [6].

A relatively lower heating treatment process is therefore required to reduce the volatility associated with such elements. Hence, sol-gel process has particularly sparked the interest among scholars in KNN fabrication [7–9]. More specifically, it is due to the use of low annealing temperature (i.e., commonly below 700 °C) and more importantly, it is reportedly easier to control the stoichiometry of the starting material to ensure higher homogeneity [5]. However, it is worth highlighting that an improper selection of annealing temperature may result in the formation of unwanted secondary phase and it may therefore deteriorate the film's crystallinity. For example, Ahn et al. [6] observed and reported the formation of such unwanted secondary phase in the course of annealing process at 700 °C. In addition, thin films which are made

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from sol-gel route may require several coating layers to help films achieve smooth morphology and uniform thickness. In a series of repetitive coating-pyrolysis processes, the residual stress may inevitably be induced in thin films due to the crystal structure volume changes and thermal expansion mismatches which lead to deterioration of piezoelectric properties such as electromechanical coupling factor, permittivity and dielectric loss [8,10]. However, a comprehensive review of literature reveals that studies, which have looked into the number of coating layers, are scarce and a number of such studies did not clearly spell out the basis for selection. For instance, the study of Wang et al. [9] coated the KNN film for 8 times and produced 1.6 µm thick films in comparison with Kang et al. [4] who repeated the coating process for 15 times with a resulting total thickness of about 320 nm. Considering the frequencies of coating as reported in these two studies, it can be seen that they are remarkably different. It can therefore be argued that such inconsistencies without clearly spelling out may not serve as useful guidelines for researchers to choose an appropriate number of coating cycles to obtain highly crystalline, dense, and cracks-free KNN films.

Considering the discussion in the foregoing, the present study therefore intends to investigate the effects of different annealing temperature. In addition, various coating layers towards both the structural and electrical properties of KNN thin film along with the optimum conditions are reported with scientific evidences. It is hoped that the present study may further facilitate the researchers to decide on choosing more appropriate processing conditions for KNN thin films fabricate via low cost sol-gel spin coating technique.

2. Experimental procedures

Two experimental designs are presented in this section. The first section describes a facile route to produce KNN films in contrast to the next section, in which the characterization method is discussed.

2.1. Fabrication of KNN thin films

The KNN solution for the present study was prepared using sol-gel synthesis. Two alkaline precursors, namely potassium acetate (i.e., Alfa Aesar, 99%) and sodium acetate (i.e., Alfa Aesar, 99%) were used as starting chemicals. The stoichiometry of reactants selected was the K: Na (0.5: 0.5) in mol ratio. These chemicals were subsequently dissolved in 20 mL of polar organic solvent, 2-methyoxyethanol with a constant stirring at room temperature ~25 °C for approximately 30 min. Separate from the previous processes, 1 mol of niobium (V) ethoxide (Sigma Aldarich, 99.95%) was dissolved in a mixed solution of 20 mL of 2-methyoxyethanol (Sigma Aldarich, > 99.9%) and acetylacetone (chelating agent) for approximately 30 min with a constant stirring. It is noteworthy that the ratio of niobium (V) ethoxide to acetylacetone (Sigma Aldarich, > 99.9%) was kept as 1:1. Upon the completion of a vigorous stirring for an estimated 30 min at room temperature, a mixed solution of niobium ethoxide and acetylacetone was added dropwise to the prepared KN precursor. The resulting mixture was left to remain for an hour at 80 °C in order to create a clear and homogenous solution. The thin films were then produced when the mixed solution was spun onto the Si substrate with dimension of 1 cm × 1 cm at 3000 rpm for 60 s. This was followed by the pyrolysis, in which the wet films were dried at 250 °C for 1 min. The coating and pyrolysis processes were carried out repeatedly in order to form dense and homogenous structure of the films. This step was followed by the films being annealed at various temperatures by means of rapid thermal annealing furnace (RTP-1000D4, MTI) at a rate of 5 °C/s for 5 min. In this regard, Fig. 1 depicts the preparation process of pure KNN thin films.

2.2. Characterization of KNN thin films

Thermal stability of KNN dried sample was gauged by the thermo

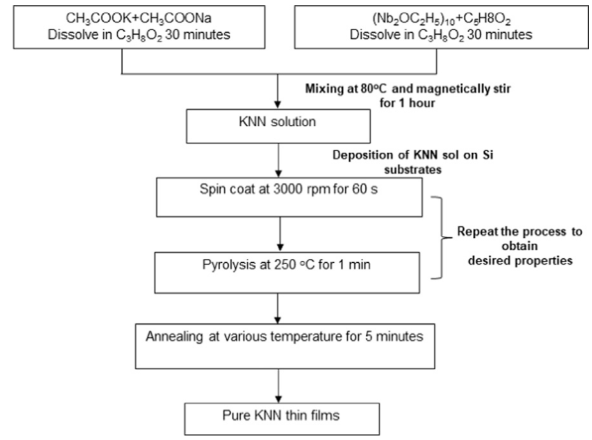

Fig. 1. Flow charts showing the synthesis procedure of KNN thin films via sol-gel spin coating technique.

gravimetric analysis (TGA) and dynamic thermal analysis (DTA). It has to be noted that these analyses were performed simultaneously by means of Hitachi STA 7300 with a heating rate of 10 °C/min from room temperature to 700 °C. In order to avoid any potential misleading reactions involved in the chamber atmosphere, inert gas, nitrogen (N_2) was supplied at 200 mL/min as a precautionary measure. Next, the XRD was used to analyze the formation of both the phase and crystallographic properties of KNN thin films by means of PANanalytical X'Pert Pro3. The scanning speed was set at 0.05 °C/s using Kα radiation. The 2θ scan range was fixed between 20° and 70°. For the thin films, the grazing angle was used to make the XRD measurement more sensitive to the interested surface region and simultaneously eliminate the contribution of the substrate to the diffraction response. Hence, the grazing angle was set at 0.1° for this experiment. Both qualitative and quantitative analysis of XRD profiles were performed by means of the PANanalytical X'Pert Highscore Plus software. The surface morphology of the thin films was examined by means of field emission scanning electron microscopy (FESEM, Hitachi 51400) operating at 10 kV. In addition, mapping analysis was performed to analyze the atomic distribution at the KNN phase. To measure the size of the grains for FESEM images, image J software was utilized. Finally, the resistivity of KNN films was characterized by four-point resistivity measurement by means of the I-V Keithley probe (2400 source-meter).

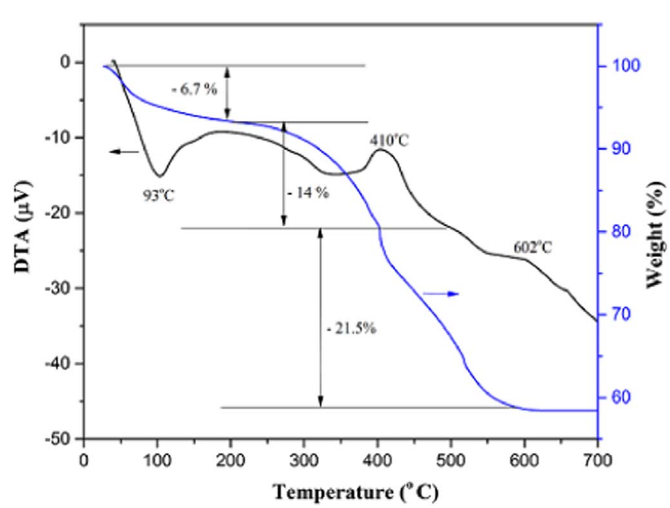

Fig. 2. TGA/DTA curves of dried KNN gel.