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Full Length Article

Effects of two-stage post-annealing process on microstructure and electrical properties of sol-gel derived non-stoichiometric NKN thin films

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ABSTRACT

Highly (100)-oriented lead-free $Na_{0.5}K_{0.5}NbO_3$ (NKN) + 40 mol% Na(I) and K(I) thin films are fabricated on $Pt/Ti/SiO_2/Si$ substrates via a sol-gel processing method. A two-stage post-annealing process consisting of rapid thermal annealing (RTA) at various temperatures in the range of 650 ~ 850 °C followed by tube furnace (TF) treatment at a temperature of 700 °C is then employed to modify the microstructure and chemical bonds of the NKN films in an attempt to improve their dielectric and ferroelectric properties. It is shown that the optimal values of the dielectric constant (ε = 658 at 100 kHz), dielectric loss (tanδ = 0.113 at 100 kHz), remnant polarization ($2P_r$ = 17.1 $\mu C/cm^2$ at 1 kHz), and coercive field ($2E_c$ = 372 kV/cm at 1 kHz) are obtained when using an RTA temperature of 750 °C. The superior electrical properties of the NKN film are the results mainly of an improved crystallization, a higher film density and a denser grain structure. It is shown that the ferroelectric properties of the NKN film are maintained for more than 25000 cycles in thermal environments of less than 150 °C. Hence, it is inferred that NKN has good thermal stability and endurance for ferroelectric devices.

1. Introduction

Lead-free ceramic materials have attracted great interest in recent decades due to the persistent trend toward environmentalism, which has led to an increasing requirement for non-toxic products [1–4]. Among the various ceramic materials available, sodium-potassium niobate (($Na_{0.5}K_{0.5}$)NbO_3, NKN) has attracted particular attention due to its relatively good dielectric, ferroelectric and piezoelectric properties [5–8]. Thin NKN films have found extensive use in such applications as variable reactance devices (varactors) [9], ferroelectric non-volatile memory (NVM) devices [10], voltage-controlled acoustoelectric devices [11], hydrogen sensing devices [12], energy harvesters [13], resistive random access memory (ReRAM) devices, and nanogenerators (NGs) [14].

Various methods are available for the synthesis of NKN films, including pulsed laser deposition (PLD) [15], radio-frequency (RF) magnetron sputtering [16], and metal-organic chemical vapor deposition (MOCVD) [17]. Compared to such methods, sol-gel processing has the advantages of a lower cost, a more effective synthesis outcome, and a better control of the film properties [18]. However, the thickness of the liquid film produced in a typical spin-coating process followed by heat treatment (e.g., dried at 150 °C on a hot plate, pyrolyzed at 300 °C in an oven, and calcined in a rapid thermal annealing (RTA) furnace at 600 °C) is only around 50 nm [19]. Thus, the experimental procedures must be repeated 10 times to obtain a total film thickness of 500 nm (i.e., the thickness typically required in ferroelectric NVM applications). In other words, the samples must be calcined 10 times, resulting in a time-consuming fabrication process; particularly in the cooling-down stage. In addition, the 500-nm NKN film must then be post-annealed at 700 °C for a further 2 h in air in a tube furnace (TF).

The aim of this study is therefore to replace the repeated (i.e., 10-time) RTA process described above with a single RTA process

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in order to simplify the fabrication procedure and shorten the processing time. Accordingly, the present study examines the effects of a two-stage post-annealing process consisting of RTA at various temperatures (650, 700, 750, 800 and 850 °C) followed by fixed temperature TF annealing (700 °C for 2 h) on the microstructure, chemical bonds, and electrical properties of NKN films produced using a 10-time spin-coating process. In general, the results show that the RTA-induced growth of the NKN microstructure and the formation of chemical bonds have a significant effect on the electrical properties of the film. Moreover, the results suggest that the proposed two-step post-annealing process is beneficial in enhancing the thermal stability and endurance of the ferroelectric properties of the film.

2. Material and methods

NKN films were prepared using a sol-gel technique. Sodium ethoxide (C_2H_5ONa, 96%, Aldrich), potassium ethoxide (C_2H_5OK, 95%, Aldrich), and niobium ethoxide ($C_{10}H_{25}NbO_5$, 99%, Aldrich) were mixed with 2-methoxyethanol solvent (99.8%, anhydrous, Aldrich) and used as precursors. Small quantities of acetic acid (CH_3COOH, 95%) and acetylacetone ($C_5H_8O_2$, 99%, Aldrich) were added as chelating agents to stabilize the gel (with a concentration of 0.3 M). The gel was then stirred at 50 °C for 15 min to obtain the final solution. To compensate for the loss of alkaline metals during annealing, non-stoichiometric (excess amounts of 40 mol%) Na and K were added in accordance with the findings of a previous study by the present group [19]. Prior to film deposition, the substrate ($Pt/TiO_2/SiO_2/Si$) was cleaned with acetone, isopropanol, deionized water and alcohol, and then treated with ultraviolet-ozone cleaner (UVO-42, Jetlight) for 20 min at room temperature (RT). Thereafter, a liquid film was deposited on the substrate by a spin coater (PM490, Swienco) rotating at 3000 rpm for 30 s. The liquid film was dried at 150 °C on a hot plate for 10 min. Finally, the dried film was pyrolyzed at 300 °C for 10 min to evaporate organic compounds. The procedure was repeated 10 times to obtain a total sol-gel film thickness of around 500 nm. The samples were annealed via RTA (650, 700, 750, 800 and 850 °C) with a heating rate of 40 °C/s and then TF annealed (700 °C) for 2 h in air. Finally, Pt top electrodes with a diameter of 50 μm and a thickness of 100 nm were patterned on the NKN films using a photolithography technique and thermal deposition method.

The crystallographic phases of the prepared samples were investigated by means of standard θ–2θ X-ray diffraction (XRD, Bruker D8 Advance) using CuKα radiation (λ = 1.5408 Å). The film density was analyzed by X-ray reflectometry (XRR) using the same instrument. The morphology and element ratios of the thin films were characterized by a high-resolution scanning electron microscope (HR-SEM, Hitachi SU8000) equipped with an energy dispersive spectrometer (EDS). Analyses and measurements of the chemical bonds were performed using X-ray photoelectron spectroscopy (XPS, JAMP-9500F field emission Auger microprobe, JEOL). The dielectric properties were measured using an impedance analyzer (Agilent 4294A). Finally, the ferroelectric properties were analyzed under various thermal environments using a precision multiferroic tester (Radiant Technologies).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the NKN films processed at different RTA temperatures. For each sample, four NKN peaks (100, 110, 210 and 211) and two Pt peaks (111 and 200) are observed (refer to JCPDS Card No. 01-079-7690 for cubic NKN powders and the XRD patterns presented in [20] for another NKN thin film). Taking the intensity of the Pt (111) peak for comparison purposes, it is seen that the samples processed at RTA temperatures of 650–750 °C have more pronounced NKN (100) and (110) orientations than those processed at higher temperatures [21]. In other words, the films have a perovskite structure and good crystallinity when annealed at temperatures of 750 °C, or lower. Table 1 shows the peak area ratios (i.e., A_{100} ((100)-oriented))/A_{total} ((100, 110, 210 and 211)-oriented)) of the various NKN films. (Note that the area ratio results are calculated directly from Fig. 1(a)). It is seen that the NKN film processed at 750 °C has the highest peak area ratio of the various films (i.e., A_{100}/A_{total} = 0.387). In other words, the film has the most pronounced (100)-orientation of all the films, and has a better dielectric property as a result [22]. However, at RTA temperatures higher than 750 °C, the volatility of Na and K results in a slight element-ratio imbalance, which degrades the crystallinity and orientation of the NKN film [23]. Fig. 1(b) shows the XRR critical angles (θ_c) of the NKN films processed at different annealing temperatures. In general, θ_c has a value in the range of tenths of a

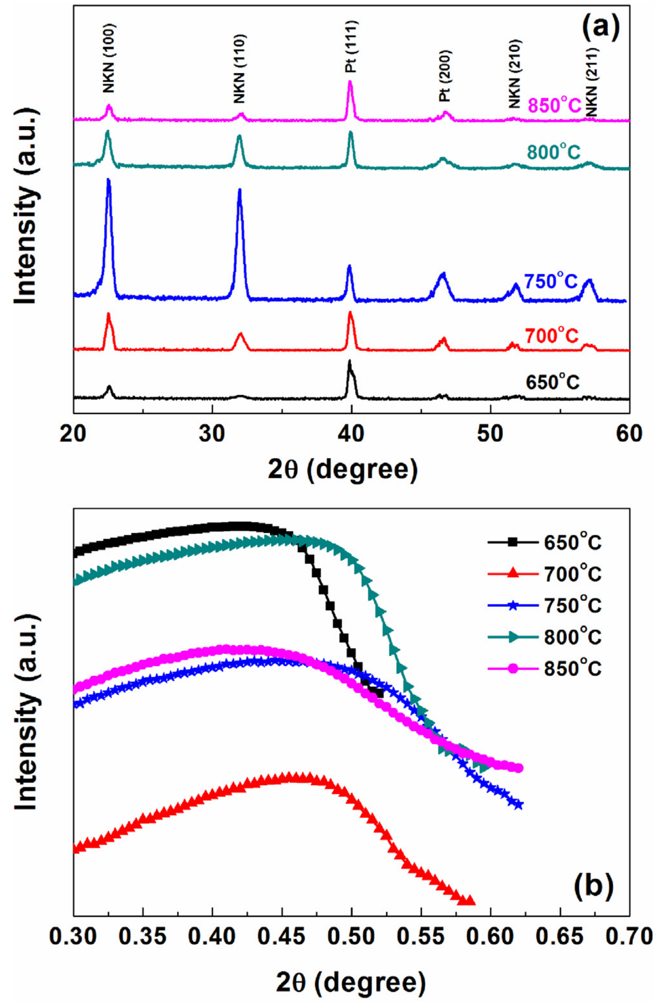

Fig. 1. (a) XRD patterns and (b) XRR critical angle plots of NKN thin films processed with various RTA temperatures.

Table 1
Peak area ratio (A_{100}/A_{total}) of NKN films processed at different RTA temperatures. (Note that the peak areas are computed from the XRD results in Fig. 1(a) by Gaussian deconvolution using Origin® software (Ver.8).).

RTA temperature (°C)	650	700	750	800	850
A_{100}/A_{total}	0.295	0.324	0.387	0.355	0.333