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To cite this article: U.A.A. Azlan et al 2018 J. Phys.: Conf. Ser. 1082 012053

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Optimization of Sodium Potassium Niobate Thin Films with Different Deposition Layers

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Abstract. Sodium Potassium Niobate, KNN with different deposition layers on Si substrate was successfully prepared by sol-gel spin coating and subsequently annealed at 650°C for 10 min. Several deposition layers of KNN were systematically studied with different characterizations. The KNN thin films with five deposition layers showed a good result in terms of its homogeneity and uniformity of thickness that was measured to be around 280 nm. Further study on the surface roughness was obtained by AFM and its value of around 1.698 nm was recorded from the scanned area of 1 µm × 1 µm of thin films. It was also reported that the NbO₆ octahedral vibrational modes of υ₆, υ₅, υ₄, υ₂, υ₁, υ₃, υ₁+υ₅ was detected in a wide range of 200 cm⁻¹ to 900 cm⁻¹, shown by Raman analysis. The elemental composition was also studied and the results were confirmed with deconvolution of XRF spectrum.

1. Introduction

For the past 10 years, ferroelectric ceramics with a perovskite structure, a tungsten bronze structure and bismuth layer-structured (BLSF) have been reported to replace the lead-based materials. Recently, there is more findings with better results has been reported from various perovskite-structured ferroelectrics such as barium titanate, bismuth titanate, bismuth sodium titanate, potassium niobate, sodium potassium niobate [1]. Among these, sodium potassium niobate (K₀.₅Na₀.₅NbO₃) or KNN has been nominated as one of the most promising candidate to replace the wide usage of lead-based materials especially the lead zirconate titanate [2]. This compound is a combination of solid solution ferroelectric KNbO₃ and anti-ferroelectric NaNbO₃ that has been the most studied lead-free piezoceramics materials due to its relatively high piezoelectric constant (416 pC/N) and high Curie temperature (420°C) [3-5].

Thin film is a layer of material that resembles a coating with a thickness ranging from nanometres into micrometres. In general, the precursor can be made by various wet chemistry techniques. One of them is a sol-gel process, whereby it is typically accomplished by two primary reactions of hydrolysis and condensation. The most common starting materials, or precursors, used in the preparation of the sol are water-sensitive metal alkoxide complexes (M(OR)x, whereby R = alkyl group (e.g., CH₃, C₂H₅, CF₃,
etc.). Metal alkoxides are good precursors because they readily undergo hydrolysis; that is, the hydrolysis step replaces an alkoxide with a hydroxide group from water and a free alcohol is formed [6]. There are a few methods that have been used for deposition of the thin films. Evaporation, sputtering, spin coating, pulsed laser deposition (PLD), molecular beam epitaxy (MBE) and aerosol deposition are the physical deposition techniques. Additional deposition techniques that have been used are chemical-based deposition, chemical vapour deposition (CVD), metal chemical vapour deposition (MCVD), plating, spin coating, plasma enhanced chemical vapour deposition (PECVD), atomic layer deposition (ALD) and chemical solution deposition (CSD). Among these techniques, spin coating is chosen to fabricate a good physical film with uniform coating layers. In this work, a study on KNN thin films with different deposition layers was reported in this paper.

2. Experimental study

The precursor was started by dissolving CH₃COOK and CH₃COONa into 2-ME in a beaker with constant stirring at room temperature. Nb₂(OC₂H₅)₁₀ was also prepared with a constant stirring at room temperature in another beaker containing 2-ME with the addition of acetylacetone. Both of the precursors were mixed together for another constant stirring at 60°C for an hour. After that, the deposition process was done by depositing the precursor onto the Si substrate with different layers using the spin coating machine. One minute of pyrolysis was taking place between each of the layers. To end the deposition process, the wet films were annealed at 650°C for 10 minutes by using the rapid thermal processing (RTP) furnace. The deposition process can be clearly seen as shown in Figure 1.

Raman spectroscopy has been used to investigate the molecular vibration modes for KNN thin films to find the octahedral bonding between the Nb and O ions. The samples were measured by UniRAM-II Micro Raman Mapping System in single mode laser with 532 nm DPSS laser. A FESEM (Model: Hitachi 51400) was used to investigate particle morphology, thickness and grain microstructure of the annealed thin films. Electron microscopic images were taken at various magnifications using secondary electron (SE) mode and back-scattered electron (BSE) mode with the high electron high tension (EHT) was set at 10 kV. Hitachi AFM5100N was employed to measure the roughness of KNN thin films. This instrument uses a cantilever with a sharp probe tip that scans the surface of the specimens. The results of this analysis will be presented in 3D image form. The scan was conducted on 1 μm x 1 μm area of thin films. Elemental analysis for the thin films samples was conducted using XRF microscope and EDX. This analysis was conducted by Micro-XRF on SEM (Bruker) with the x-ray source of 50 kV, a current of 600 μA and rhodium (Rh) as the X-ray source of the target.

![Deposition process of KNN using spin coating technique.](image)
3. Results and discussion

The Raman spectra for KNN with different deposition layers are shown in Figure 2. The profile in Figure 2 is consistent with the previous report, claimed that the scattering mode of secondary phase are not detected in spectrum [7]. It was also reported that the vibrations of the NbO$_6$ consisted of $1A_1g(\nu_1) + 1E_g(\nu_2) + 2F_1u(\nu_3, \nu_4) + F_2g(\nu_5) + F_2u(\nu_6)$, whereby $1A_1g(\nu_1) + 1E_g(\nu_2)$ are the stretching modes and the rest are the bending modes [8]. The NbO$_6$ octahedral vibrational modes of $\nu_6$, $\nu_5$, $\nu_4$, $\nu_2$, $\nu_1$, $\nu_3$, $\nu_1+\nu_5$ appear in a wide range of 200 to 900 cm$^{-1}$. Notably, $\nu_1$ (617 cm$^{-1}$) and $\nu_5$ (301 cm$^{-1}$) that were detected in this analysis are also having the relatively strong scattering in the single layer deposition of KNN. At the signal of 520 cm$^{-1}$ it was found that a high intensity peak for each deposition layer is attributed by Si peak. As reported, the broad peak at both modes $\nu_1$ and $\nu_5$ is a clear signal disorder in symmetry perovskite as detected in Raman spectrum [9]. Besides that, these modes are also common in the perovskite structure of KNN, showing that the distortion of perovskite structure through Nb-O bonding.

![Raman spectra analysis for KNN with different deposition layers: (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5.](image)

The FESEM images of annealed KNN thin films with different deposition layers are shown in Figure 3. As seen, the diverse sizes of grain in each deposition layers can be seen clearly without any crack and with a smooth surface. The inhomogeneity of KNN particles can be seen on the lowest deposition layer of KNN thin films in Figure 3(a) due to the rapid volatilization of K and Na elements thus, reducing the formation of the uniform particle at a single layer of KNN films. However, the films deposited with three deposition layers in Figure 3(b) showing some agglomeration of particles due to the high temperature annealing process. The thin films with five deposition layers in Figure 3(c) showed a better improvement in homogeneity and uniformity as compared with one and three deposition layers. In addition, the thin films with five deposition layer also pleasantly denser from the other films. The uniformity of KNN thin films is also in agreement with a report of PZT thin films for the fifth deposition layer with dense uniform grains and compact crack-free structure [10]. In Figure 3(d), the thickness of the films with five deposition layers was measured to be around 284 nm. Further analysis was also
carried out on the films with six deposition layer. Nevertheless, the formation of cracks on the sixth deposition layer was found clearly in the FESEM image as shown in Figure 3(e). This can be explained that the repetitive process of coating and pyrolysis for each deposition layers also contributed to the thermal expansion of thin film that exceeded the substrate and leads to change in crystal structures volume which resulted in residual stresses induced in thin films propagating the severe cracks [11]. Figure 3(f) shows the AFM images of KNN thin films with five deposition layers. From the AFM analysis of the surface morphology and topography, the root mean square roughness (Rq) was determined. The value of surface roughness was obtained from the scanned areas of 1 µm × 1 µm of thin films which indicated that all the deposited films have nano-crystalline growth patterns of 1.698 nm.

![Figure 3. FESEM images of KNN thin films with different deposition layers: (a) 1, (b) 3, (c) 5, (d) thickness of KNN with 5 layers deposited on Si substrate, (e) formation of cracks at six deposition layers and (f) AFM images of 5 deposition layers.](image-url)
The elemental composition of KNN with five deposition layers was confirmed with de-convolution of XRF spectrum as shown in Figure 4. Elements which are K, Na, and Nb are present in the KNN compound. Note that Rh is the X-ray source, which is used as Rh target. XRF penetrated deep into the layers and does not detect the gaseous type of elements, thus the oxygen gas was not presented in the analysis graph. Distribution in KNN grains was consistent with its XRF spectrum which portrays the lower excitation energy that shows the stability of alkaline elements (K and Na). The result in Figure 4 was found to be consistent with the EDX spectrum in Figure 5, which also portrays the lower excitation energy that shows the stability of alkaline elements of both K and Na due to the volatility of these materials which highly reacted with moisture. It shows that the composition of all elements is slightly changed from the actual numbers because of thermal effect due to alkaline ions character that is easy to volatile on high temperature.

**Figure 4.** XRF spectra analysis for elemental compositional of KNN thin films.

**Figure 5.** EDX spectrum analysis of K, Na, Nb and O elements.
4. Conclusion

The KNN thin films with different deposition layers was successfully prepared by sol-gel spin coating. It can be concluded that the KNN with five deposition layers are well distributed in terms of homogeneity and uniformity of its morphology. The thickness of the same films was around 284 nm. The surface roughness was measured to be around 1.698 nm with nano-crystalline growth patterns. The presence of the following elements, K, Na, and Nb was confirmed with de-convolution of XRF spectrum.

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