Effects of Annealing Temperature of Potassium Sodium Niobate Thin Film

Mohd Warikh Abd Rashid[1,*], Hidayah Mohd Ali Piah[1], Umar Al-Amani Hj Azlan[2] and Maziati Akmal Mohd Hatta[3]

[1]Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka,
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[2]Faculty of Mechanical and Manufacturing Engineering Technology, Universiti Teknikal Malaysia Melaka,
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[3]Faculty of Engineering, International Islamic University Malaysia, Jalan Gombak,
53100 Kuala Lumpur, Malaysia

[*]Corresponding e-mail: warikh@utem.edu.my

Keywords: Potassium sodium niobate, annealing, thin film

ABSTRACT – Potassium Sodium Niobate (KNN) thin films were grown on Si substrate by using sol-gel spin coating method and the annealing temperature is manipulated. The as-deposited thin films were undergo 250 °C pyrolysis of for 5 min and then was annealed at the range temperature which are from 610°C to 650°C. Following this, a series of material analysis such as X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) on the effects of annealing temperature is carried out. The electrical properties of KNN thin films were characterized using resistivity testing. Looking into the results, it was discovered that 650°C is the optimum annealing temperature as it shows the best crystallization of KNN grain and good resistivity value of 104 Ω cm.

1. INTRODUCTION

In the new market research report "Piezoelectric Devices Market by Material, Product, Application - Global Forecast to 2022", the market of piezoelectric devices is expected to have continuously growth till the year of 2022 with a growing rate of Compound Annual Growth Rate (CAGR) of 4.88 % [1]. With that also predicted the need on PZT will increase. Despite of the advantages and flexibility of PZT as material in making electrical components, the lead waste produced during manufacturing and recycling would cause serious hazard to humans and the environment. Hence, the ideal of switching the PZT to KNN is supported by the Waste Electrical and Electronic Equipment (WEEE)'s law in 2006 and the usage of certain Hazardous Substances in electrical and electronic equipment (RoHS) is restricted due to protect the health and environment [2].

Anyhow, inadequate study shows the optimum temperature among 610°C to 650°C. Hence, one of the way to optimize the properties of KNN thin film is by investigating the fabrication parameters variances mentioned above and explore any relationship of these parameters which could improve the structural and electrical properties of KNN thin films for future use in electronic appliances.

2. METHODOLOGY

2.1 Synthesis of KNN thin film

The sol-gel process was started with preparation of KNN solution. Two alkaline precursors, specifically potassium (K) acetate (i.e., Alfa Aesar, 99%) and sodium (Na) acetate (i.e., Alfa Aesar, 99%) were used as starting chemicals. These chemicals with ratio of reactants chosen was the K: Na (0.5: 0.5) in mol were later dissolved in 20 ml of polar organic solvent, 2-methyoxyethanol with a continuing stirring at room temperature for about 30 min. Upon the completion of a vigorous stirring, the mixed solution of niobium ethoxide and acetylacetone was intercalary dropwise to the KN precursor which had been prepared earlier, then left for constant stirring about an hour at 80°C.

The thin films were then spun onto the Si substrate at 3000 rpm for 60s once the mixed resolution is ready. The Si substrate dimension is 1 cm × 1 cm. Then, it was followed by pyrolysis which the wet films were dried at 250°C for 1 min. The coating processes were carried out repeatedly 5 times so as to create dense and homogenous structure of the 5-layer films. After that, the films being annealed at various temperatures as proposed (610°C-650°C) at a rate of 5°C/s for 5 min. Fig. 1 depicts the preparation method of pure KNN thin films.

2.2 Characterization of KNN thin film

The crystallographic properties of the KNN films were analysed by using X-ray diffraction (PANanalytical). The glancing angle was set at 0.10 for the thin film in order to avoid the effect of radiation on the Si substrate. On top of that, the surface morphology of the samples was examined by using scanning electron microscopy (SEM). Besides, four-point resistivity method (Jandel RM3000) was used to measure the electrical resistivity of KNN thin films.

3. RESULT AND DISCUSSION

Figure 1 demonstrates the XRD patterns for KNN thin film grown on the Si substrate that were annealed at various temperatures. All films had the pronounce peaks at planes (1 0 1), (1 1 1), (2 2 0), (1 1 0), (2 1 1) and (2 0 2) beginning from 20°< 2θ < 70° which indicate that KNN thin films are polycrystalline in nature. All in all, there are not any auxiliary part distinguished and furthermore the outcomes were observed to be as per KNN orthorhombic structures.

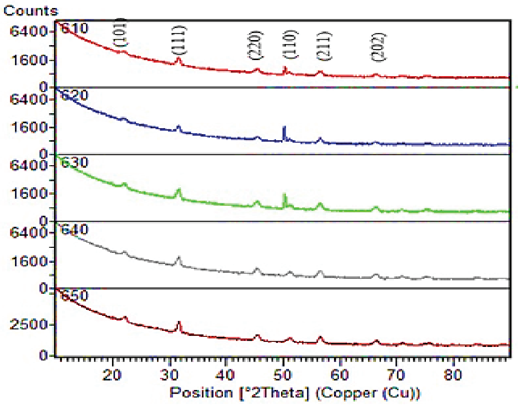

Figure 1 XRD patterns for KNN thin film

Figure 2 depicts the surface morphology of KNN thin films. At the annealing temperature of 610°C, the grain structure is less obvious and smaller in size. Previous study has proved that the temperature of 610°C is not high enough to allow the complete crystallization of KNN thin films [3]. Though, the crystallization is start to occur at the temperature of 620°C as the grains structure can be clearly observed compared to 610°C. It can be clearly seen that the grain size is increasing with the increasing of annealing. On contrast, at the high annealing temperature which is 650°C, the KNN grains are seem denser than KNN thin film annealed at 640°C. It shows that the grains are more toughened when annealed at high temperature. Therefore, 650°C can be selected as the optimum annealing temperature to obtain highly crystalline KNN thin film.

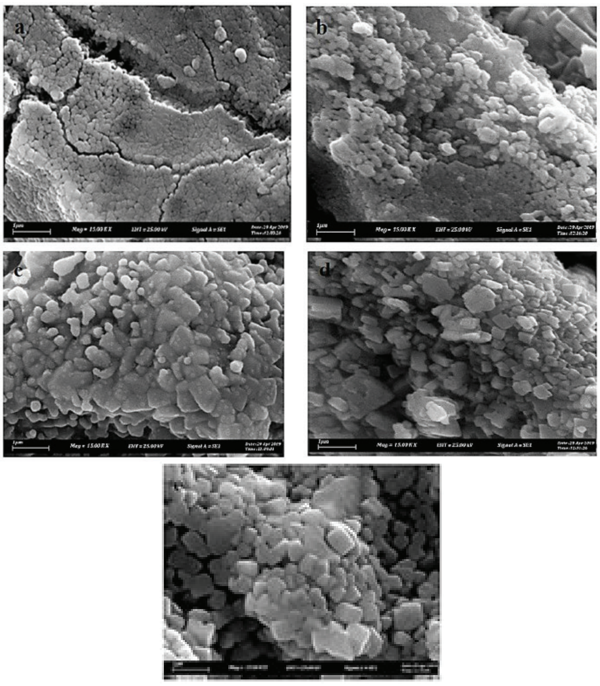

Figure 2 SEM micrograph at annealing temperature (a) 610ºC, (b) 620ºC, (c) 630ºC, (d) 640ºC, (e) 650ºC

Based on the Table 1, when the annealing temperature is increased, the value of the resistivity of the KNN thin film is decreasing. Other study has proved that the resistivity of the piezoelectric material is decreasing when the annealing temperature increasing [4]. As noted, the resistivity value in this study ranging from 10^5 to 10^8 Ω cm. According to this Wu et. al, resistivity values are reasonable for piezoelectric application and the lower resistivity demonstrates the electrons were easily moves from grain to grain within KNN structure due to improved densification of grains at high temperature [3].

Table 1 Resistivity for KNN thin film at different annealing temperature

Annealing temperature (°C)	Resistivity (Ωm)
610	0.27 x1 0^{4}
620	0.20 x10^{4}
630	0.11 x1 0^{4}
640	0.05 x 10^{4}
650	0.03 x 10^{4}

4. CONCLUSIONS

Annealing process is an important stage in fabricating the thin films to ensure that the films are fully crystallize on the Si substrate. For this study, the annealing temperature selected are 610 to 650°C, respectively. Accordance to the results obtained, the degree of crystallinity is increasing with the annealing temperature. For the morphology analysis, SEM images shows the grain size is increasing with the temperatures which attributed to the toughening factor and at 650°C and shows the polarization will be easy to occur at high temperatures. Finally, it can be concluded the 650°C is the optimum annealing temperature to obtain highly crystalline and dense KNN thin film for integration of KNN thin film in electronic devices specifically for piezoelectric applications.

ACKNOWLEDGEMENT

Authors are grateful to Universiti Teknikal Malaysia Melaka and the Ministry of Higher Education, Malaysia under the Fundamental Research Grant Scheme (FRGS), grant no.: FRGS/1/2021/FKP/F00475.

REFERENCES

[1] C.H. Hong, H.P. Kim, B.Y. Choi, H.S. Han, J.S. Son, C.W. Ahn and W. Jo, "Lead-free piezoceramics – Where to move on?", *Journal of Materials*, vol. 2, pp. 1–24, 2016.

[2] J. Wu, D. Xiao and J. Zhu, "Potassium-sodium niobate lead-free piezoelectric materials: past, present, and future of phase boundaries", *Chemistry Review*, vol. 115, pp. 2559–95, 2015.

[3] S.R. Burns and M. Dolgos, "Sizing up ($K_{1-x}Na_x$) NbO_3 films: a review of synthesis routes, properties & applications", vol. 45, pp. 7408-7436, 2021.

[4] M.H.M. Akmal, A.R.M. Warikh, U.A.A. Azlan, M.A. Azam, T.J.S. Anand and T. Moriga, "Structural evolution and dopant occupancy preference of yttrium-doped potassium sodium niobate thin films", *Journal of Electroceramics*, vol. 37(1), pp. 50-57, 2016.