A NEW LEAD-FREE (K,Na)NbO_3 PIEZOELECTRIC MATERIAL AND ITS MICROFABRICATION FOR MICRO ENERGY HARVESTER

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Abstract: In this paper, a new lead-free piezoelectric (K,Na)NbO_3 (KNN) film is presented as a promising, environment-friendly alternative to the conventional piezoelectric thin film materials like PZT, etc. with regard to applying into piezo-MEMS devices in general and micro-energy-harvesting devices in particular. The KNN films deposited by the RF magnetron sputtering deposition system were revealed excellent transverse piezoelectric coefficient of 120pm/V and high figure of merit (FOM) of $22\ \mathrm{GJ.m^{-3}}$. The microfabrication of KNN films was investigated by both dry etching and wet etching while there are few publications about etching the material. Under the FAB condition – 3kV anode-cathode voltage, 25mA current, and 5.6sccm SF_6 flow rate, the KNN-etching rate is approximately 10nm/min. Wet etching is also studied as an alternative method. Various high-concentration HF solutions are delved into etching KNN thin film. The 77nm/min KNN-etching rate in 40% HF solution is achieved.

Keywords: Lead-free piezoelectric, (K,Na)NbO_3 film, KNN thin film, KNN etching, energy harvesting

I. INTRODUCTION

Micro-energy-harvesting devices have attracted attention from both industrial and scientific communities for their potential applications, such as wireless sensor nodes, portable electronic devices, human-implanted devices, etc. Energy harvesting devices based on piezoelectric materials are one of the direct methods converting vibration sources into electrical energy. Lead piezoelectric materials and PZT ($PbZr_{1-x}Ti_xO_3$) in particular have exploited to fabricate many piezo-MEMS applications as well as energy harvesters [1-3]. However, the conventional PZT thin film material contains lead over 60 weight percent which is a toxic element, though the material possesses outstanding piezoelectric properties.

In this paper, we presented a new lead-free material, KNN, obtaining a high FOM factor and excellent transverse piezoelectric coefficient. The microfabrication of KNN films was addressed by using both dry etching and wet etching methods.

II. (K_{1-x},Na_x)NbO_3 MATERIALS

($K_{1-x}Na_x$)NbO_3 (KNN) films were synthesized by using RF magnetron sputtering at Hitachi Cable Ltd. [4,5]. A Pt/Ti/SO_2/Si substrate was prepared for KNN film deposition. The bottom electrode (111)Pt of 200nm with a Ti-adhesive layer of 2nm was deposited on the SiO_2(200nm)/Si(525μm) substrate by using the RF magnetron sputtering. A composition-desired KNN ceramic was utilized as the sputtering target for sputtering KNN film. At a substrate temperature of 500^oC and an Ar/O_2 ambient pressure of 1.3Pa, the KNN deposition on Pt/Ti/SiO_2/Si is achieved at relative high growth rate of 0.7μm/h [4]. In the Figure 1, the cross-section SEM image of the typical 3μm-thick KNN film on 4inch wafer is shown. The as-deposited KNN film was annealed at 750^oC in air for 2 hours [5].

In order to investigate and optimize the piezoelectric coefficient, the KNN films with different composition stoichiometry are deposited by using RF magnetron sputtering of the respective KNN ceramic target. The chemical compositions of both as-deposited KNN film and the KNN targets were determined by using EDS [4].

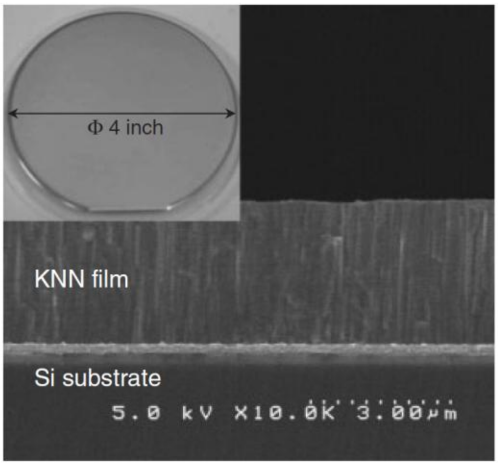


Figure 1: SEM image of KNN film deposited on Pt/Ti/SiO_2/Si substrate[5].

The transverse piezoelectric coefficient (d_{31}) at 20V and the relative dielectric constant (ϵ_r) for the KNN films as a function of the Na/(K+Na) ratio as shown in Figure 2. The KNN films were revealed excellent transverse piezoelectric coefficient. The maximum piezoelectric coefficient and dielectric constant were approximately 120pm/V and 1100, respectively at the Na/(K+Na) of 0.55 [4]. Hence, the figure of merit (FOM) defined as $\mathrm{FOM_{KNN}} := \frac{e_{31}^2}{\varepsilon_0 \varepsilon_{33}^T}$ is approximately $22GJ.m^{-3}$, which is high value for fabricating piezoelectric energy harvesters in comparison with contemporary piezoelectric energy harvesters based on PZT and AlN materials [2].

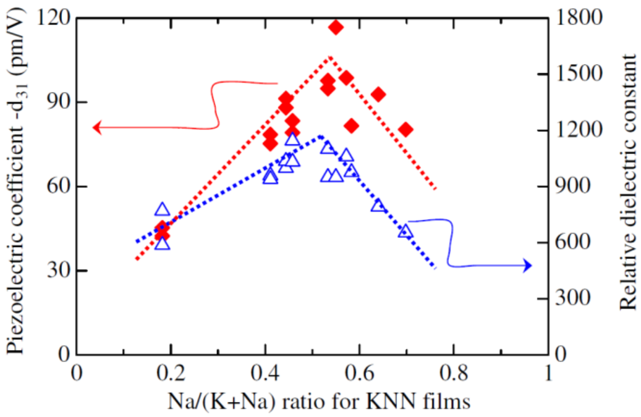


Figure 2: Transverse piezoelectric coefficient –d_{31} and relative dielectric constants for KNN films as a function of Na/(K+Na) ratio[4].

II. $(K_{1-x},Na_x)NbO_3$ MICROFABRICATION

The high values of FOM and high transverse piezoelectric coefficient are attractive to apply the KNN film in energy harvesting. Hence, it is necessary to study on microfabrication technique for KNN film in order to exploit this excellent material. In our study, both wet etching and dry etching methods of KNN were investigated.

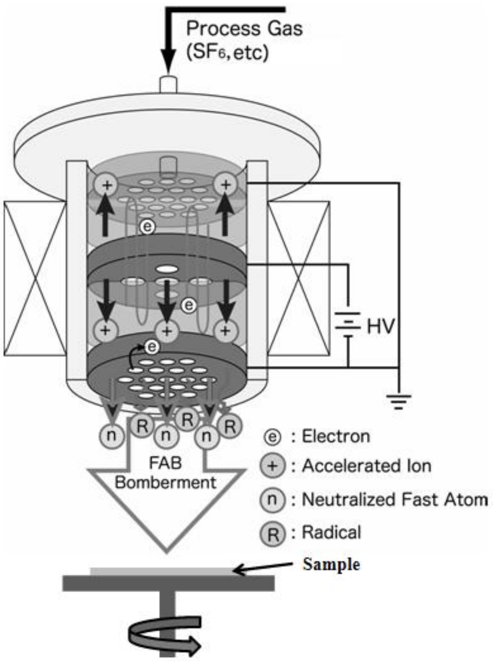


Figure 3: The schematic structure of FAB apparatus.

SF_6 FAB etching KNN

A Fast Atomic Beam (FAB) technique which generates the energetic neutral particles to bombard the etched materials is selected for etching KNN films. The advantage of this technique enables to fabricate fine, precise structures for high anisotropy etching [6,7].

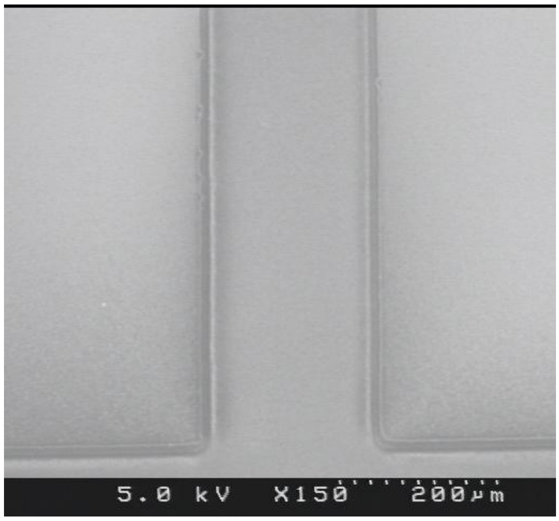


Figure 4: KNN pattern by SF_6 FAB etching technique.

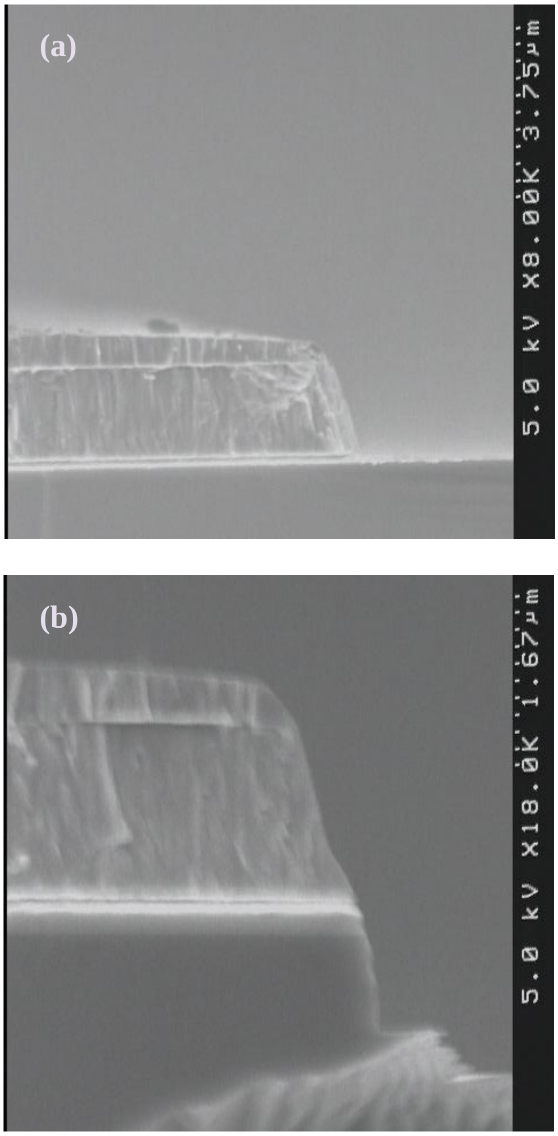


Figure 5: Cross-section SEM images of etching KNN patterns by SF_6 FAB.

Figure 3 illustrates the principle and configuration of the FAB apparatus (FAB-60ML EBRA). The FAB etching of KNN films has been carried out by using SF_6 gas. The etching rate of KNN film depends on the gas species, gas pressure, wafer temperature, and discharge conditions. In our experiment, the etching conditions are as following: gas flow rate of 5.6sccm, an anode-cathode voltage of 3kV, and a discharge current of 25 mA.

Figure 4 shows the KNN pattern by SF_6 FAB etching. The cross-sectional SEM images of the pattern are exhibited in Figure 5. The etching pattern obtained smooth edges and and vertical side wall. The etching rate is approximately 10nm/min. However, the SF_6 FAB etching is likely to have no selectivity between KNN material and Pt bottom electrode (Figure 5b).

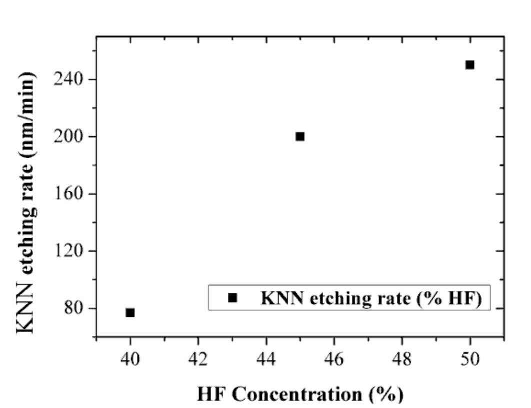


Figure 6: Etching rate of the KNN thin films in various concentrations of HF solution.

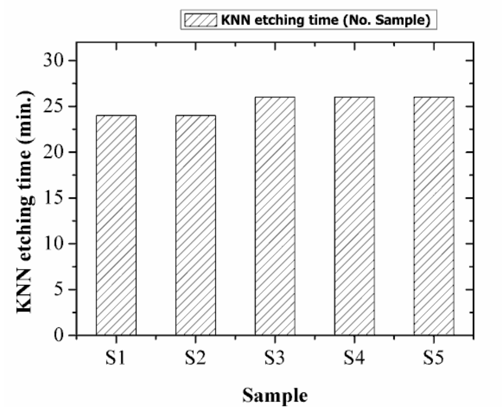


Figure 7: The repetition of etching KNN sample in 40% HF solution.

Wet etching KNN films

While SF_6 FAB of etching KNN has possessed a good etching pattern, the wet etching of this material has its own advantages. The high etching rate and good selectivity between bottom electrode and KNN materials were taken into consideration. As a perovskite ceramic material, it is well-known for hardly etching materials. It is evident that the 25% HF solution is likely not to etch KNN film while this concentration is likely to etch PZT materials. Therefore, finding a solution for etching KNN is very necessary and important. In our experiments, the high-concentration HF acid solutions are investigated for etching KNN material. The weigh concentrations of HF solutions are ranged from 50% to 40%. Figure 6 shows the etching rate of KNN films depending on the concentration of HF solution. The high etching rate of 50%HF solution is over 240nm/min. However, high concentration HF solutions are very corrosive. Therefore, the 50%HF solution attack adversely to protective mask. Moreover, it is likely to be difficult to control the KNN etching pattern when the side etching is very fast as well. According to our experiment, the 40%HF solution can etch KNN with a reasonable etching rate of 77nm/min. Hence, the 40% HF solution etched the KNN of 2µm in thick for approximately 25 min in average. Figure 7 displays the repetition of etching 5 KNN samples in 40%HF solution. The positive photoresist OFR800-200cp/Cr was utilized as a protective mask for the etching process. The KNN pattern achieved by wet etching in 40%HF solution was exhibited in Figure 8.

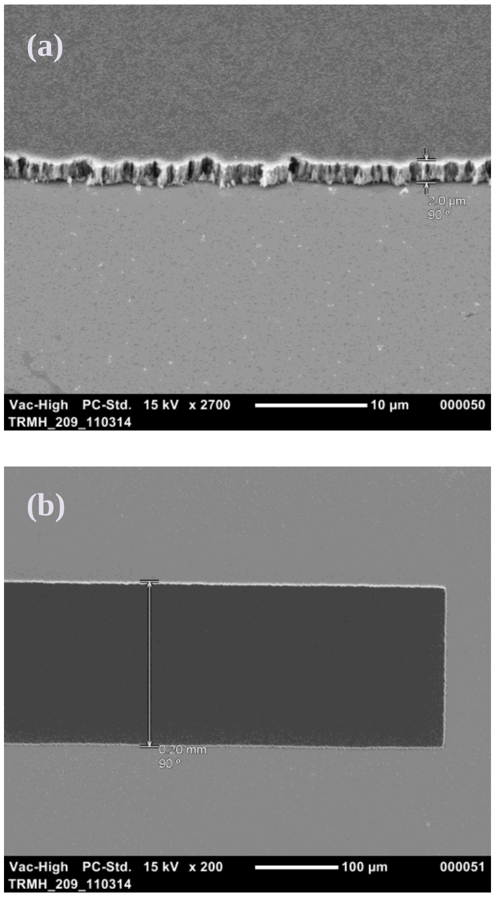
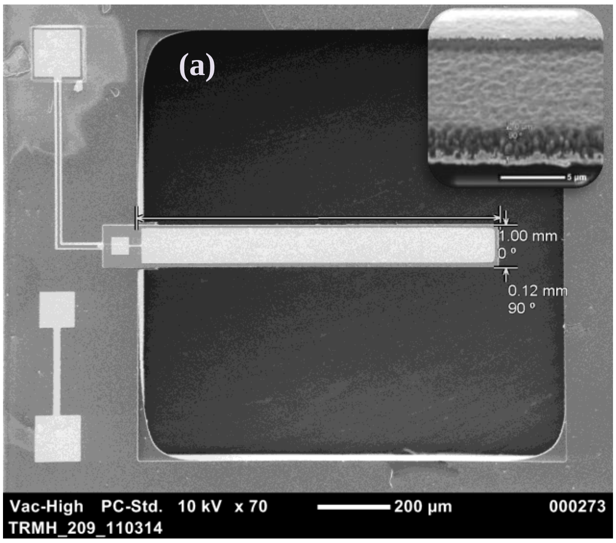


Figure 8: SEM images of KNN patterns by 40%-HF wet etching. (a) 45^o-tilted image (b)top view image

Cantilevers based on KNN films

The micro cantilevers were fabricated using microfabrition process. The KNN film of 2µm was used for the fabrication. The KNN cantilever with dimension of $1000 \times 120 \times 2\ \mu m^3$ was fabricated successfully. Both d_{31}-mode and d_{33}-mode of the free standing KNN cantilevers are shown in Figure 8. The top electrode was Au(200nm)/Cr(20nm) film and The bottom electrode was Pt thin film.



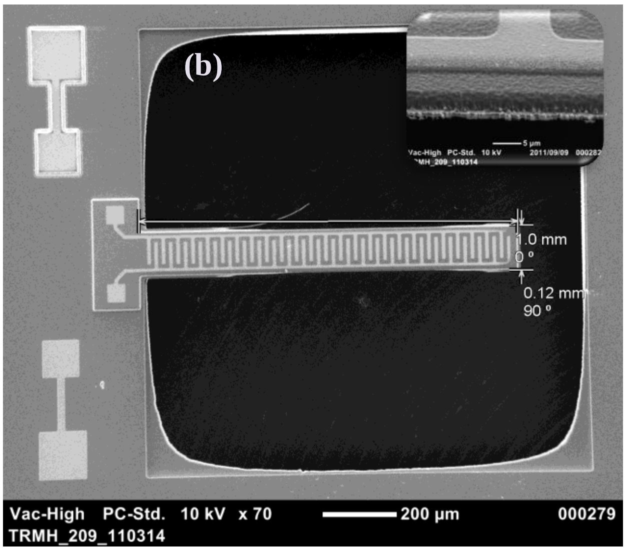


Figure 9: SEM images of KNN/Si cantilever: a) d_{31}-mode cantilever and inset of the 45^o-tilted image b) d_{33} -mode cantilever and inset of the 45^o-tilted image

CONCLUSION

In this paper, we presented a new lead-free thin film material – KNN film - as a potential material for energy harvesting. The 2μm-thick KNN films with mole ratio x=0.55 between Na and K achieved the high FOM. The microfabrication of KNN film was investigated by either SF_6 FAB etching method with 10nm/min etching rate or 40%HF solution with 77nm/min etching rate. These etching techniques were implemented to fabricate sucessfully micro-cantilevers of KNN in dimensions of $1000 \times 120 \times 2\mu m^3$ for micro energy harvesting.

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