



Master of Science

Epitaxial growth of lead-free (K, Na)NbO₃ – based thin films by rf sputtering and pulsed laser deposition

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Epitaxial growth of lead-free (K, Na)NbO₃ – based thin films by rf sputtering and pulsed laser deposition

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Abstract

Piezoelectric devices, since the first discovery of direct piezoelectric effect by Pierre Curie and Jacques Curie in 1882 [1], have been playing major roles in many industrial fields, medical diagnosis, medical treatment, etc [2-4]. Thin-film piezoelectricity is one of the key factors for MEMS technologies with novel applications in piezoelectric transducers, pyroelectric IR sensors, actuators, electro-optical devices, and nonvolatile ferroelectric memories [5]. The most successful and practical piezoelectric materials have been the lead-based type such as PZT or Pb(Zr,Ti)O₃ due to the exceptional electromechanical properties [6-8]. However, since most lead-based materials contain higher than wt. 60% Pb, they are considered toxic, and poses a serious threat to the environment. Consequently, regulations of hazardous substances (RoHS) have been established by the European Union to restrict their usage in electronic devices [6]. Many studies have been carried out in finding the alternatives, and among the most promising candidates are $K_{0.5}Na_{0.5}NbO_3$ (KNN)-based materials, with KNN ceramic's piezoelectric strain coefficient $d_{33} = 416$ pC/N comparable to that of PZT-based. In the meantime, KNN-based ceramics have been considered to possess the closest characteristics with respect to PZT [8-12].

As lead-based materials had been continuously researched, developed and optimized for several decades since it was first discovered in 1950s until the numerous reports of its toxicity [6], KNN based materials are now constantly focused and improved. KNN thin films have the potentials for great applications, especially in medical science for being biocompatibility. Extensive efforts have been made to fabricate both KNN and KNN-based thin-films, however their qualities and piezoelectric properties are much inferior in compared to those of their ceramic counterparts. Up until recently, reports on d₃₃ of all KNN-based thin-films are in the range of 40-74 pm/V, regardless of the fabricating process [9, 13-17]. The significant inferiority of thin-films KNN-based is reported to originate from the severe volatility of alkaline elements during the deposition process, leading to the deviation from compositional stoichiometry, the formation of secondary phases, and consequently high leakage current density. Many studies have been carried out to overcome the high leakage problem of KNN and KNN-based thin-film. Kizaki *et al.*,[18] in 2006,

reported the improvement in leakage control in Mn-doped single crystal KNN. Kondo *et at.*,[19] and Lee *et al.*,[20] respectively reported on the improvement of chemically deposited KNN-based thin-films by Mn-doping. However, the drawback of chemical synthetic route involves early aging, formation of micro-cracks across the film, and the necessity of post annealing treatment for the crystallization of KNN-based film. Lopez-Juarez *et al.*,[21] and Wang *et al.*,[22] reported the successfully fabricated Mn-doped KNN ceramic, in 2015, with improvements in dielectric, ferroelectric and electrical properties. Consequently, this has opened an opportunity for physically fabricated Mn-doped KNN film.

The scope of this work, firstly, involves successful synthesis of high density and good quality Lead-free Mn-doped Potassium Sodium Niobate (K,Na)NbO₃-based ceramic targets. Next, Mn doped KNN thin films are grown by using the rf magnetron sputtering and pulse laser deposition (PLD). Insight studies on the influence of thin-film fabrication parameters, effect of substrate temperature, substrate orientation, O₂ partial pressure, post deposited thermal treatment and protecting Al₂O₃ layer will be carried out. Investigation and analysis on structural phases, grain morphologies, electrical properties and ferroelectric properties such as dielectric permittivity, ferroelectric polarization, and piezoelectric responses, and electrical leakage current will be carried out for confirming the reduction in leakage current density and good piezoelectric properties. Finally, the applications of KNN-based films for the sensors, the energy harvesters, and energy storage devices are addressed, and current challenges and prospects for future work will be discussed.

Keywords: thin films, ferroelectric, piezoelectric, lead-free, Mn doped (K,Na)NbO₃-based, epitaxial, hysteresis.

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Chapter 1. Introduction

1.1. Dielectrics

In the physical world, there are many materials are called dielectric materials (or possess dielectric properties) such as wood, glass, chalk, plastics, papers, or even distilled water. The unique property of an ideal dielectric is that it does not contain free charges which can move from molecule to molecule. The charges are, instead, tightly bound to the atomic or molecular structure, however, the charges can still travel a small distance from their binding centers. If an electric field is applied to an ideal dielectric material, positive and negative charges tend to move in opposite direction in response to the applied field, henceforth, creating a separation between two opposite charged centers [23, 24]. This separation is described as the dipole moment **p**, defined as the product of charges and distance between the charges. The accumulation of all dipole moments in a unit volume Δv generates a polarization **P**.

$$\mathbf{P} = \lim_{\Delta \mathbf{v} \to 0} \frac{1}{\Delta \mathbf{v}} \sum_{i} \mathbf{p}_{i}$$
(1.1)

In a dielectric material, the induced polarization is proportional to the external electric field **E**, and can be expressed as:

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \tag{1.2}$$

With ε_0 as the permittivity of vacuum and χ is the dielectric susceptibility. Dielectric displacement **D** can be described by:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi) \mathbf{E} = \varepsilon_0 \varepsilon_r \mathbf{E}$$
(1.3)

where $(1 + \chi)$ is the relative permittivity ε_r , corresponding to the degree of polarization in the dielectric materials.

1.2. Ferroelectrics and piezoelectrics

1.2.1. Piezoelectrics

Piezoelectricity is a physical phenomenon of electric charges accumulating in certain materials when being applied with a mechanical stress. It was first discovered by Pierre Curie in 1880 [1]. It is the accumulation of electric charges on the surfaces of certain crystals when external mechanical stress is applied. Materials that display a piezoelectric effect are called piezoelectrics.

The piezoelectric effect is described as a linear electromechanical interaction between mechanical and electrical state in solid materials, in addition, the reverse effect is also applied. The origin of the piezoelectric effect is closely related to the occurrence of electric dipole moments in solids. The latter may either be induced for ions on crystal lattice sites with asymmetric charge surroundings or may directly be carried by molecular groups [23]. The dipole density or polarization can be calculated for crystals by adding up the dipole moments per volume of the crystallographic unit cell. Dipoles near each other tend to be aligned in regions called Weiss domains. The domains are usually randomly oriented but can be aligned using the process of poling, by which a strong electric field is applied across the material, usually at elevated temperature [23].

The most important aspect of piezoelectric effect is the change of polarization \mathbf{P} when being applied a mechanical stress. This might be resulted from either by a reconfiguration of the dipole-inducing surrounding or by reorientation of molecular dipole moments under the influence of the external stress. Piezoelectricity occurs in a variation of the polarization strength, its direction or both, with the details depending on, firstly, the orientation of \mathbf{P} within the crystal, secondly the crystal symmetry, and thirdly the applied mechanical stress. The difference in \mathbf{P} manifests as a variation of surface charge density upon the crystal faces. However, piezoelectricity is not caused by a change in charge density on the surface but by dipole density in the bulk. The polarization vector \mathbf{P} is mathematically described by:

$$\mathbf{P}_{\mathbf{i}} = \mathsf{d}_{\mathbf{i}\mathbf{j}\mathbf{k}}\sigma_{\mathbf{i}\mathbf{j}\mathbf{k}} \tag{1.4}$$

The parameter d_{ijk} is known as piezoelectric moduli, constitute a tensor of the third order totaling $3^3 = 27$ components. According to classical theory, 18 piezoelectric moduli are necessary to describe piezoelectric properties. The number decreases with the increasing symmetry of the crystal. Of the 32 crystal classes, 21 are non-centrosymmetric (not having a center of symmetry), and of these, 20 exhibit direct piezoelectricity (the 21^{st} is the cubic class 432). Ten of these represent the polar crystal classes, which show a spontaneous polarization without mechanical stress due to a nonvanishing electric dipole moment associated with their unit cell and which exhibit pyroelectricity. Nevertherles, If the dipole moment can be reversed by the application of an electric field, the material is said to be ferroelectric [23].

1.2.2. Ferroelectrics

Ferroelectric materials exhibit spontaneous electric polarization due to the atomic displacement of the body-centered atom (in the perovskite structure), coming from the balance between the long-range Coulomb force and short-range interaction, and this character can be reversed by the application of external electric field. Thus, all ferroelectrics are pyroelectric with additional feature of having natural reversible electric polarization. Ferroelectric crystals possess regions with uniform polarization called ferroelectric domains, in which dipoles are aligned in the same direction. The boundaries between adjacent domain are called ferroelectric domain walls (or in shortened form domain walls).

Normally, a ferroelectric material is in a multi-domain state due to the tendency of lowest of total electrostatic and elastric energies. When an electric field is applied, domains can be switched, and the polarization aligned with the direction as close as possible to the direction of the applied field. This is one of the most important properties of ferroelectric materials, and the electric field-induced domain switching process can be described by the hysteresis loop (P-E loops). The hysteresis is related to the influence of the magnitude and direction of the external field on the spontaneous polarization, domains switching, domain wall growth ability, and accompanied by a change of strain.

The polarization reversal is described through a ferroelectric hysteresis shown in **figure 1.1.** As the applied electric field strength is increased, the domains start to align in the positive direction, rapidly increase the polarization. At very high field level, the polarization reaches a saturation value. The polarization does not fall to zero even if the external field is removed, some of the domains remain aligned in the positive direction, preserving the remnant polarization P*r*. The material cannot be completely depolarized until a field of magnitude Ec is applied in the opposite (negative) direction. The external field needed to reduce the polarization to zero is called the coercive field strength and depicted as Ec. If the opposite field is further enhanced, the direction of polarization flips, and hence a hysteresis loop is obtained. The value of the spontaneous polarization P*s* is obtained by extrapolating the curve onto the polarization axes (B-E line).



Figure 1.1. A polarization versus electric field (*P-E*) hysteresis loop of a typical ferroelectric material.

Phase transition is also very important character in ferroeletric materials, depending on how the polarization changes. Commonly, as temperature rises, bulk polarization in ferroeletric materials decreases and become zero abruptly when temperature reach Curie temperature $T_{\rm C}$ value. This is phase transition similar to that in ferromagnet when temperature is above its Curie temperature or in solid at above melting point. When the temperature decreases through the Curie temperature, a ferroelectric crystal undergoes a structural phase transition from a paraelectric phase to a ferroelectric phase. When the temperature is above $T_{\rm C}$, the crystal does not exhibit ferroelectricity. On the other hand, when the temperature is below $T_{\rm C}$, the crystal exhibits ferroelectricity [23].

1.3. Perovskite structure (ABX₃)

Among the most common structures of ferroelectric materials is the perovskite structure, described by the chemical formula ABO₃, where the valence of the A site can be +1, +2, or +3 and the valence of the B site can be +3, +4, +5, or +6. The corners and body-centered positions of the unit cell are occupied by A-site and B-site cations, respectively, while the O²⁻ ions are located on the face-centered positions **figure 1.3**.



Figure 1.2. Schematic of a perovskite structure ABO₃.

An ideal perovskite material has a cubic structure. It can also be described as consisting of BO₆ octahedra sharing corners with intermediate A-site cations in 12-fold coordination sites. A cubic perovskite shows neither ferroelectric nor piezoelectric properties because of the coincidence of positively and negatively charged centers. The paraelectric cubic structure can evolve into tetragonal, orthorhombic, or rhombohedral with lower symmetry, originating from

thermal- or stress-induced lattice distortions. **Figure 1.3** shows a schematic of ferroelectric hysteris loop and unicell of a typical perovskite crystal. Significant perovskite materials involve lead titanate (PbTiO₃), lead zirconate titanate PZT, barium titanate BaTiO₃, strontinium titanate (STO), potassium niobite (KNbO₃), sodium niobite (NaNbO₃), and potassium sodium niobate (KNN) [23]



Figure 1.3. A typical ferroelectric hysteresis loop and unit cell of ABO₃ type perovskite structure.

1.4. Lead zirconate titanate PZT

PZT is by many standards the most successful and leading piezoelectric and ferroelectric material, allowing numerous practical applications. PZT-based materials are used in components of most commercial ultrasound tranducers, ceramic capacitors, STM/AFM actuators, FeRAM chips, infrared imaging sensors, etc. The excellent properties are the high longitudinal electromechanical coupling coefficient (k_{33}) and piezoelectric coefficient (d_{33}) [6, 7, 23-25]. PZT, like other piezoelectric materials, possess ABO₃ structure, however particularly easy to change its composition. The superior compositional adjustability originates from its wide range of possible B-site stoichiometry and substituents [23]. Highest achieved piezoelectric coefficients $d_{33} \sim 2500$ pC/N was reported so far [6], with electromechanical coupling factor k_{33} of approximiate 95% in "33" mode.

The exceptional properties of PZT are from its morphotropic phase boundary (MPB). After being poled, where its temperature is raised past its Curie point, ferroelectric domains align and create a remanent polarization. The phase transitions, from rhombohedral (R) to tetragonal (T) to cubic (C), undergo at certain temperature, depending on the molar percentages between its two component PbZr_xO₃ and PbTi_{1-x}O₃. In the region of around 45-52% PbZrO₃ and 48-50% PbTiO₃, the PZT structure, after polling, undergoes the full phase transitions from R to T to C, and is called morphotropic phase boundary; hence produce the enhancement in piezoelectric properties. Noheda 1999 discovered that at MPB compositions, PZT actually exhibits monoclinic phase, bridging the transition between the R and T phases [6]. The monoclinic symmetry allows the ferroelectric polarization vector to rotate continuously in plane, leading to the enhanced polarization and strain.

1.5. Lead-free (K,Na)NbO₃ materials

Even with the all amazing performance and quality of PZT materials, tremendous environmental pollution, human health's harm are being generated by the disposal of waste lead-based electronic products. All lead-contained materials are now deemed as hazardous substances, and there required alternatively safer solutions. KNN emerges as one of the best candidates for lead-free and environmentally friendly piezoelectric material. Good piezoelectric performance and relatively high Curie temperatures $T_{\rm C}$ promise the high potential of KNN. Highest reports on KNN-based piezoelectric materials give d₃₃ of ~ 700 pC/N and planar coupling coefficient k_p of 61% [7]. The figures are still a long way to reach the level of top of the art PZT-based materials, however it is comparable to the average polycrystalline PZT-based materials.

Pure KNN is a solid solution of ferroelectric KNbO₃ and antiferroelectric NaNbO₃. Upon heating, the KNbO₃ undergoes the following sequence of phase transitions: rhombohedral orthorhombic at -50 °C, orthorhombic tetragonal at 220 °C, and tetragonal paraelectric cubic at 434 °C [26]. The phase transition sequence of the NaNbO₃ upon heating is: ferroelectric monoclinic, antiferroelectric orthorhombic at -55 °C, antiferroelectric orthorhombic paraelectric orthorhombic at 355 °C, paraelectric orthorhombic paraelectric pseudotetragonal paraelectric pseudotetragonal at 430 °C, paraelectric tetragonal paraelectric pseudotetragonal at 470 °C, paraelectric pseudotetragonal paraelectric tetragonal at 530 °C, and paraelectric tetragonal paraelectric tetragonal paraelectric pseudotetragonal paraelectric pseudotetragonal paraelectric tetragonal at 530 °C, and paraelectric represented tetragonal paraelectric tetragonal at 530 °C, and paraelectric tetragonal paraelectric tetragonal at 470 °C, paraelectric pseudotetragonal paraelectric tetragonal at 530 °C, and paraelectric represented tetragonal paraelectric tetragonal at 530 °C, and paraelectric tetragonal paraelectric tetragonal paraelectric tetragonal paraelectric pseudotetragonal paraelectric pseudotetragonal paraelectric pseudotetragonal paraelectric tetragonal at 530 °C, and paraelectric properties when Na was substituted by 50 mol% K, leading to the well-known composition K_{0.5}Na_{0.5}NbO₃. **Figure 1.4** shows the phase diagram of KNN, published by Li *et al.* [27] based on the work of Jaffe *et al.* [24] and Ahtee *et al.* [23].



Figure 1.4. K_xNa_{1-x}NbO₃ phase diagram. The symbols are P: paraelectric, F: ferroelectric, A: antiferroelectric, C: cubic, T: tetragonal, O: orthorhombic, R: rhombohedral, MON: monoclinic and M: multiple cells [23].

Normally, KNN manifests a polymorphic phase boundary (PPB) [10]. However, precisely calibration of the composition of KNN yield the desired MPB, similar to that of PZT systems. As shown in phase diagram, around the vicinity of 50% NaNbO₃, MPB appears and provides the highest remnant polarization. The MPB exhibits rhombohedral to orthorhombic ($T_{\text{R-O}}$), orthorhombic to tetragonal ($T_{\text{O-T}}$) and tertragonal to cubic (T_{C}) transitions from low temperature to high temperature.

1.6. KNN thin film, promises and challenges

Nano technology has been playing very important roles in modern technologies and industries. Since piezoelectric materials possess the unique property of electromechanical coupling, they provide excellent sensors and actuactors. The ability to generate electric dipoles from elastic strain and to produce mechanical deflections from applied electric field assure piezoelectric the dominant role in numerous sensing and actuating applications [2].

PZT remains the main materials, however, recent reports show that KNN can generate comparable power densities to those of PZT energy harvester [28]. One reported that 3 μ m KNN and PZT thinfilms with the same fabrication condition via rf sputtered with annealing temperature of 600 °C give very close performance [6]. The relative dielectric constant (ε_r) of the sputtered KNN and PZT films was 744 and 872, respectively. The tranverse piezoelectric coefficients, e_{31} of the KNN film approximate 11 C/m², and d_{31} varying between -96.3 to - 138.2 pC/N, almost the same with what PZT film achieved [7]. The cantilever made from both materials yield 1.1 μ W and 1.0 μ W average power output for KNN and PZT, respectively [6]. Biomedical field also see a lot of thin film applications from piezoelectric materials, however, lead-based materials are not suitable due to their high toxicity [29]. KNN has been proven to be biocompatible and safe for use as implants, with suggestion of being pressure sensor for pacemakers [3].

There are a lot of promises and potentials for KNN thinfilm, however, many challenages also present. The biggest issue of KNN materials is the volatility of alkaline elements during fabrication process, leading to unachievable MPB composition ratio, and much inferior performance. Alkaline ion vacancies and oxygen vacancies in KNN thin film are generally formed due to the volatilization of alkali elements [22]. It is reported that the volatility of K⁺ and Na⁺ would leave oxygen vacancies in the KNN film crystal structure. In turn, the oxidization of those oxygen vacancies leads to the forming of holes as charge carrier [30].

$$V_0^{"} + \frac{1}{2}O_2 \to O_0 + 2h^{"}$$
 (1.5)

where $V_0^{"}$ and O_0 denote the oxygen vacancy and oxygen at normal site, respectively; h⁻ is associated with free hole-carrier. Introducing Mn²⁺ would lead to the following reactions:

$$Mn^{2+} + h^{\cdot} \to Mn^{3+} \tag{1.6}$$

$$Mn^{3+} + h' \to Mn^{4+} \tag{1.7}$$

Therefore, with the oxidation of Mn ion into higher valance state would reduce the concentration of hole-carrier in the film and hence the leakage current as well. **Figure 1.5** shows that the schematic of Mn doping in KNN structure. However, this is what reported to happen in Mn-doped KNN ceramic as well as the chemically deposited KNN-based film, where Mn is doped directly in the deposited solution. It has yet been investigated the role that Mn doping play during the sputtering process from Mn-doped KNN target. Other reports showed much lower K concentration in compared to Na concentration in KNN films deposited by rf sputtering. In other word, the formation of holes can decrease the amount of oxygen vacancies but results in the increase in leakage current [13].

It has been confirmed experimentally that there are normally non-ferroelectric interfacial layers at the interfaces with the (metal) electrodes resulting in the detrimental effects on the ferroelectric functionality of thin films. On the other hand, it is possible that this interface layer can be utilized constructively to improve the reliability of a ferroelectric capacitor under certain circumstances by-electrode charge injection is blocked by this layer. arguably, this layer should not interfere with polarization switching otherwise ferroelectric switching would become problematic. In this sense, it would be ideal to develop an interposed tunnel switch layer that turns on only during ferroelectric domain switching but off immediately after ferroelectric switching, and remains in the off state during ferroelectric non-switching to prevent by-electrode charge injection during the retention time [31]. The switch can be a highly insulating dielectric layer, such as a thin Al_2O_3 layer, as in this study.



Figure 1.5. Schemactic of Mn doping in KNN structure.

Chapter 2. Experiments

2.1. Experimental methods

2.1.1. Ceramic targets fabrication

a. Fabrication of rf sputtering ceramic targets

0.5 mol% Mn doped KNN (KNMN) ceramic targets were prepared by mixing the high purity oxides, Na₂CO₃, K₂CO₃, MnO₂, and Nb₂O₃ in desired molar ratio using the conventional solid-state reaction method.

The mixture underwent wet ball-milling for several hours at 380 rpm in isopropanol using 3mm diameter Y_2O_3 stabilized zirconia milling media prior to calcination. After milling, the slurry was further washed with isopropanol, separated from milling media through a sieve and solution removed by drying at 100 °C for 12 hours. Then the dried material was crushed, sieved through a 150 microns mesh and undergone calcination at 700 °C for 5 hours. Calcination causes the constituents to interact by inter-diffusion of their ions and reduces the extent of the diffusion that occur during sintering in other to obtain a homogeneous body. This process is repeated twice.

The calcined powder was then uniaxially pressed into a cylindrical shap in a steel mold at 6 tons pressure. The sintering was at 1120 °C for 4 hours in ambient atmosphere. Sintering's purpose is to convert compacted powder into a denser structure of many particles joined together via grain boundaries. The mechanism lies in the reduction of surface energy by elemental diffusions from the interior of grains along the grain boundaries to the adjacent empty space which will eventually be filled. Grain boundaries serve as vacancy sinks because of their intrinsic disorder. The whole ceramic process is presented in the schematic in **figure 2.1.**



Figure 2.1. Schematic of fabrication process for rf sputtering ceramic targets.

b. Fabrication of PLD ceramic targets

In addition, the effect of excess K and Na on the crystal structure and electrical properties of the film have not yet been sufficiently investigated. In order to avoid the deficiency of 'K' and 'Na' ions at high sintering temperature, an excessive amount of Na₂CO₃ and K₂CO₃ powders were added initially, before ball milling, to maintain the stoichiometry of the target. For PLD target preparation, a 0.5 mol% Mn doped KNN ceramic contained about 6 mol% excess K and 4 mol% Na for the compensation of loss element due to volatility during the deposition [30, 32-35] was prepared by mixing the high purity oxides. One-inch diameter KNMN target was sintered at 1060 °C for 2 h. The final target density was 4.1 g/cm³. A KNMN ceramic target with Na- and K- enriched composition easily reform NaOH and KOH hydroxides. To avoid the formation of NaOH and KOH, the sintered target was kept in the electric furnace at 100 °C. After the NKN target was mounted to the PLD chamber, the vacuum state was maintained in order to avoid the moisture.

2.1.2. (K,Na)NbO₃-based thin films: rf magnetron sputtering

2.1.2.1. Substrate preparation

The substrate employed in thin study is coated on the *p*-type silicon (100). The coatings were accompanied by 20nm SiO₂, 50nm Ti and 150nm Pt (111), the multilayer sandwich structure is abbreviated by Pt/Ti/SiO₂/Si (GMEK Inc., Korea). The substrate was cleaned with ultra sonic cleaner (Branson 1210, Bransonic, U.S.A) before deposition and summarized the cleaning conditions in the table 2.1.

Beaker Number	Cleaning Reagent (Temperature: 75 °C)	Duration
А	Distilled Water	5 minutes.
В	Ethanol	5 minutes.
С	Isopropanol	5 minutes.

Table 2.1. Cleaning procedures for Pt/Ti/SiO₂/Si substrate

2.1.2.2. Thin films fabrication

KNMN was fabricated by reactive rf-magnetron sputtering method using the target made previously in a home-built system with schematic shown in **figure 2.2**. The films were deposited on the $Pt(111)/Ti/SiO_2/Si(100)$ substrated in Ar and O₂ mixture environment at 10/4 ratio. Substrate temperature was set at 500 °C, and placed directly opposite from the target with substrate-target distance of 3.5 cm. Base pressure was achieved with diffusion vacuum system up to 10^{-6} Torr. Working pressure was maintain at 10mTorr through a contiuous injection of gas mixture into the chamber via a four channels mass flow air controller. The sputtering power was kept at 80W, and sputtering duration was 4 hours. The sputtering condition is summarized in **table 2.2**.

Substrate	Pt(111)/Ti/SiO ₂ /Si(100)
Rf-power	80 W
Substrate temperature	500 °C
Base pressure	10 ⁻⁶ Torr
Working pressure	10 mTorr
Ar/O ₂ ratio	10/4
Sputtering duration	4 hours
Substrate-target distance	3.5 cm

Table 2.2. Rf sputtering deposition condition

HEATER SUBSTRATE SHUTTER TARGET MFC RF-GENERATOR DIFUSION PUMP

Figure 2.2. Schematic diagram of the rf sputtering system.

After deposition, the thin films were annealed at 750 $^{\circ}$ C using rapid thermal annealing furnace (RTP-1200, Nextron) at a rate of 10 $^{\circ}$ C/s for 5 minutes by using oxygen partial pressures. The purpose of post annealing is to improve crystallization and quality. The annealing condition is shown in **table 2.3**, and the annealing system is shown in **figure 2.3**.

Annealing temperature (°C)	750
Annealing time (min)	5
Annealing ambient	O_2
Gas flow rate	1 litre/min

Table 2.3. Annealing condition for deposited films



Figure 2.3. Schematic diagram and picture of the rapid thermal annealing system.

2.1.3. (K,Na)NbO₃-based thin films: pulse laser deposition

2.1.3.1. Substrate preparation

 $SrTiO_3$ (STO) (001) substrates were prepared using a deionized (DI) water, BHF (buffered hydrofluoric acid) etching and subsequent annealing. Firstly, using the tweezers to soak STO substrates in the DI water container (beaker) for 30 minutes and then transfer the STO substrates into the BHF carefully. Let the sample etch for 1 minutes and 30 seconds. When the BHF etch is complete, put the STO substrates into a tube furnace at 900 °C in 4 hours. After deionized-water, BHF etching procedure and a step thermal-annealing, topography measured

by atomic force microscopy shows the evolution of substrates from a rough to step-terraced surface structure. The surface step terraces can be clearly resolved in the AFM images.

2.1.3.2. Thin films fabrication

Pulsed laser deposition uses energy from a laser source to excite the target surface. This energy results in electronic excitation, heating and physical ablation of the surface atoms/molecules. The atoms/molecules which are ablated from the surface then form a plasma plume which is directed to the substrate where deposition may occur. The physical and chemical processes which occur at both the target and substrate surface are complex and depend on the target chemistry, laser energy, laser intensity, distance from the target to substrate and the carrier gas in the chamber (often PLD is performed under vacuum but may deliberately contain oxygen if oxidized surfaces are desired). By controlling these parameters, the species arriving at the substrate may vary between individual atoms, small molecules and molten globular clusters. The topography of the resulting thin film may then vary between relatively smooth and micro-roughened surfaces exhibiting "island" formations [36]. In fact it is conceptually and experimentally simple. Figure 2.4 shows a schematic diagram of a pulsed laser deposition apparatus. To avoid interaction with the ambient atmosphere, both target and substrate are placed into a vacuum chamber. The focused pulsed laser beam enters the chamber via a suitable window. Some devices to control the pressure, to insert a gas, to heat the substrate, or to control the substrate temperature are generally used.



Figure 2.4. Schematic diagram of a pulsed laser deposition apparatus.

KNMN thin films were synthesized using pulsed laser deposition system at different substrate temperatures. Initially, the PLD chamber was vacated until a base pressure of 7×10^{-7} Torr was reached. Then, the oxygen gas was inserted into the chamber to maintain a pressure of 20 mTorr inside the chamber. The LSMO target (La_{0.7}Sr_{0.3}MnO₃) were ablated inside the PLD chamber by focusing KrF Excimer Laser (wavelength, = 248 nm) on the target surface at a power of laser of 0.83 W and reiteration rate of 5 Hz. The separation between the target and substrate was set to be 3.5 cm (**Table 2.4**). The bottom LSMO film was deposited at 650 °C. Thin films of KNMN were continuously deposited by ablating the respective ceramic target. The power of laser was set as 0.43 W and the repetition rate was kept to be 5 Hz. The working gas pressure was maintained at 100 mTorr. The consequence of substrate's temperature on the growth of KNMN thin films on STO substrates was studied. The substrate temperature was varied from 520 °C to 600 °C during deposition. KNMN samples was annealed inside the PLD chamber at 100 Torr oxygen atmosphere.

Substrates	STO
Laser	Excimer KrF laser
Power of laser	0.43 W
Target	K _{0.53} Na _{0.52} Mn _{0.006} Nb _{0.994} O ₃ [1-inch diameter]
Ambient gas	100% oxygen
Deposition temperature	From 620 °C to 600 °C
Deposition pressure	100 mTorr
Target to substrate distance	3.5 cm
Repetition rate	5 Hz

Table 2.4. PLD deposition parameters

2.1.4. Top electrode deposition

In order to study the electrical properties of the KNMN thin films, the Pt capacitors with contact area of 2.5×10^{-4} cm² were deposited by dc sputter coater (Cressington 108, Cressington, Inc., USA) on the surface of thin films through a shadow mask. Argon was used as the sputtering ambient, the sputtering pressure and time were 6×10^{-2} mbar and 10 minutes, respectively. After that of Pt top electrode deposition, the MFM (metal/ferroelectric/metal) capacitor structure was built up as schematically shown in **figure 2.5** and **figure 2.6**. These films were annealed at 550 °C for 5 minutes in oxygen atmosphere using a tube furnace by direct insertion (as shown in the **figure 2.7**). **Table 2.5** shows the evaporation condition of Pt top electrode for ferroelectric properties measurement.

Evaporation Pressure	0.06 mbar
Evaporation Temperature	25 °C
Current	30 mA
Evaporation Time	10 min
Top electrode Area	$2.5 \text{ x } 10^{-4} \text{ cm}^2$

Table 2.5. Evaporation conditions of the top electrode



Figure 2.5. The MFM (metal/ferroelectric/metal) structure of KNMN thin films fabricated by rf sputtering.







Figure 2.7. Schematic diagram of tube furnace system.

2.2. Characterization

2.2.1. Crystal structure and surface morphology

The phase and orientation of the thin films were determined by the standard x-ray diffraction studies (XRD RAD III, Rigaku, Japan). The Cu-K α radiation of x-ray through Nickel field was utilized to scan the specimen at accelerating voltage of 30kV and current of 20mA, the scattering angle 2 θ ranging from 20° to 60°.

The surface and cross-sectional morphology was studied by scanning electron microscopy (SEM-EDS, S-4200, Hitachi, Japan). SEM has a combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation. The magnification and scanning radius, in this study, were set to 5×10^4 times and 20m respectively.

X-ray photoelectron spectroscopy (XPS) measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material.

2.2.2. Piezoelectric properties

In order to study the electrical properties, Pt top electrodes with contact area of 2.5×10^{-4} cm² were deposited by dc sputter coater (Cressington 108, Cressington, Inc., U.S.A) on the surface of thin films through a shadow mask. Argon was used as the sputtering agents, the sputtering pressure and time were 6×10^{-2} mbar and 10min respectively, the input current was 30mA.

After that of Pt top electrode deposition, the MFM (metal/ ferroelectric/metal) structure was built up as shown in **figure 2.5** and **figure 2.6**. Polarization-field (*P-E*) or Displacement-field (*D-E*) loops of the ferroelectric samples was measured using the Sawyer-Tower circuit. In general, *P-E* measurement of thin film using RT66A (Ferroelectric tester, Radiant Technology, U.S.A) was attained with the Sawyer-Tower and the virtual ground mode.

The dielectric and capacitance-voltage (*C*-*V*) studies were conducted with a HP4192A LF Impedance Analyzer (Hewlett Packard, Inc., U.S.A) which was controlled by a computer. In the frequency range of 10 kHz ~ 13 MHz, the capacitance was measured as a function of small voltage which ranged from 10mV to 100mV.

Current-voltage (*I-V*) characteristic, as shown in **figure 3.4**, was studied with a Keithley-237 electrometer (Keithley Instruments, Inc., U.S.A) which was also controlled by a computer. The furnace and temperature controller were included in the assembly to measure the temperature dependance, the metal envelop works as a shield to surmount external electric noise.

Chapter 3. Results and discussions

- 3.1. Fabrication of (K,Na)NbO₃-based thin films using rf magnetron sputtering
- 3.1.1. Morphology measurements



Figure 3.1. XRD patterns acquired over the 2θ range of 20–50° for KNMN film (a) RTP annealed at 750 °C, in 5 minutes (b) As-grown (500 °C, 4h), (c) AFM image of as-grown KNMN film (500 °C, 4h), and (d) AFM image of RTP annealed KNMN film at 750 °C, in 5 minutes.

Figure 3.1.(a), (b) shows the XRD patterns of 0.5 mol% Mn-doped KNN films with different treatment process. In this figure, the as-grown KNMN film shows single perovskite structure under orthorhombic symmetry with (110) prefer orientation. No secondary phase was observed, indicating the possibility of Mn totally subsite into the lattice of KNN perovskite crystal structure [37]. However, the RTP annealed KNMN film shows the appearance of little signal corresponding to secondary phases, together with enhanced signal from the previous orientations, indicating the better crystallization but with introduction of new crystal formation due to reaction of film with oxygen during rapid thermal treatment process. The diffusion of oxygen into KNMN lattice would lead to either reaction of Nb⁴⁺ becoming Nb⁵⁺ or the oxidation of ion-oxy vacancies into oxygen at deficient site and holes. Suggesting the thermal treatment in oxygen atmosphere could be both good and bad in improving leakage of the film. Appropriate temperature and treatment time needed to be carefully controlled in order to effective improving electrical properties. However, the introduction of Mn would eliminate the forming of holes, and hence effective improving leakage current density of KNMN film. Figure 3.1.(c), (d) show the AFM scanning of the surfaces of Mn-doped KNN films. The annealed films' surfaces were uniform with overall roughness at 8.7 nm, referring to a good crystallization state. The films' thicknesses were measured to be of around 600 nm using Scanning Electron Microscopic technique.

3.1.2. X-ray photoelectron spectroscopy

The XPS spectra were taken to reveal the chemical states of the films, checking the effect of Mn doping upon the crystal of KNN and whether Mn entered the lattice structure. The binding energies of sodium, potassium, niobium, oxygen, and atomic elements ratio were investigated. **Figure 3.2.(a)** shows the atomic ratio of all elemental species in the films with respect to etching time and depth of scan. Mn signal is around 0.5%. The ratio of Na and K elements are equivalent at 4% of total amount. The distribution of Na and K elements are uniformed with respect to the depth of film. It is clearly observable that for the RTP treatment sample, the uniformity is of both surface and deep inside the thickness of the film. Ratio of (Na+K)/Nb of the films are at 20%, which is equivalent to other reports

on KNN-film rf sputtered under 30% partial oxygen pressure [38]. In addition, ratio in concentration of Na/(Na+K) is approximate 0.533, promising the MPB effect. It is reported by Weng *et at*, 2016 that the main defects in KNN-based materials come from the volatility of Na₂O and K₂O, and the effect of the former is greater than the later [39]. This would lead to the un-equality in concentration of NaNbO₃ and KNbO₃ in the structure, consequently the occurrence of secondary phases happened. In **figure 3.1.(a)**, however, the concentration of Na is even higher than that of K, suggesting the effectiveness of Mn doping in lowering volatility of the Na₂O and K₂O, and keeping the balance of the two species at the same time.

Figure 3.2.(b), (c) shows the XPS spectra for all the element of the as-grown and annealed KNMN films, except for Mn, where the Mn2p scan was undetectable. The background correcting was conducted from the as obtained XPS spectra, using the Shirley algorithm [40], and the chemically different species' signals were resolved using Gaussian fitting procedure. The O1*s* spectrum of the films show two convolutions with binding energies at 530.7 eV and 532.5 eV, corresponding to oxygen mostly in lattice position (90%) and oxygen at ion-oxy vacancy cites (deficient site) (10%), respectively. Higher binding energies of oxygen at deficient sites indicate the corresponding higher electrochemical potential, suggesting the lacking in oxygen at such sites.



Figure 3.2. (a) Relative concentration percentage of KNMN film's species at consecutive etching level, and (b) XPS of elemental profiles for as-grown KNMN film, (c) RTP annealed film at 750 °C.

The Nb 3*d* scans show three different spin orbital pairs, corresponding to three different Niobium species in the KNN matrix. The Nb 3*d*_{5/2} peak corresponding to NbO_δ state (where $1 < \delta < 2$) at 203.36 eV weight 38% of total Nb signal. Nb 3*d*_{5/2} peak at 204.69 eV weight 17% totally and is corresponding to the lacking oxygen state of the perovskite structure. Significantly, the Nb 3*d*_{5/2} peak at 206.80 eV weight 45% totally and is corresponding to the true Nb in KNN matrix (or Nb-KNN) [38]. Hence, this indicates Nb did not attain completely desirable state Nb₂O₅ of KNN perovskite structure. Instead, the presence of lower valence Nb species suggest the likeliness of acquiring secondaries Nb phase to compensate the loss of alkaline species due to the low ratio between concentration of (Na+K) and Nb. Moreover, the lower in concentration of Nb⁴⁺ (Nb^{*}) to Nb⁵⁺ (Nb^{*}) in RTP sample could be explain through an redox reaction [41]:

$$\frac{1}{2}O_2 + 2Nb' + V'' \to 0^* + 2Nb^*$$
(3.1)

where V'' designate oxy-ion vacancy site and O* is the O^{2-} at the oxy-ion vacancy site. This equation explains the forming of oxygen at ion-oxy vacancy site as well as the turning of Nb⁴⁺ into Nb⁵⁺ (or KNN–Nb) due to the reaction with atmosphere oxygen, or the diffusion of atmosphere oxygen into the lattice.

The K $2p_{1/2}$ peak at 295.18 eV and K $2p_{3/2}$ peak at 292.48 eV binding energies are corresponding to K in KNN perovskite structure [42]. This is first report ever achieve mono chemical species of potassium in KNN-based films [9, 30, 43-45]. Consequently, no secondary phase of potassium would be presented, preserving the equality between ferroelectric phase and anti-ferroelectric phase in the MPB nature of this materials. It is reported that the volatility of K₂O and Na₂O would leave ion-oxy vacancies in the KNN film crystal structure. In turn, the oxidization of those oxygen vacancies leads to the forming of holes as charge carrier [30, 41].

$$V'' + \frac{1}{2}O_2 \to O^* + 2h^{-1}$$
 (3.2)

where h is associated with free hole-carrier. Since the Nb⁴⁺ was is completely turned into KNN-Nb, the forming of hole carriers is high and hence leakage current density is equivalently large. Introducing Mn^{2+} would lead to the following reactions [30, 41]

$$Mn^{2+} + h' \to Mn^{3+}$$
 (3.3)

$$Mn^{3+} + h^{\cdot} \to Mn^{4+} \tag{3.4}$$

Therefore, with the oxidation of Mn ion into higher valance state would reduce the concentration of hole-carrier in the film and hence the leakage current as well. However, this is what reported to happen in Mn-doped KNN ceramic as well as the chemically deposited KNN-based film, where Mn is doped directly in the deposited solution. It has yet been investigated the role that Mn doping play during the sputtering process from Mn-doped KNN target. Other reports show much lower K concentration in compared to Na concentration in KNN-films deposited by rf sputtering [38, 46, 47]. Apparently, Mn ion entered and subsite into the lattice positions of KNN perovskite structure, efficiently preventing the loss of K element during deposition process at 500 °C. It can be observed from the XPS spectra that Mn-doped KNN film show higher binding energies for all element in compared to undoped film, from the effect of higher bonding due to Mn doping [48].

3.1.3. Polarization-electric hysteresis loop



Figure 3.3. (a) P-E Loop of as-grown sample (b) P-E Loop of RTP 750 °C in 5mins.

Figure 3.3 shows the polarization – electrical (*P*-*E*) hysteresis loops of the as-grown and annealed KNMN films. The hysteresis loops are observed to be slightly leaky ferroelectric at high electric field of 1000 kV/cm (with as-grown sample) and 1300 kV/cm (with annealed sample), however it is first reported the presence of remanent polarization (P_r) and coercive field (E_c) of as-deposited KNMN film at 500°C without any post treatment process. The value of P_r of 18.8 μ C/cm² and coercive field of 198.6 kV/cm was obtained at an applied electric field of 1000 kV/cm. this is remarkable, since most of KNMN film, irrespective of deposition method, require post annealing process to acquire polarization remanent. Nevertheless, this result also confirmed the effect of rapid thermal treatment in improving ferroelectricity of the KNMN films. However, since the concentration of Nb⁴⁺ in RTP sample was still high, even though much lower than that of as-grown sample, suggesting the need for longer heat treatment time.

Mn-doped lead free KNN films K and Na elements volatility was effectively reduced with the subsite of Mn ion into KNN lattice structure. The equivalent amount of Na and K indicates the balance in the phase boundary state of the material, promised the high ferroelectric properties of the films. Nb⁴⁺ was shown to turned into Nb-KNN with rapid thermal treatment. Effective reduction in hole carriers by Mn-doping is confirmed. Leakage

current density of Mn-doped KNN films is much lower and more resistant in compared with the undoped counterparts.

3.1.4. Leakage current density

Leakage current density was measured using DC Keithley semiconductor characteristic system. Figure 1 shows the leakage current density (*J*) versus applied electric field (*E*) of both as-grown and RTP annealed KNMN films deposited by rf sputtering. The better *J*-*E* character of annealed sample shows low conducting state as applied electric field increased, followed by drastically surge in current density at above E = 85 kV/cm. The dielectric breaks down occurred at 90 kV/cm. the current density was $J = 10^{-9}$ A/cm² at E < 85 kV/cm, then the leakage current density was $J = 10^{-7}$ A/cm² at E > 90 kV/cm. The breakdown at high DC electric field was caused by the accumulation of charge carrier across the electrodes of the KNMN films.



Figure 3.4. *J-E* characters of different KNMN films after RTP anneal and as-grown respectively.

The log(*J*) versus log(*E*) presented in the figure, show the law of conductivity by the relationship of *J* proportionate to E^n . For leaky electric field region, the *J*-*E* relationship was $J \sim E^{0.7}$, with the exponent of n was 0.7, indicating Ohmic-like conduction. At high electric field and breakdown region, due to the accumulation of charge carriers and the avalanche of charges as breakdown happen, various conduction mechanism took place [44]. The measured leakage current density measured at 10^{-9} kV/cm is significantly lower than undoped film about 10^2 times [44].

3.2. Fabrication of (K,Na)NbO₃-based thin films using pulsed laser deposition

3.2.1. Morphology measurements

a. X-ray diffraction (XRD)



Figure 3.5. XRD patterns acquired over the 2θ range of 20–60° for KNMN film (a) without Al₂O₃ layer and (b) with Al₂O₃ layer.

Figure 3.5 shows that both thin films (KNMN film without Al_2O_3 layer and KNMN with Al_2O_3 layer) retain in good condition, since a single phase of perovskite structure with (100) orientation is still observed and no other diffraction peaks are observed.

b. Atomic force microscopy (AFM)

The AFM images of both samples with and without the Al₂O₃ layer show that they are slightly changing in root mean square (RMS) roughness but not much different.



Figure 3.6. AFM images of KNMN film (a) without Al₂O₃ layer and (b) with Al₂O₃ layer.

3.2.2. Polarization-voltage hysteresis loop

The hysteresis loops are leaky for both samples with and without the Al_2O_3 layer, with the slightly better remanent value belongs to the pristine sample. So far, the novel effect of Al_2O_3 have upon the ferroelectric properties of KNN films has not yet any significant improvements, but a little margin of detriment. However, judjing from **figure 3.7**, the coecertivity of sample with additional Al_2O_3 layer is larger, suggesting a higher reverse field needed to drive the magnetization of the film to zero due to the higher magnetic potential stored in the polarization state. This could promise a better, more stable and more durable ferroelectric properties of the $Al_2O_3/KNMN$ film.



Figure 3.7. (a) *P-V* loop of KNMN thin film without Al₂O₃ layer (b) *P-V* loop of KNMN thin film with Al₂O₃ layer.

3.2.3. Switching current measurements

The current characteristics of KNMN and Al₂O₃/KNMN are shown in **figure 3.8**. The voltage starts at the maximum negative value, reachs the maximum positive value, and repeat the cycles. There is one peak observed for both films suggesting the switching of ferroelectric domains in both samples. When the voltage increases from zero to negative maximum or positive maximum, current density value of both samples increase gradually, then have a sudden jump and reduce immediately after that. The voltage associated with the peak current value of sample with Al₂O₃ layer is higher that that of pristine sample, and the maximum peak current density of pristine sample is at twice the value of modified sample. This is corresponding to the novel effect of the Al₂O₃ layer in improving the ferroelectric domain switching, preventing by-electron charge injection during the retention, and consequently improve the overall ferroelectric properties of the film.



Figure 3.8. (a) Switching current of KNMN thin film without Al₂O₃ layer (b) Switching current of KNMN thin film with Al₂O₃ layer.

Chapter 4. Summary and implications

4.1. Summary

Lead-free Mn-doped Potassium Sodium Niobate (K_{0.5}Na_{0.5}NbO₃) thin films were fabricated by reactive rf sputtering method under O₂ and Ar mixed atmosphere on Pt/Ti/SiO₂/Si substrate. X-ray diffraction results indicated that KNNM thin films show single perovskite structure under orthorhombic symmetry with (110) prefer orientation. The KNMN films show mediocre ferroelectric polarization, however the ferroelectric polarization-electric field (*P*-*E*) loops were well shaped at room temperature for both as-grown and rapid thermal treatment films. The remnant polarization P_r of as-grown sample was observed to be 18.2 μ C/cm2 at 1000 kV/cm, and the coercive electric field E_c was 198.6 kV/cm. The leakage current densities of the films were remarkably reduced to 10⁻⁹ at 85 kV/cm via 0.5% mol Mn doped. Our results suggest that KNNMn-0.0050 lead-free film have a great potential for future environmentfriendly piezoelectric devices.

Developing from the success of Mn dope KNN film by rf sputtering, state of the art PLD technique was employed to further develop this KNN-based material. Initial result show good quality ferroelectric properties, significant improvements from the rf sputtered films. Moreover, adopting the novel idea of adding an Al₂O₃ layer on top the the KNMN film to prent by-electron charge injection during the retention, there is high potential in prolong the lifetime of KNMN piezoelectric film for practical applications. Preliminary results suggest the real effect of the Al₂O₃ upon improving the stability and durability of the KNMN films. However, there are much more extensive studies required involing retention and fatique tests for a long period of time in order to confirm the validality of this study.

4.2. **Implications**

KNMN have proven to be a promising material to substitute PZT as the practical, commercial piezoelectric material. The PLD study has only recently been started, and there has been many promising preliminary results. Futher studies on calibrating the fabrication condition of KNMN films via PLD are required for the optimized quality films. In additions,

extensive researches on the novel effect of Al_2O_3 are also needed, since the initial results are showing promising improvements. More importantly, should the studies on $Al_2O_3/KNMN$ films be successed, developing the practical harvesting devices based on KNMN films is of high possibility and practicability.

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