Optimization of $K_{0.5}Na_{0.5}(NbO_3)$ Thin Films Using Pulsed Laser Deposition

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Abstract

In environments where wind, or solar energy harvesting are not accessible, piezoelectric microelectromechanical systems (PiezoMEMS) that include $Pb(Zr_xTi_{1-x})O_3$ (PZT), use vibration energy to provide clean energy. Due to concerns about lead exposure during the processing of lead-based materials, $K_xNa_{1-x}NbO_3$ (KNN) is being explored as a lead-free replacement. Pulsed laser deposition (PLD) was used to deposit a 500 nm $K_{0.5}Na_{0.5}NbO_3$ thin film onto a platinized silicon substrate.

By varying deposition parameters, such as temperature, pressure, target to substrate distance and even the energy density provided to the target, the optimal KNN thin film can be fabricated. Studying the microstructures and chemical composition of PLD deposited KNN thin films revealed an average grain size of 1.5 μm at 400mTorr and 2 cm of separation between the target and substrate. But X-ray diffraction scans show many unidentified peaks which infer the existence of many potassium and sodium deficient secondary phases. Additional work needs to be done in order to identify the deposition parameters that will create the most piezoelectrically efficient KNN thin film.

Introduction

Piezoelectric materials are widely used in piezoelectric microelectromechanical systems (piezoMEMS) devices such as actuators, sensors, and energy harvesters (Muralt 2009). Their ability to convert mechanical stresses to electrical energy makes these materials useful as a local source of renewable energy for low power applications, which is of interest for powering sensors for the internet of things. Lead zirconate titanate (PZT) is commonly utilized in piezoMEMS devices because it exhibits superior piezoelectric properties compared to other piezoelectric materials. However, health concerns about lead exposure during the processing and disposal of lead-based materials have driven research into alternative lead-free piezoelectric materials. Studies show a strong correlation between children exposed to lead and reckless adult behaviors such as theft and murder (Wolpaw, 2007). During processing, lead deposits coat the inside of the vacuum chamber and the resulting wafers can potentially contaminate tools that come into contact with the lead containing material.

Although protocols to handle potential cross-contamination from PZT-coated wafers have been developed by companies producing ferroelectric random-access memories, interest exists in alternative materials that have high actuation authority without containing lead.

Lead-free materials in piezoMEMS, such as potassium sodium niobate (KNN), present possible alternatives. However KNN's properties, a piezoelectric constant (d_{33}) of ~80 pC/N and a coercive field (E_c) of ~19 kV/cm (Dai, Zhang, & Chen, 2009), make it less efficient than PZT for many applications. Additional work is therefore needed. The goal of this work is to determine optimal growth parameters for KNN thin film with reasonably good piezoelectric properties. For this purpose, pulsed laser deposition (PLD) was used to deposit KNN films onto platinized silicon substrates; the films' microstructures and chemical composition were determined as a function of the deposition parameters. This paper investigates the effects of deposition temperature, pressure, and target to substrate distance on the measured d_{33} and E_c in KNN thin films. To implement films into energy harvesters more information needs to be collected on how piezoelectric energy harvesters work.

The crystal structure and composition of KNN is important in understanding how a piezoelectric energy harvester works. PZT and KNN have the same perovskite crystal structure (see Figure 1) with different atoms placed at the A and B-sites of the crystal. Pb populates the A-site of a PZT perovskite structure while K and Na populate the A-sites of a KNN crystal. The B-site (located at the center of the unit cell) is occupied by the ferroelectrically active ion. In PZT, the ion is zirconium but in KNN it is niobium; the displacement of this atom off the center of the unit cell gives it piezoelectric characteristics.

The maximum piezoelectric response occurs when the film composition is on the verge of going through a phase transition. The morphotropic phase boundary (MPB) is a nearly temperature independent boundary between two different ferroelectric distortions. In KNN, at the $K_{0.5}Na_{0.5}(NbO_3)$ composition, the maximum piezoelectric response comes from crossing the MPB between two orthorhombic phases (Dai et al., 2009). By depositing KNN films on this composition, higher piezoelectric responses are obtained. The correct chemical composition not only places the film on a favorable MPB for energy harvesting but, it is also one of the many deposition parameters that can affect film growth.

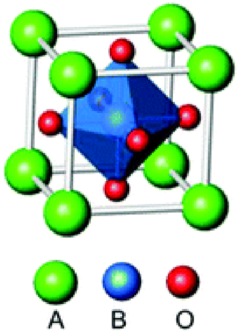

Figure 1. Schematic of a perovskite unit cell

The structure zone model proposed by John A. Thornton explains the mechanisms that drive thin film microstructure during growth; thermal energy and kinetic, or bombardment energy (Thornton, 1988).

When growing films via a physical vapor deposition process, such as PLD, a higher amount of thermal energy applied to the substrate allows for surface diffusion of ions. According to the structure zone model, the ratio of substrate temperature (T) to melting temperature of the material deposited (T_m) determines the film microstructure. The first type of growth, called zone 1, occurs when the atoms stick to the spots where they arrive on the substrate with minimal surface diffusion ($T/T_m < 0.3$). This process is dominated by the transport of atoms from the surface of the target to the substrate. The next type of film growth is when $T/T_m < 0.5$ and the atoms have sufficient thermal energy that surface diffusion dominates the process. This produces columnar growth the zone 3 condition ($T/T_m > 0.5$) occurs when bulk diffusion dominates over surface diffusion (Thornton, 1988).

By studying the MPB composition of KNN thin films, and parameters that affect thermal and bombardment energy, the fabrication of these films can be optimized. The parameters that align to create KNN films with reasonably good chemical composition and microstructures using PLD can be transferred to more industrial deposition techniques. Sputtering is a good candidate for mass producing KNN thin films for use in handheld energy harvesting devices due to its similarities to PLD and ability to deposit on four-inch wafers. Before mass production of films can begin, the deposition parameters, using PLD, must be determined.

Materials and Methods

A one-inch $K_{0.5}Na_{0.5}(NbO_3)$ target with 5 mol% excess potassium carbonate (K_2CO_3) and 2.5 mol% excess sodium carbonate (Na_2CO_3) was sintered using standard bulk ceramic processing techniques. This was used for growth of KNN films on 0.25 cm^2 pieces of $Pt/Ti/SiO_2/Si$ wafers. Excess alkali metals were added to offset the volatilization of these elements during high energy depositions. The substrate was ultrasonicated for cleaning in acetone, ethanol, and isopropyl alcohol for ≥5 minutes in each solution. While the substrate was ultrasonicated, pre-ablation of the target was performed at 20 Hz for 1200 pulses. After cleaning, the substrate was bonded to the substrate heater using Alpha Aesar silver paste cured at 300^oC to ensure uniform thermal contact. Once the substrate was securely attached to the heater and aligned with the target, the system was pumped down to a base pressure in the 10^{-7} Torr range. Using the (ozone generator) the atmosphere inside the system was kept at a 10/90 mix of O_3/O_2 with a flow rate of 26 sccm.

1.) Optimization

To optimize the thin film growth parameters, depositions varying temperature, pressure, and target to substrate distance were performed. For high quality KNN thin films, atoms need to have enough thermal energy for surface diffusion to occur and the right amount of bombardment energy to crystallize the perovskite phase. Different deposition parameters affect atom mobility and the type of growth that occurs on the film. Atom mobility is mainly coupled with the amount of thermal energy available to the ions to undergo surface diffusion. Changing deposition temperature to achieve various T/T_m ratios allows for observation of different film microstructures. In this study, 650^oC was chosen as the optimal deposition temperature in order to get a T/T_m ratio of 0.5 which corresponds to columnar growth. The other contributing factor to film growth, bombardment energy, can be modified through parameters such as target to substrate distance and deposition pressure.

Since the plasma plume shape changes at different pressures, becoming skinnier and shorter as deposition pressure increases from 100 mTorr to 400 mTorr, it was hypothesized that the substrate position within the plume would have an effect on the quality of the KNN film. To test this, films were deposited at three different positions within the plume: at the widest point, just inside the tip, and at the tip. To observe the effects of deposition pressure, the experiment was performed at different chamber pressures ranging from 100mTorr to 400mTorr (see Table 1.).

Table 1. Target to Substrate Distances at Various Deposition Pressures

"Optimal Distance" (cm.)	5.8	5.7	5.3	5.1
Wide Plume Width Distance (cm.)	2	2	2	2
Tip of Plume Distance (cm.)	6	6	5.6	5.7
Temperature (°C)	650	650	650	650

2.) Characterization

After deposition, X-ray diffraction (XRD), using the Malvern Panalytical Empyrean X-Ray Diffractometer, was utilized to determine crystallinity and identify any secondary phases that arose from potassium and sodium deficiencies. Each scan was done using copper as the anode material in the X-ray tube with a 40-mA current and 45 kV voltage. The scans were 17 minutes in duration, ranging from 0-70° 2-theta. Next, each film was imaged using the Leo 1530 Field Emission Scanning Electron Microscope (FESEM) in order to see the surface microstructures and grain size (determined by the line intercept method). The imaging distance was 3 mm, and an acceleration voltage of 5 kV was used.

Results

Observations of the microstructure through X-ray diffraction revealed that KNN thin films deposited at the tip of the plume crystallized into the perovskite phase with minimal pyrochlore phase.

Depositions done at the widest part of the plume showed the most sodium and potassium deficient secondary phases. The [100] orientation axis peak was further intensified as deposition pressure rose from 100 mTorr to 400 mTorr. This shows that the perovskite phase crystallized at

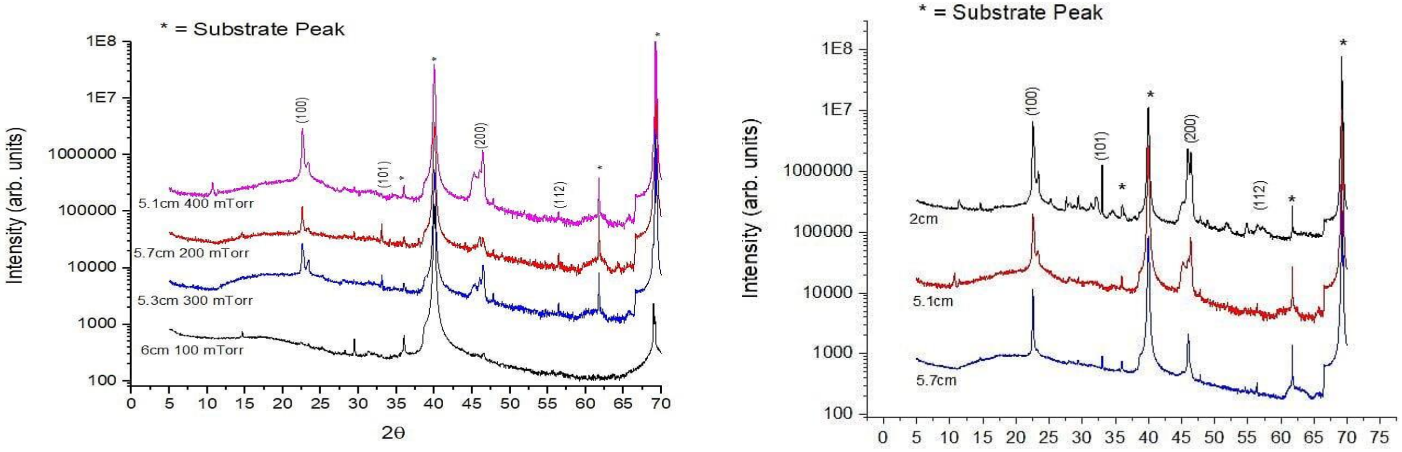

Figure 2. X-ray diffraction pattern of "optimal" target to substrate distance at 100, 200, 300 and 400 mTorr (left). Also pictured on the right, an x-ray diffraction pattern for depositions at 400mTorr at 2 cm, 5.1 cm, and 5.7 cm target to substrate distances.

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FESEM images revealed further information about the microstructure and type of film growth achieved with respect to target to substrate distance. At a distance of 2 cm and pressure of 400 mTorr, the average grain size was 1.5 μm. As the target to substrate distance increased from 2 to 5.8 cm, the average grain size was reduced to 0.09 μm. Observing the KNN films with the naked eye shows a dull gray color (which is consistent with the high surface roughness visible in FESEM imaging).

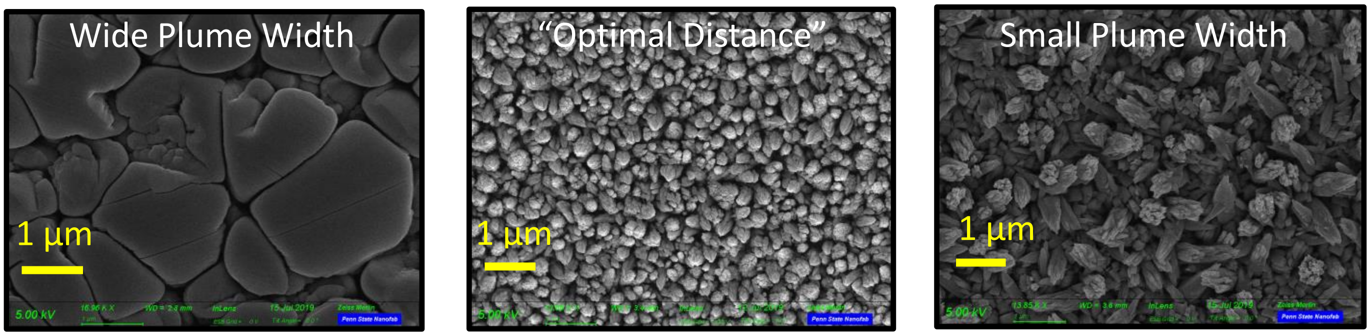

Figure 3. FESEM images of surface at 400 mTorr and each target to substrate distance

Further observation of film growth with respect to deposition pressure revealed that at 100 mTorr there was too much bombardment energy. It is possible the resulting re-sputtering promoted the appearance of secondary phases. As the pressure was increased up to 400 mTorr, the porosity of the films increased. Even with reasonably good perovskite phase crystallinity, due to the porosity and high surface roughness of the films, electrical measurements were not attempted.

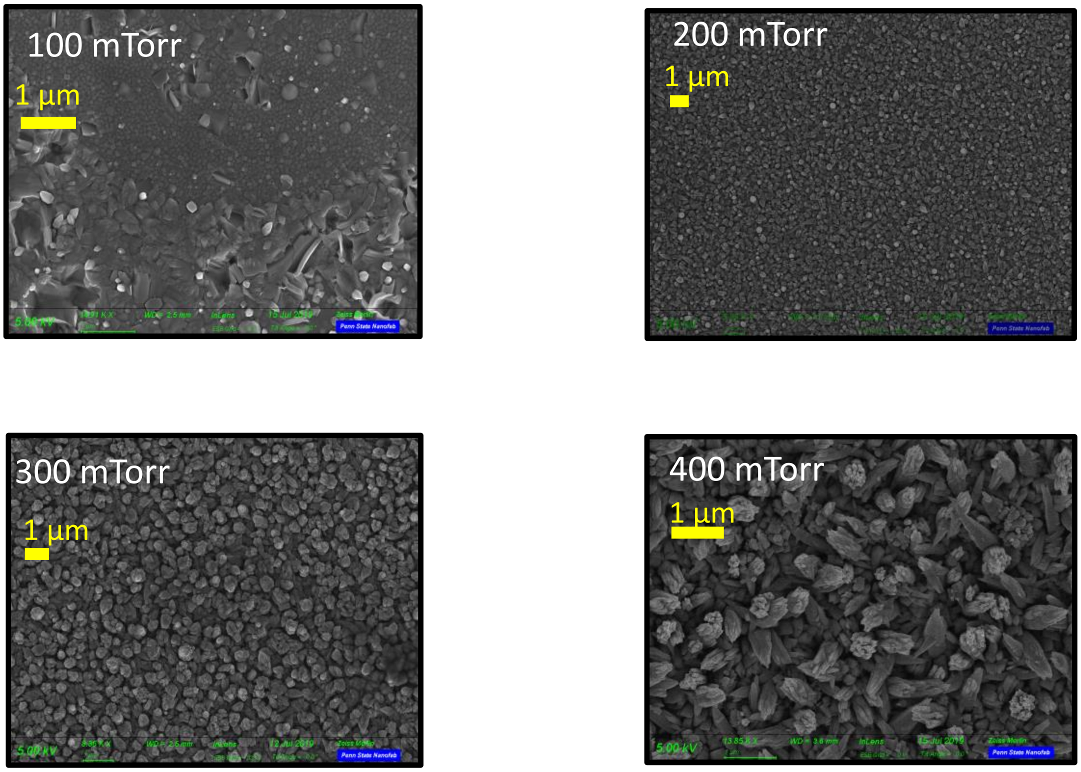

Figure 4. FESEM images of surface of depositions at “optimal” target to substrate distance. These distances are 5.8 cm at 100 mTorr, 5.7 cm at 200 mTorr, 5.3 cm at 300 mTorr, and 5.1 cm at 400 mTorr.

Conclusions

While strides have been made towards finding the correct target to substrate distance and deposition pressure, further optimization of the microstructures needs to be done in order to fabricate a KNN thin film that could replace PZT in piezoelectric energy harvesting devices. Parameters such as laser pulse frequency, target composition, and temperature can be changed in order to alter the film growth. To address the issue of surface roughness, deposition temperature can be changed in order to allow more surface diffusion. This study will be continued in order to find the deposition parameters to create films with better microstructures and phase purity for use in piezoelectric energy harvesting devices.

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