

Improved Sputtering Conditions for *in situ* Crystallization of PZT Thin Films

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Abstract:

The applications of piezoelectric microelectromechanical systems based on $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, or PZT, thin films could be expanded by the use of flexible metal foil substrates. Strongly oriented $\langle 001 \rangle$ PZT thin films showing high piezoelectric response with a low dielectric constant have been grown on flexible nickel foil substrates by chemical solution deposition (CSD), which improved the figure of merit for piezoelectric energy harvesters [1]. The goal of this research was to develop a process for growing comparable films by high temperature sputtering, thereby simplifying the deposition process for obtaining desired film thickness with high density and allowing for *in situ* crystallization.

Introduction:

Lead zirconate titanate ($\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, or PZT) has been used for various applications including transducers, sensors, actuators [2] and energy harvesters. Typically, research on these thin films involves platinized silicon substrates. Using flexible metal substrates, such as nickel foil, could vastly improve the uses of PZT thin films due to the improved mechanical durability and flexibility of the metal foil, and because the foil does not mechanically constrain the PZT layer as much as a rigid substrate.

Growth of films greater than $\sim 0.2 \mu\text{m}$ by CSD requires that the spin deposition-pyrolysis-crystallization process be run multiple times. Developing a process for sputtering PZT onto flexible metal substrates would allow for just one deposition step to be done using *in situ* crystallization, thereby eliminating potential drawbacks caused by CSD.

In this experiment, PZT was sputtered onto platinum/titanium/silicon dioxide/silicon substrates with and without a PZT seed layer. This substrate was used because the passivated nickel (Ni) foil requires additional processing steps. Controlling both chamber pressure and oxygen flow during the deposition alters the lead content of the deposited film, which is vital for obtaining pure perovskite PZT without the presence of the non-piezoelectric pyrochlore phase. Temperature was also adjusted to determine the *in situ* crystallization temperature for perovskite PZT.

Experimental Procedure:

PZT thin films were deposited by radio-frequency (RF) magnetron sputtering. The target used for the process

was $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, or PZT (52/48), with 10 mole percent excess lead oxide. Additional PbO compensated for loss due to evaporation and/or resputtering, since the sputtering occurred at elevated temperatures and PbO is easily volatilized.

Before the deposition started, the substrates were first gradually heated up and stabilized at a desired temperature. The heating dwell time for the samples in this experiment was set at 90 minutes.

After that, the deposition was run for 15,000 seconds at 90 watts RF power in an argon atmosphere, under varying conditions of temperature, chamber pressure, and oxygen flow. The conditions were optimized sequentially based on the results of previously sputtered samples. Films were sputtered onto the non-seeded and the seeded PZT substrates at the same time. Half of each sample was then rapid thermal annealed (RTA) at 700°C in O_2 to check for phase and microstructure changes.

X-ray diffraction (XRD) patterns, microstructure images taken by field-emission scanning electron microscopy, and electrical characterization (low field dielectric constant and polarization hysteresis data) were obtained to analyze each sample.

Results and Conclusions:

For the first series of experiments, the chamber Ar pressure was increased. At higher chamber pressures, the bombardment of the growing films is reduced. This, in turn, reduces the presence of the pyrochlore phase. The set temperature was also adjusted in the range of $600\text{--}700^\circ\text{C}$.

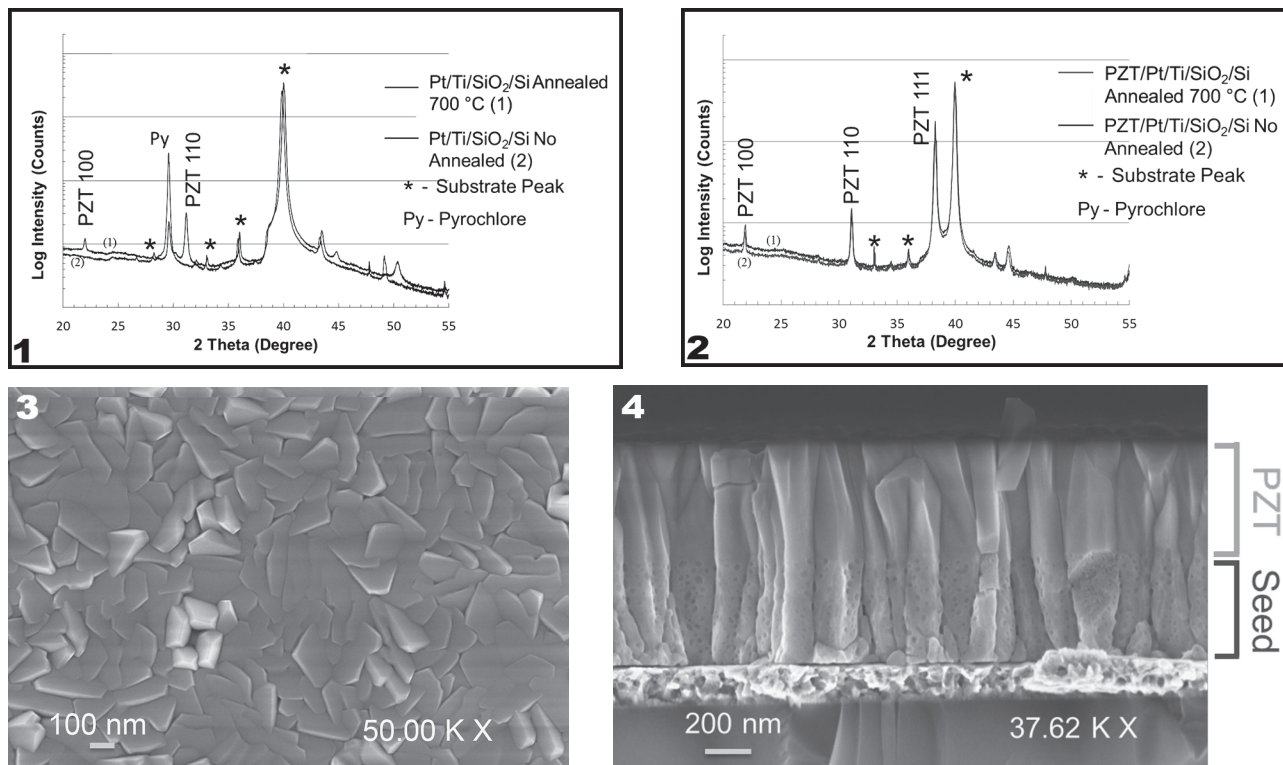


Figure 1, top left: XRD pattern of PZT films without seed layer sputtered at 9 mTorr, 670°C, with 3% oxygen flow. **Figure 2, top right:** XRD pattern of PZT films with seed layer sputtered at 9 mTorr, 670°C, with 3% oxygen flow. **Figure 3, below left:** Top view field-emission scanning electron microscopy (FESEM) image of non-annealed sample with seed layer sputtered at 9 mTorr, 670°C, with 3% oxygen flow. **Figure 4, below right:** Cross section FESEM of non-annealed sample with seed layer sputtered at 9 mTorr, 670°C, with 3% oxygen flow.

It was found that changing only the Ar pressure did not lead to phase-pure perovskite films. Without oxygen flow during sputtering, the best sample was grown at 12 millitorr and 670°C. However, the non-seeded sample showed pyrochlore and the seeded sample showed low intensity perovskite peaks. The seeded sample did show saturated polarization hysteresis loops. These experiments indicated that 670°C was around the crystallization temperature. Neither the XRD perovskite peak intensity nor the microstructure for samples sputtered at this temperature showed much change after annealing.

It has been shown that introducing oxygen into the sputter gas can help initiate perovskite growth on Pt/Ti/SiO₂/Si [3]. In addition, increasing the ratio of oxygen to argon in the sputter gas decreases the lead content of the deposited film [4]. For the next series of experiments, samples were sputtered at 670°C with either 3 or 5% oxygen flow rate in the sputter gas, at different set pressures. It was found that having 3% oxygen flow in the sputter gas, as opposed to 5%, better reduced the pyrochlore present on the XRD patterns. The best sputter conditions of 670°C, 9 mTorr with 3% oxygen flow resulted in an intense pyrochlore peak for the non-seeded sample (Figure 1), yet very intense perovskite peaks for the seeded sample (Figure 2). Samples sputtered under these conditions but with lower pressure showed decreased perovskite crystallinity and increased pyrochlore. It was also shown that sputtering at higher temperatures led to dense films, as seen in Figures 3 and 4.

Moving Forward:

In future work, electrical characterization is needed for films grown at a 9 mTorr chamber pressure at 670°C with 3% oxygen in the sputter gas. It is likely that final optimization will be done by iterative experiments based on structural and electrical characterization. After optimum conditions are found, Ni foil substrates will be used.

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