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Correlation between Nano-Mechanical and Piezoelectric Properties of Thin Films: An Experimental and Finite Element Study

Hussein Nili,^{†,§} Guang Cheng,^{‡,§} T. A. Venkatesh,^{*,‡} Sharath Sriram,[†] and Madhu Bhaskaran^{*,†}

[†] Functional Materials and Microsystems Research Group, RMIT University, Melbourne, Victoria 3001, Australia

[‡] Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794, United States

*E-mail: t.venkatesh@stonybrook.edu, madhu.bhaskaran@gmail.com

[§] These authors contributed equally.

ABSTRACT

Piezoelectric materials perform mechanical-to-electrical energy conversion and have unique and enhanced properties, particularly in the thin film form. In this work, the nanomechanical properties of strontium-doped lead zirconate titanate thin films are investigated by nanoindentation. Finite element modeling of the nanoindentation process allows for a comparison of the simulated and experimentally measured load–displacement curves. New insights correlating the nanomechanical and piezoelectric properties of thin films have been obtained which will enable more efficient design of piezoelectric energy harvesting devices.

Keywords: Thin films; Piezoelectric response; Nanoindentation; Elastic modulus; Instrumented indentation method (IIM)

Piezoelectric materials have been traditionally used in a variety of sensing, actuating, and transduction applications [1,2]. Now, they are increasingly studied in energy harvesting applications to harness mechanical energy in the form of pressure transitions and vibrations [3–6]. This has resulted in an impetus to understand the nanomechanical and electromechanical behavior of piezoelectric materials in their bulk, thin film, and nanowire form [3–6].

The adoption of thin film technology for energy harvesting applications is increasingly favored given the ability to incorporate thin film materials on silicon-based devices and flexible electronic platforms [5,6]. These approaches provide opportunities for micro- and nano-patterning to realize complex energy amplification structures [5,6].

Lead zirconate titanate compounds [$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT)] are well-known for their exceptional piezoelectric properties [7,8]. The addition of strontium (Sr) to PZT compounds to realize strontium-doped PZT (PSZT) enhances piezoelectric and ferroelectric properties of the compound both in bulk and thin film structures [9–13]. Longitudinal piezoresponse (d_{33}) values as high as 892 pm/V on gold-coated silicon [13] and 1,450 pm/V on platinum-coated silicon [14] are reported for the piezoelectric response of $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ compounds under the converse piezoelectric effect. Nanomechanical properties of PZT and PSZT thin films play an important role in the functionality of the microelectromechanical systems (MEMS) and energy transduction applications that use these films.

Nanoindentation, with controlled forces (as shown in **Fig. 1**), has been utilized with *in situ* electrical measurements to study energy generation from piezoelectric thin films at the nanoscale [5,15,16]. Such load–displacement and quantified energy generation measurements will be enhanced by a fundamental understanding of the influence of nano-electro-mechanical properties of the materials on the nanoindentation measurements. Furthermore, such thin film systems are influenced by surface roughness, interface, and substrate effects. Development of

finite element models which can account for materials property variations, and enable correlation with measurements will prove valuable.

This study has two main aspects. First, nanoindentation experiments were performed on thin films of strontium-doped lead zirconate titanate (Sr-doped PZT or PSZT) using a Hysitron Triboindenter [5] and the corresponding load–displacement curves were recorded for a range of forces from 0.1–10.0 mN. It should be noted that the conductive indenter tip was electrically grounded during all measurements, and is electrically isolated from the displacement transducer. Second, a finite element model was developed to characterize the influence of the electromechanical properties on the effective nanoindentation response of PSZT thin films.

The PSZT thin films were deposited by RF magnetron sputtering, onto pre-cleaned platinum-coated silicon substrates. The platinum thin film coating on the substrate was 200 nm thick, with an adhesion layer to silicon of titanium dioxide (TiO₂). The PSZT thin films were deposited at 350 nm/h to attain thicknesses of 700 and 1400 nm. Full details on the sample preparation and deposition processes can be found in our earlier work [17,18]. The synthesized films exhibited strong preferential orientation with their *c*-axis normal to the substrate [14,17].

The load–displacement curves obtained for the 700 and 1400 nm thick PSZT films are shown in **Fig. 2**, with the maximum applied force indicated. In general, there is a non-linear increase in the indentation load with an increase in the indentation depth for both the piezoelectric thin films. Significant tip displacement at very low loads is also observed for the 1400 nm film, which is not observed in the case of the 700 nm film. This is attributed to the higher surface roughness of the thicker films (R_a of ~25 nm for the 1400 nm films, as against ~11 nm for the 700 nm films), which influences the tip–surface interaction during the initial loading phase [19].

A major challenge is the ability to model and quantify the interaction between a defined geometry of the nanoindentation tip, the material surface, and the penetration depth. This is overcome by the use of the instrumented indentation method (IIM) [20–23]. The constitutive relationships for a piezoelectric material that exhibits coupling characteristics between its electrical (i.e., dielectric) and mechanical (i.e., elastic) properties are given by:

$$\begin{aligned}\sigma_{ij} &= C_{ijkl}^E \varepsilon_{kl} - e_{ijk} E_k \\ D_i &= e_{ikl} \varepsilon_{kl} + \kappa_{ij}^E E_j\end{aligned}\tag{1}$$

where, σ = stress tensor, ε = strain tensor, E = electric field vector, D = electric displacement vector, C^E = elasticity tensor with the superscript ‘ E ’ indicating that the elasticity tensor corresponds to measurement of C at constant or zero electric field, κ^E = permittivity tensor with the superscript ‘ ε ’ indicating that the permittivity tensor corresponds to measurement of κ at constant or zero strain, and e = piezoelectric coupling tensor. Equation 1 is the most general representation of the constitutive equation and has 21 elasticity, 18 piezoelectric, and 6 permittivity (or dielectric) constants that are independent material properties. The nanoindentation response of a piezoelectric material is influenced by its elastic, piezoelectric, and dielectric properties.

The instrumented nanoindentation method involves indenting a substrate material with a conical, spherical, or flat indenter and measuring the complete load–displacement (force–depth) relationship during the loading and the unloading cycle [20–23]. Within the context of piezoelectric materials, depending on the electrical boundary conditions introduced into the indentation set-up, the electric field or voltage generated (open loop) or electric charge or current generated (closed loop) in the indentation process can be determined as a function of indentation depth as well.

The load–displacement characteristics observed in the nanoindentation response of two PSZT thin films were then compared to the results of a finite element model (FEM) of the

nanoindentation process, the details of which are as follows. Modified two-dimensional axisymmetric models were developed to simulate the indentation response of PSZT thin films with thicknesses of 700 nm and 1400 nm (Fig. 1). We only constrain the bottom side of the sample from any vertical displacement and the left side (which is actually the center of the specimen) from any horizontal displacement. The top side and the right side are not constrained mechanically. Our substrate dimensions were chosen to match with experimental specimens. A commercially available software package, ABAQUS, was used for developing the model. For the 700 nm film, the finite element model had about 23464 nodes comprising of 23315 elements, which included 6337 four-node axisymmetric (CAX4E) elements and 16978 four-node bilinear, reduced integration axisymmetric (CAX4R) elements. For the 1400 nm film, the model had about 21978 nodes with 21810 elements, which included 11972 CAX4E and 9838 CAX4R elements. The model was designed such that it was large enough to minimize end-effects and the mesh was fine enough in the indented regions for improved accuracy.

The PSZT thin films were considered as exhibiting elastic and dielectric properties that were similar to bulk PZT materials but with different piezoelectric properties (i.e., d_{33} and d_{31}). This modification in the piezoelectric properties is due to the fact that PSZT thin films have a piezoresponse coefficient d_{33} of 800-1,000 pm/V, [5,13,14] which is about 2.0-2.5 times greater than that of bulk undoped PZT-5A with d_{33} of 374 pm/V [24] (d_{31} is normally 30-45% of d_{33} in magnitude, but opposite in sign [3]).

The FEM was used to simulate the nanoindentation of the commercial piezoelectric PZT-5A in bulk and thin films forms, with variation in materials properties to account for doping to enhance d_{33} . The electromechanical properties of the piezoelectric materials used in the IIM are presented in **Table 1**.

Figure 3 presents the load–displacement data obtained employing the IIM approach for 700 and 1400 nm thick films utilizing the considerations described above and the parameters listed in Table 1. Firstly, the nanoindentation of bulk PZT-5A is modeled by the IIM approach. The results obtained are typical of experimental results reported for PZT ceramics and thin films, with ~70 nm penetration at 1 mN load [25–28]. Secondly, the piezoelectric properties of the material were modified to relate to an intermediate d_{33} of 600 pm/V and then to 1000 pm/V (as in Table 1). This resulted in a noticeable increase in the stiffness of the load–displacement data (diamond green marker and triangular gold markers in Fig. 3), with a force of 1 mN only having a penetration of ~60 nm (~14% lesser than bulk PZT-5A). These initial results highlight the influence of piezoresponse coefficients on nanomechanical response of materials.

From Fig. 3, it is evident that the nanoindentation load–displacement response predicted by the finite element model depends strongly on the piezoelectric properties of the substrate material. In general, the indentation responses are observed to be stiffer with increased piezoelectric properties. However, there is little difference in the load–displacement curves obtained from the finite element modeling of nanoindentation of bulk and thin film PSZT. This can be attributed to the fact that the depths of indentation are very small compared to the thickness of the PSZT films.

Overall, there is good agreement between the results of the finite element model and the experimental load-depth response obtained from the nanoindentation experiments on PSZT thin films. In particular, the nanoindentation response of 1400 nm PSZT thin films are captured very well by the finite element model. This could be attributed to the lack of substrate effects, which become prominent only beyond 10% of the films thickness (140 nm in this case). On the other hand, there is lesser agreement between simulation and measurement for the 700 nm films. It is expected that further refinements of the finite element

models to account for surface roughness effects and residual stresses will enhance the observed agreement with experimental results, especially for the thinner films.

In summary, high response piezoelectric thin films of Sr-doped PZT of two thicknesses (700 and 1400 nm) were deposited by RF magnetron sputtering. These films were characterized by nanoindentation and observed to exhibit load–displacement slopes that are higher than that observed in standard PZT materials. Finite element models were developed to characterize the nanoindentation response of PSZT and PZT piezoelectric materials in the bulk and thin film form. The modeling results demonstrate that the increased slope of the nanoindentation response curve observed for PSZT originates from its increased piezoelectric coefficient d_{33} . This shows that materials with higher piezoresponse are stiffer, which has implications for design of mechanical–electrical energy harvesters. This highlights that nanoindentation can be very useful in correlating the nanomechanical and piezoelectric properties of thin films.

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GRAPHIC ABSTRACT

TABLE (WITH CAPTION)

Table 1. The electromechanical properties of PZT-5A invoked to characterize their indentation response.

Materials and Properties	Elastic (10^{10} Pa)						Piezoelectric (pm/V)			Dielectric (10^{-9} C/Vm)	
	C_{11}^E	C_{12}^E	C_{13}^E	C_{33}^E	C_{44}^E	C_{66}^E	d_{31}	d_{33}	d_{15}	ϵ_{11}	ϵ_{33}
PZT-5A ($d_{33} = 374$ pm/V)	12.1	7.59	7.54	11.1	2.11	2.26	-171	374	583	8.11	7.35
PZT-5A ($d_{33} = 1000$ pm/V)	12.1	7.59	7.54	11.1	2.11	2.26	-300	1000	583	8.11	7.35

FIGURE CAPTIONS

Figure 1. Schematic illustrating nanoindentation of PSZT thin films: the experimental set-up (left) and finite element modeling (right).

Figure 2. Typical experimental load–displacement curves obtained at various maximum forces from the nanoindentation of PSZT thin films of thicknesses: (a) 700 nm and (b) 1400 nm.

Figure 3. The load–displacement response obtained from the nanoindentation of PSZT films are compared to the finite element simulations of a standard PZT-5A thin film and PZT-5A thin films with enhanced d_{33} properties. Results are shown for film thickness of (a) 700 nm and (b) 1400 nm.