Surface Morphology Induced Localized Electric Field and Piezoresponse Enhancement in Nanostructured Thin Films

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ABSTRACT Nanostructured piezoelectric and ferroelectric thin films are being increasingly used in sensing and actuating microdevices. In this work, we report the experimental discovery of localized electric field enhancement in nanocolumnar piezoelectric thin films and its significant impact on piezoresponse. The magnitude of electric field enhancement is associated with nonflat surface morphologies and is in agreement with theoretical and finite element models. The influence of this surface morphology induced enhancement on piezoresponse is demonstrated using phase field simulations, which also illustrates surface morphology induced strain enhancement. The observed enhancement can be effectively harnessed to improve the sensitivity of related piezoelectric thin film applications.

KEYWORDS: piezoelectric thin films · piezoresponse · surface roughness · electric field enhancement · enhancement factor · phase field simulations

Piezoelectric materials are used in a wide range of multidisciplinary applications encompassing such fields as acoustics (*e.g.*, microphones), biomedicine (*e.g.*, drug delivery systems, micropumps), fluid sensors, and nanotechnology (*e.g.*, accurate stages for sample positioning). In the pursuit of miniaturization and efficiency enhancement of such devices, bulk crystals are gradually being replaced by thin film coatings of piezoelectrics on ceramic, polymeric, or silicon substrates. This has driven the widespread research in piezoelectric thin films and the characterization of their performance.

In some cases, especially on single crystal ceramics, the piezoelectric thin films tend to be grown epitaxially.[1,2] In most cases, however, the films tend to be polycrystalline with a definite grain structure.[1] Piezoelectric response is predominantly due to the local inversion of the polarization and re-alignment of domains in the material to produce piezoelectric response under an applied force or electric field, for the direct and inverse effects, respectively. In order to maximize this piezoelectric response (henceforth referred to as piezoresponse), and the related piezoelectric charge coefficient d_{33}, preferential crystalline orientation is desired.[1,3] Piezoelectric materials with a tetragonal or rhombohedral unit cell tend to have high response,[1−3] and films oriented with their longer unit cell axis (the *c*-axis) perpendicular to the substrate are especially desirable to achieve enhanced performance (enabling greater polarization and strain). In the case of polycrystalline thin films, preferential *c*-axis growth results in columnar grain structure perpendicular to the substrate, with grain widths varying from tens of nanometers to a few micrometers, depending on the method of synthesis.[1,4] In general, the surfaces of such columnar films are not planar. When a potential difference is applied across such films, the nonplanar surface morphology results in an inhomogeneous distribution of the electric field within the material. Recently, it has been shown that such electric field inhomogeneity can significantly reduce the applied electric field required to initiate polarization switching process in ferroelectric thin films.[5] In this work, we investigate the influence of such inhomogeneous electric fields on the piezoresponse of such films using experimental measurements, finite element modeling, and phase field simulations.

The paper is organized into three main sections. First, we briefly outline the experimental details; including a description of the

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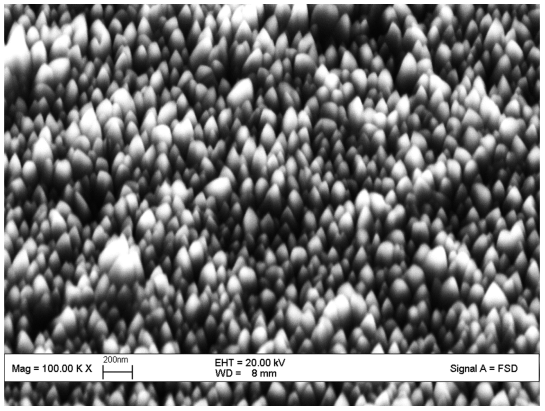

Figure 1. Field emission gun scanning electron micrograph of the PSZT thin film surface. This highlights the regularity of the grain structure and the typical surface morphology (sample tilt: 70°).

materials, the piezoresponse measurements process, and the piezoresponse results. Next, we describe a series of finite element calculations that show the presence of an electric field enhancement associated with the nonplanar morphology. Finally, we present the results of phase field simulations of piezoresponse enhancement in films with nonplanar surface morphology.

Piezoelectric Response Results. One of the most widely used piezoelectric materials is lead zirconate titanate (PZT). It is a frequent choice because of its relatively high piezoresponse and its strong electromechanical coupling. Low concentration doping of strontium in place of lead has been shown to enhance piezoresponse of PZT.[6,7] For this work, we deposit strontium-doped PZT (PSZT) thin films on platinized silicon substrates by RF magnetron sputtering from a $(Pb_{0.92}Sr_{0.08})(Zr_{0.65}Ti_{0.35})O_3$ target. The platinized substrates had a 200 nm layer of platinum with a 20 nm adhesion layer of titanium dioxide (TiO_2), both deposited at room temperature by electron beam evaporation. The PSZT deposition required 4 h to produce a film of nominal 1200 nm thickness. Further details of the deposition process can be found in previous publications[4,8] and in the Supporting Information.

To assess the surface morphology and grain structure, the PSZT films were analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1 presents a SEM micrograph of the as-deposited PSZT thin films. A nanostructured surface is clearly evident. Figure 2 presents results from the cross-sectional TEM analysis of the PSZT thin film samples. This analysis showed the existence of a well-defined, densely packed columnar nanostructure, with the nanocolumn width varying from 80 to 120 nm and a height of ~1200 nm. On the basis of the average column width and the film thickness, the aspect ratio (ratio of height to width) of the columns in the film is ~12. The surfaces showed a regular roughness with an amplitude of ~50 nm.

We next quantified the piezoelectric charge coefficient d_{33}. We have previously reported a technique for

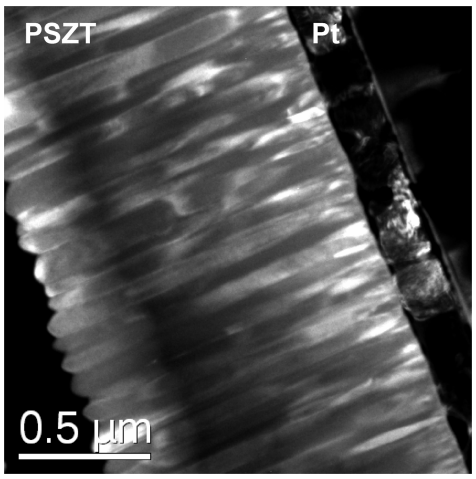

Figure 2. Cross-sectional energy filtered dark field transmission electron micrograph of PSZT thin films deposited on $Pt/TiO_2/Si$ highlighting the nanocolumnar grain structure.

quantitative measurement of d_{33} *via* the inverse piezoelectric effect by applying an electric field across the thin film and measuring the thickness variations normal to the plane using an atomic force microscope (AFM).[9,10] Figure 3 illustrates this measurement technique. An AFM tip is used to measure the local film thickness variation of a piezoelectric sample subjected to an electric field.[10] After careful calibration of the AFM using standards, the sample to be tested is introduced into the test setup. The tip location is kept constant, but an oscillating field is applied and the vertical displacement is thus recorded as a function of time. Over the course of developing this technique, rigorous tests were undertaken to ensure the integrity of the measurements. Samples of nonpiezoelectric silicon dioxide were shown to produce null response, expected values of piezoresponse were measured for aluminum nitride thin films, the variation of electric field parameters was studied, and mapping to determine uniformity of piezoelectric response over the thin films surface was carried out. Details of these aspects of the d_{33} measurement approach used are presented in refs 9 and 10.

Since the applied voltage is a well-defined function of time, the lateral axes of the AFM image can also be interpreted as corresponding to the applied voltage.[10] From the ratio of the peak-to-peak thickness variation to the applied peak-to-peak voltage, d_{33} can be determined as

$$d_{33} = \frac{\Delta L}{\Delta V} = \frac{\Delta L}{L \Delta E} \quad (1)$$

where ΔV is the peak-to-peak applied voltage, L the average film thickness, ΔL the peak-to-peak thickness variation associated with the applied voltage (the piezoelectric effect), and ΔE the corresponding electric field variation.

Measurements were carried out to determine d_{33} of the PSZT thin films deposited on $Pt/TiO_2/Si$ substrates

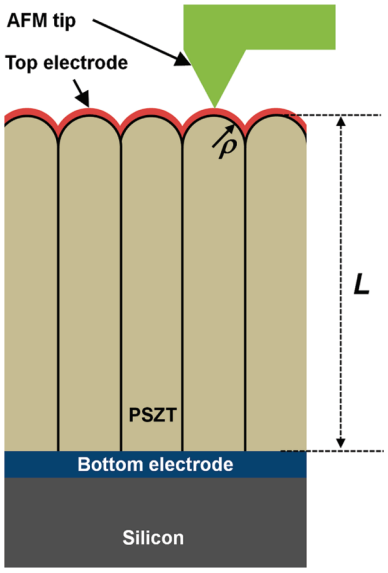

Figure 3. Schematic representation of the thin film sample used for the piezoresponse measurements.

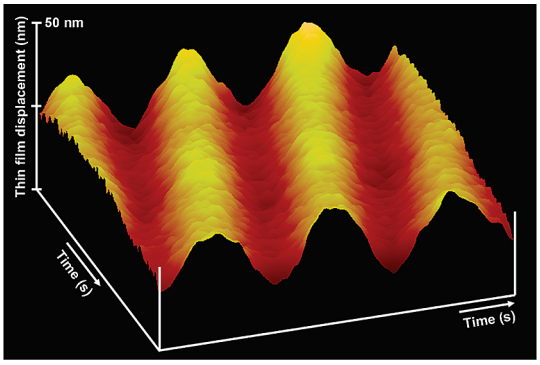

Figure 4. Piezoelectric response measurement results collected using an atomic force microscope. Thickness variations at a point under an applied sinusoidal electric field are recorded against time (as a raster scan). A peak-to-peak thickness variation ΔL of 23.2 nm was observed for a peak-to-peak applied voltage ΔV of 6.4 V.

using the AFM-based piezoresponse technique.[10] The AFM image in Figure 4 presents the results for an applied peak-to-peak voltage ΔV of 6.4 V with a frequency of 2 Hz. From this measurement, a peak-to-peak displacement ΔL of 23.2 nm (with ~5% error) was extracted. This result is typical of measurements made at various points on the thin film surface. These results show that significant film thickness variation, related to piezoelectric strain (%$\Delta L/L$) of over 2%, can be attained for applied voltages of less than 10 V.

Using eq 1, the effective d_{33} for these nanocolumnar PSZT thin film samples is 3625 pm/V. Previously reported d_{33} values are in the range of 200−600 pm/V for PSZT and similar PZT compounds, especially in the form of preferentially oriented polycrystalline material.[3,6,7,11] We have previously reported d_{33} values of up to 892 pm/V for similar, smooth PSZT thin films (with measurements performed under identical experimental conditions).[9,12] The observed piezoresponse for the nanocolumnar PSZT thin films is clearly much higher than these previous reports. We have been careful to maintain accurate control over the applied voltage and are confident of the calibration and measurement of thickness variations and, thus, believe that this measured enhanced piezoelectric coefficient is valid. Conventional approaches to explain such a high value of d_{33}, such as enhanced domain switching,[2] fail to account for this 4-fold increase in piezoresponse. This led us to consider other sources influencing measurements.

In formulating a model that could explain this enhanced piezoelectric response, it will be valuable to discuss the nature of induced piezoelectric strain in this type of material. Equation 1 states simply that the thickness variation is proportional to the applied field with d_{33} being the constant of proportionality. While this may be true for cases such as single domain ferroelectrics,[1,2] the case for PSZT is more complex. The PSZT thin films are of the relaxor ferroelectric type, given the strontium doping and 65:35 ratio of Zr/Ti, where the piezoelectric response is mostly due to inversion of polarized domains. The dynamics of polarization inversion in response to an applied voltage can be complex, but for slowly varying fields, the piezoelectric response is closely related to the nucleation of inverted domains at the high potential surface.

A recent report has shown that nanoscale surface morphology can generate strong local electric fields which can significantly enhance the nucleation of inverted domains in thin film ferroelectrics[5] with a consequent reduction in the electric field required for polarization switching. Our PSZT film (as shown in Figure 1 and Figure 2) also exhibits sharp nanoscale surface topology which may similarly lead to strong local electric fields and enhanced domain switching. To establish whether electric field enhancement can be expected, we perform finite element simulations of the static electric field that would be expected across our nanotextured thin film.

Finite Element Modeling. The distribution of static electric field for the nanocolumnar thin films structure in Figure 2 (and schematic in Figure 3) was modeled using the finite element method (FEM),[13] which solves the Laplace's equation for the electric field given the static voltage applied between electrodes. Surface morphology variations and the dielectric properties of PSZT were considered. Figure 5 shows the simulated static electric field distributions for a representative sinusoidal surface morphology of dimensions corresponding to the film geometry. Extreme surface morphologies such as semicircular and triangular surface features, which will have points of singularity, are discussed in the Supporting Information.

The enhancement factor is calculated by normalizing the maximum electric field in Figure 5 by the electric field of the corresponding flat case with a

height of 1200 nm. The FEM results clearly highlight that there is a pronounced increase in the electric field near the minima in the surface height. The magnitude of the electric field enhancement is between 2.0 and 2.5.

This enhancement factor of 2.0−2.5 compares well with field enhancement factors estimated for low macroscopic field electron emission,[14] with such phenomenon having been observed before in piezoelectric thin films[15] and metal-coated oxide nanostructures.[16] Unified expressions for the field enhancement parameter (γ) were first presented by Rohrbach.[17,18] On the basis of the unifying equation derived by Rohrbach to account for all field enhancement contributions

$$\gamma \approx 2 + \frac{h}{\rho} \qquad (2)$$

where h and ρ correspond to the height of the structure and the radius or half-width of the structure, respectively. For the "hemisphere on a surface" model, which corresponds to the surface of the nanocolumnar thin film structure, h and ρ are equal, resulting in an enhancement factor $\gamma = 3$. It should be noted that, for this study, the electrodes are separated by the dielectric thin film with a finite thickness L of 1200 nm, while the enhancement factor model assumes infinite separation. This does not greatly influence the calculation of the enhancement factor, with only about 4% decrease in its value, to γ of 2.88 (which is closer to the upper range we quote for the FEM simulations).[19]

Utilizing this enhancement factor γ in the range of 2.0−2.5 for the nanostructured PSZT thin films and incorporating this in the calculation of d_{33}, aided by the inverse electric field dependence governed by eq 1, the piezoresponse of the PSZT thin films is calculated to be in the range of $d_{33} \approx 1450-1813$ pm/V (*i.e.*, the experimental measurement for d_{33} of 3625 pm/V is scaled using γ). These values approach the maximum piezoelectric response reported for smooth PSZT thin films of 892 pm/V.[12]

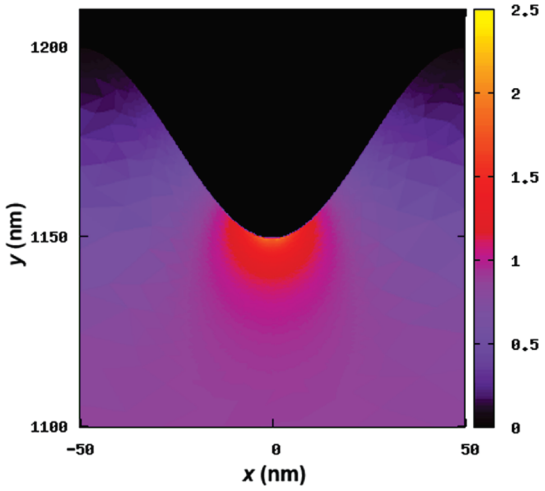

Figure 5. Simulated static electric field distribution (in V/μm) for 1 V dc applied between the electrodes is presented for a sinusoidal thin film surface with geometry corresponding to the experimental results in Figure 2. The electric field enhancement by a factor of 2.0−2.5 can be observed at the surface profile minima.

Phase Field Simulations. Motivated by the preliminary modeling results confirming electric field enhancement near the position of the nanocolumn boundary intersections with the surface in the metal−dielectric−metal system, we extended the modeling investigation to the analysis of electric field induced strain in the piezoelectric thin films. The influence of the nonplanar surface on strain enhancement was modeled using the

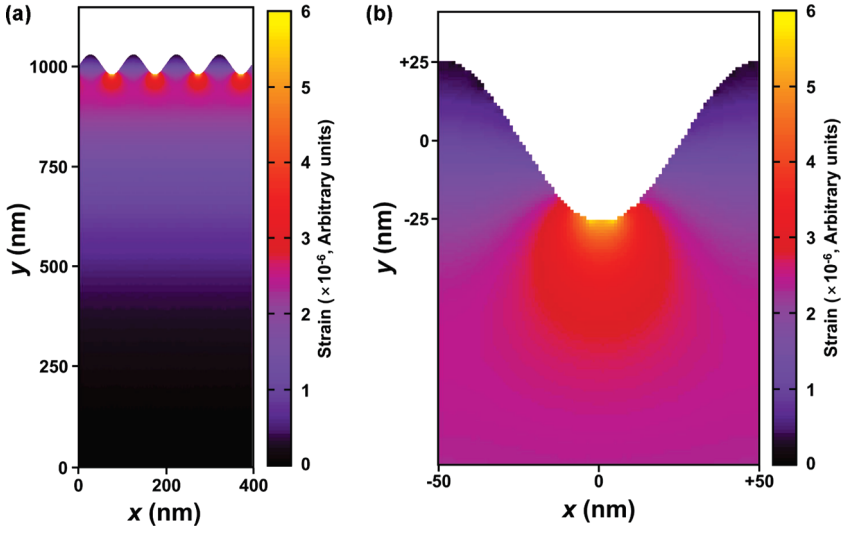

Figure 6. Distribution of strain ε_{yy} in piezoelectric thin films with sinusoidal surface modulations. The simulation area covers four piezoelectric nanocolumns. (a) Enhanced strain at the minima in these profiles (corresponding to the positions where the nanocolumn boundaries intersect the surface) is visible. (b) Magnified view of the strain enhancement observed at the boundary of the two nanocolumns, corresponding to the electric field enhancement.

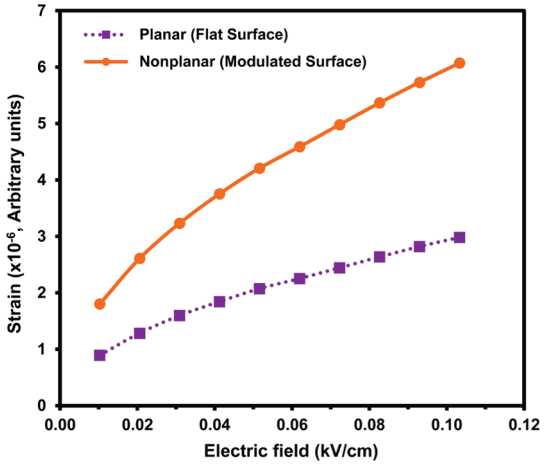

Figure 7. Maximum strain ε_{yy} *vs* average electric field is presented for the flat and the surface modulated film. The nonlinearities in these curves are associated with the nonlinearity in the piezoelectric properties of this material and the large applied electric fields.

phase field method. The phase field method has emerged as a powerful technique to simulate ferroelectric domains and polarization switching.[20] Recently, this method was used to simulate the polarization switching behavior in thin films with a nonplanar morphology.[5] We use this framework here to understand the enhancement of piezoresponse due to the nonplanar surface.

We consider a ferroelectric film in two dimensions, where the height of the film is given by the profile

$$L(x) = L_0 + A_0 \sin\left(2\pi \frac{x}{\lambda}\right) \quad (3)$$

where L_0 is the nominal film thickness, A_0 is the amplitude of the surface modulation, and λ is the modulation wavelength. To describe the geometry of the piezoelectric nanocolumns described in the experimental results (Figure 3), we assume L_0, A_0, and λ to be 1000, 25, and 100 nm, respectively. The phase field simulations were carried out using the principles, materials properties, and boundary conditions described in the Supporting Information and ref 5, with a 1 nm spatial resolution.

Figure 6 shows the strain distribution $\varepsilon_{yy}(x,y)$ in the film. This figure clearly demonstrates that the strain distribution is inhomogeneous; that is, it is highly enhanced in the region of the valley between the peaks. The enhancement in strain arises from the localized enhancement of the electric field, consistent with the electric field distribution of Figure 5. Figure 7 shows the maximum strain ε_{yy} *versus* the average applied electrical field. Note that the strain *versus* electric field curve is nonlinear. This figure clearly demonstrates the impact of surface morphology, with an overall increase in the level of maximum induced strain, related to the electric field enhancement at nanocolumn boundaries. The enhancement in strain, measured at large electric fields where the curves in Figure 7 are linear, is ~2.

CONCLUSIONS

Nonplanarity of thin film surfaces occurs commonly as a result of piezoelectric thin film deposition. This work demonstrates that such nonplanarity results in a large enhancement in piezoelectric response. The effect of nonflat surface morphologies tends to complicate electrical characterization processes and, thereby, prevent direct comparison of results from nanocolumnar thin films with corresponding data for bulk materials. The role of field enhancement in piezoresponse measurements was experimentally demonstrated for piezoelectric thin films with regular surface perturbations on the scale of 50 nm. The electric field enhancement enables large thin film displacements (ΔL of 23.2 nm) for a relatively low applied voltage (ΔV of 6.4 V). This enhancement can be effectively harnessed to improve piezoelectric applications. The computation of the piezoresponse coefficient d_{33} for such nanocolumnar and surface modulated films is influenced by the field enhancement parameter (1.5−2.5 in this case). The localization and magnitude of the electric field enhancement is determined by finite element modeling and shown to be consistent with electron emission based enhancement factor models. The influence of this electric field enhancement on piezoelectric strain is demonstrated by phase field simulations. The enhanced electric field associated with the surface morphology results in large piezoelectric displacements, even at low applied voltages. These results show that engineering surface morphology for property enhancement can be an effective approach to improve the performance of piezoelectric devices.

METHODS

Piezoelectric Thin Films Deposition. Thin films of strontium-doped lead zirconate titanate of composition $(Pb_{0.92}Sr_{0.08})(Zr_{0.65}Ti_{0.35})O_3$ were deposited by RF magnetron sputtering under conditions described elsewhere on platinized silicon substrates to achieve a nominal film thickness of 1200 nm.[3,8,21]

Electron Microscopy Analysis. The thin films were characterized by high-resolution microscopy to determine surface morphology and cross-sectional nanostructure. The analyses were carried out by field emission scanning electron microscopy and energy filtered transmission electron microscopy, respectively.

Piezoelectric Response Measurements. The piezoelectric response of smooth and nanoscale surface modulated thin films was carried out using an atomic force microscopy based technique. Thin film displacements under an applied electric field were recorded at a point, under the converse piezoelectric effect. Full details on the measurements, mapping, and d_{33} extraction are provided in the work by Sriram *et al.*[10]

Finite Element and Phase Field Simulations. The finite element modeling was performed by solving the Laplace's equation for the electric field given the static voltage applied between electrodes. Phase field simulations were carried out by determining kinetics using the time-dependent Ginzburg−Landau (TDGL) equations.[5] A full analytical discussion of this approach is provided in the Supporting Information.

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Supporting Information Available: Detailed description of experimental processes, additional finite element modeling results, and phase field model equations and parameters. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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