Effects of the top-electrode size on the piezoelectric properties (d_{33} and S) of lead zirconate titanate thin films

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The effects of a decreasing top electrode size on the electric and piezoelectric properties of tetragonal $Pb(Zr_X, Ti_{1-X})O_3$ thin films are investigated. The effective piezoelectric small-signal coefficient $d_{33,eff}$ and the piezoelectric large signal-strain S are measured using a double-beam laser interferometer. Both properties are found to decrease rapidly with decreasing size of the used Pt top electrode for the investigated dimensions of 5 mm to 100 μm edge length (square pads). While the loss of $d_{33,eff}$ is as high as 75%, the influence on the relative permittivity is only small. The source of the pad size effect on the measured piezoelectric properties is found to be the mechanics of the layered structure commonly used for piezoelectric measurements $(Pt/PZT/Pt/TiO/SiO_2/Si)$, $[PZT, Pb(Zr_x, Ti_{1-x})O_3]$ which is verified by finite element simulations. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1775306]

I. INTRODUCTION

$Pb(Zr_x,Ti_{1-x})O_3$ (PZT) ceramics exhibit superior ferroelectric, piezoelectric, and pyroelectric properties. Therefore, these materials are used in a wide range of applications such as actuators, force sensors, optical infrared sensors, and ferroelectric memories. In order to use these ceramics to their full potential, thorough research of their properties is needed.[1–3]

The double-beam laser interferometer[4,5] has been proven to be an accurate instrument for measuring the piezoelectric coefficient d_{33} and the piezoelectric field-induced sample strain S of ferroelectric thin films. Recent reports of extremely increased piezoelectric properties measured by charge integration[6] have been found to be influenced by the measurement method and the involved multilayer mechanics of the sample.[7]

Therefore, it is important to know the limitations of this method and the restrictions to the samples used for measurement.[8] One of these restrictions is the top electrode size, as for decreasing size, the correct laser alignment is becoming more difficult. Also, the beam spot on the sample could become larger than the top electrode, resulting in partial beam reflection. In order to quantify the influence of the top electrode size, we investigated the electromechanical and electric properties of different sized top electrodes on the sample.

II. SAMPLE PREPARATION AND PROPERTY MEASUREMENT

The PZT thin films are prepared using chemical solution deposition on double side polished $Pt(111)/TiO_2/SiO_2/Si$ substrates (25.4×25.4 mm^2). After spin coating and pyrolysis of three coatings, the films are annealed using rapid thermal annealing at 700 °C for 5 min in oxygen. This results in a film thickness of 130 nm. Coating and annealing are repeated in order to fabricate additional thicker films of 260 and 360 nm. Pt top electrodes are sputter deposited with electrode areas ranging from 0.01 to 1 mm^2 (130, 260 nm film) and from 0.25 to 25 mm^2 (360 nm film). The backside is finally vapor deposited with Au to achieve better reflectivity during interferometric measurements.

Film orientation is determined by standard θ-2θ x-ray diffraction (XRD) und sample thickness is measured by a DEKTAK profilometer. The effective piezoelectric small-signal coefficient $d_{33,eff}$ and large-signal strain S are measured using a double-beam laser interferometer with a minimum resolution of 0.2 pm. For small-signal measurements, the fast measurement method proposed in Ref. 5 is used. The piezoelectric coefficient is calculated according to

$$d_{33} = \frac{\Delta I}{V_{ac}}, \tag{1}$$

where ΔI is amplitude of the piezoelectrically induced sample strain and V_{ac} is the small-signal amplitude.

The relative permittivity is measured with the same setup, but using the measured electric current through the sample as input for the lock-in amplifier.[9]

III. RESULTS AND DISCUSSION

Figure 1 depicts the XRD measurements done to determine the orientation of the fabricated sample. The measured PZT (44/55) samples are highly (111) oriented and show an a/c-ratio>1.021 (calculated peak positions). No secondary orientation peaks are found, indicating no rhombohedral phase is present in the samples. Also, the absence of a (001) peak and the low intensity of the (100) peak lead to the conclusion, that most cells involved in switching are (111) oriented. All measurements investigate PZT (45/55), since

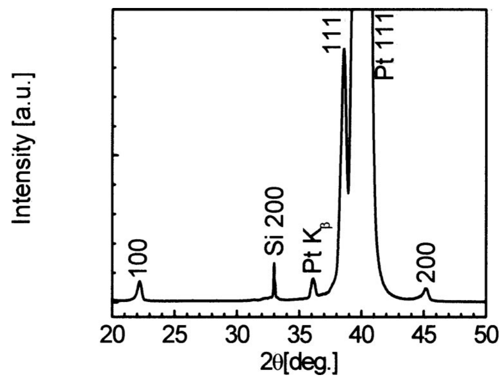

FIG. 1. X-Ray diffraction scan of 130 nm PZT (45/55) measured after complete sample preparation.

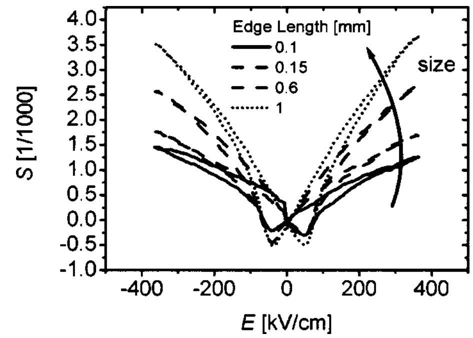

FIG. 3. Influence of the top electrode edge length on the measured piezoelectric large-signal strain S of PZT (45/55) (130 nm).

its piezoelectric response is larger than that of, e.g., PZT (40/60) or PZT (30/70) and its composition is far away enough from the morphotropic phase boundary to exhibit only tetragonal switching.[10,11]

In Fig. 2(a), the dependence of the effective piezoelectric small-signal coefficient $d_{33,\text{eff}}$ from the edge length of the used top electrode is given. As can be seen, the measured $d_{33,\text{eff}}$ decreases rapidly for smaller top electrodes. However, this decrease is not linear, but seems to grow in strength even for the lowest pad sizes measurable, with a total loss of 75% of the remanent piezoelectric coefficient $d_{33,\text{eff,rem}}$ [Fig. 2(b)]. Regarding this value, it should be noted, that measurements on pads larger than 3×3 mm^2 are influenced by either mechanical resonance or acoustic vibrations of the sample, resulting in shape distortion of the measured curve or nonstable measurements.

Also, the measured large-signal strain S of the sample decreases in a similar matter for smaller electrodes, as can be seen in Fig. 3. Since the large-signal strain in (111)-oriented thin films is mainly caused by intrinsic effects,[12,13] it is not surprising to see nearly the same decrease in the piezoelectric small- and large-signal behavior.

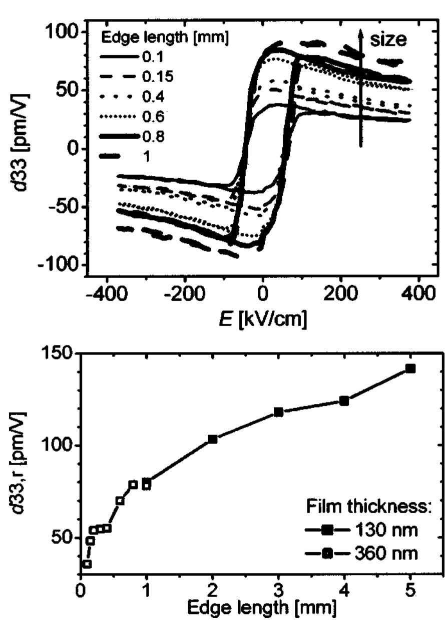

FIG. 2. Piezoelectric small-signal coefficient d_{33} of PZT (45/55) measured on different sized top electrodes. Influence of the top electrode edge length on the (a) measured curve and (b) on the remanent piezoelectric coefficient of 130 nm (gray) and 360 nm (black) thin films.

The aforementioned behavior is unexpected since d_{33} is a material parameter and should remain constant for different sized top electrodes. Even if the formula for the effective piezoelectric coefficient of clamped films is taken into account, the measured $d_{33,\text{eff}}$ should not be influenced by the used top electrode size. For films clamped perfectly on a rigid substrate, this formula reads[7]

$$d_{33,\text{eff}} = d_{33} - 2\frac{d_{31}s_{13}{}^{E}}{s_{11}{}^{E} + s_{12}{}^{E}}, \tag{2}$$

where d_{33}, d_{13} are the piezoelectric coefficients of the material and $s_{ij}{}^{E}$ are the elastic compliances. The measured behavior is also in contrast to the work of Nagarajan *et al.*,[14] which explains an increase of the measured $d_{33,\text{eff}}$ due to reduced clamping. It should be noted, however, that in Ref. 14, the geometry of the sample is transformed from that of thin films to that of near single crystals by etching the lateral dimensions of the film down to the order magnitude of the film thickness. We believe the source of the increased $d_{33,\text{eff}}$ in Ref. 14 to be mainly the freed piezoelectric strain of the ceramic edges and the largely reduced lateral dimensions.

To investigate if the edge effects also affect our measurements we measured the top electrode size dependence of the piezoelectric coefficient $d_{33,\text{eff}}$ in a sample, which capacitors were cut out from the surrounding ceramic PZT layer by reactive ion beam etching (RIBE). The results are depicted in Fig. 4. As can be seen, the influence of the top electrode size

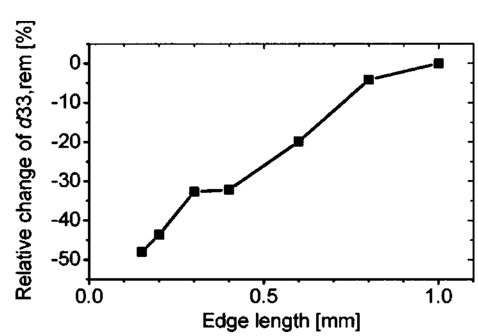

FIG. 4. Relative change of piezoelectric small-signal coefficient $d_{33,\text{rem}}$ of a PZT (45/55) thin film (260 nm) sample with capacitors etched free by RIBE. Values are based on the measured $d_{33,\text{rem}}$ at 1 mm edge length.

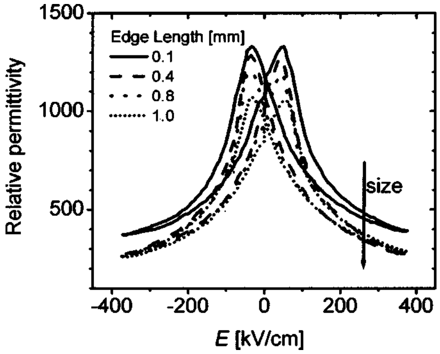

FIG. 5. Influence of the top electrode edge length on the measured relative permittivity of PZT (45/55) (130 nm).

is similar to the one measured on the other samples. Hence, the influence of the edge on the intrinsic strain of the capacitor is negligible and the main clamping effect on the ceramic layer is caused by the substrate.

In order to check for any other influences of the top electrode size on the intrinsic strain of the ceramic layer, the size impact on the relative permittivity (Fig. 5) was measured. As can be easily seen, no decrease of the relative permittivity is found when measuring smaller pads. Instead a rise of approximately 27% is found, which can be attributed to rising influences of stray fields on smaller electrodes. Since the relative permittivity is calculated from the measured small-signal current,[9] it is also an indication for the motion of the center ions out of their equilibrium state and therefore the intrinsic strain of the ceramic layer. Hence, the decrease of the measured $d_{33,\mathrm{eff}}$ cannot be attributed to a decrease of the d_{33} of the ceramic layer itself.

We therefore conclude, that the decrease of the measured piezoelectric coefficient has to be caused by the mechanics of the used layer structure of the sample, if errors produced by the measurement itself can be excluded.

IV. METHODICAL INVESTIGATION

One erroneous influence on the measurement could be caused by sample bending and has to be excluded first. According to the mechanics of bimorph structures, the displacement can be calculated by[1]

$$\Delta I = \frac{3}{4} d_{31} \left(\frac{I}{t}\right)^2 V, \tag{3}$$

where l is the length, t is the thickness of the active piezoelectric layer, and U the applied voltage. Hence, the bending of a thin film structure under voltage application should be increasing for larger top electrodes. Furthermore, the double-beam laser interferometer setup eliminates sample bending effects under perfect conditions.[4]

The primary source for errors failing to suppress bending can be a misalignment of the beam reflection points on the front and the back side of the sample. In our setup, we use a special quartz glass sample for the task of beam alignment. One side of this sample carries sputter deposited platinum spots of different sizes and the geometry of the sample is comparable to that of the thin film samples. By checking whether the back side beam and the front side beam hit the same platinum spot, while one beam is transduced through the mounted sample, the alignment of both beams can be verified. Also, an adjustable holder is used to mount the samples under a specific angle to the beams.

An additional method to check for bending influences is to measure a spot far away from the contacted top electrode. Since no measurable response was found this way, sample bending effects are negligible in our measurements.

Besides excluding possible errors in the electrical components of the measurement setup, optical effects influencing the reflected beam have to be taken into account. The former was checked by investigating the applied signal with the oscilloscope. No deviations or distortions were found during these investigations. Optical effects influencing the measurement consist of the needle used for electrical contacting distorting the laser beam and partial reflection of the beam on small electrodes. The former was rechecked by measuring the electromechanical response before and after the needle is deliberately positioned in the beam without changing the results. The latter should only affect measurements on the smaller electrodes. Also, a partial reflection would be seen in the reflected beam and therefore the resulting interference pattern. Since such influences are only seen when measuring electrodes smaller than $200 \times 200\ \mu\mathrm{m}^2$ (smallest and second-smallest pad size) and the electrode size effect is also measured for large electrodes, we believe effects of partial reflection not to be the sole source of the measured behavior. They may, however, additionally contribute to the effect.

After excluding intrinsic sources and methodical errors, the measured size effect has to be generated by the layered system of the sample itself. Since the ceramic layer is not perfectly clamped on the substrate, it is able to contract parallel to the substrate plane. This contraction influences also the platinum top and bottom electrode layers, forcing them to contract too. This will result in an additional strain of the whole layered system. In thin films, the layer thickness of the electrodes is comparable to the ceramic layer. Therefore, the additional strain caused by the electrode layers could be comparable to the strain of the ceramic layer and the resulting sample strain could be bigger than the ceramic layer strain. However, this effect should not be influenced by the size of the used top electrode since it could be investigated as locally induced and transmitted mechanical stress. Hence, only the thickness of the layer needs to be taken into account for error evaluation.

Another source causing additional strain is the substrate underneath the piezoelectrically active area of the thin film. The contraction of the film is partially transmitted through the platinum and the adhesive TiO_2 layer into the silicon substrate. Down to a certain depth into the substrate, this transferred mechanical stress should also produce additional sample strain. If this effect is dependent on the size of the piezoelectrically active area, this could be the explanation for the measured behavior.

V. NUMERICAL SIMULATION

The contributions of the single layers to the overall sample strain cannot be investigated directly with any of the

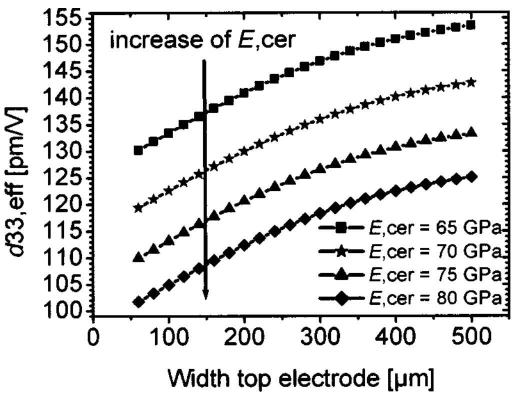

FIG. 6. Piezoelectric small-signal response of the ceramic layer in a thin film multilayer system calculated by FEM in respect of different top electrode sizes and the elastic modulus of the ceramic film.

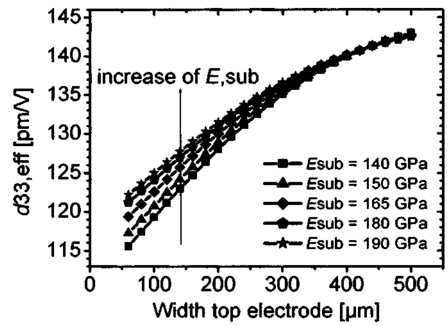

FIG. 7. Piezoelectric small-signal response of the ceramic layer in a thin film multilayer system calculated by FEM in respect of different top electrode sizes and the elastic modulus of the substrate.

known measurement techniques. On the other hand, the three-dimensional layer system is to complex to be fully calculated by analytical methods. Simulation by coupled finite element modeling (FEM) is one method to investigate whether the size effect is caused by the layered system. However, due to possible dependence of the measured electromechanical properties of the system from its geometry, literature values of thin films regarding the piezoelectric coefficients should not be taken into account.

It is therefore better to start with a simplified model consisting out of four layers: a substrate, two electrode layers and a piezoelectric, ceramic layer. Such a model can be used as indication whether the size dependence can be caused by a layered system itself or if a more complex model is needed.

Using this simple model, it is possible to use the program ANSYS to build and calculate variations of the two dimensional model. This includes the variation of the top electrode edge length between 60 and 1000 μm but also changes of the ceramic and Pt film thickness and different coefficients of elasticity for the ceramic layer and substrate. Material characteristics of the ceramic layer used in the simulations are: Young's modulus $E_{\mathrm{PZT}}=70$ GPa, Poisson's ratio $\nu_{\mathrm{PZT}}=0.3$, piezocoefficients $d_{31}=-93$ pm/V, $d_{33}=220$ pm/V, and $d_{15}=265$ pm/V, which are close to the literature values of bulk PZT. However, due to the simplicity of the model, several effects influencing thin films, are not taken into account. For example, it does not simulate mechanical stresses induced to the sample by thermal processing during sample fabrication. Hence, the calculated strain may deviate from the previously measured values.

For each model the strain at the sample surface in the middle of the top electrode is extracted with an applied static voltage of 1 V (intrinsic strain). As can be seen in Fig. 6, the FEM calculations show a qualitative similar behavior of the piezoelectric coefficient for decreasing top electrode sizes. The effective piezocoefficient $d_{33,\mathrm{eff}}$ drops about 15% ($E_{\mathrm{cer}}=65$ GPa) when the top electrode size is reduced from 500 to 60 μm.

According to our observations above, the piezoelectrically induced strain S of the ceramic layer does not vary for different edge lengths of the top electrode. Hence, the observed size effect is believed to be caused by additional substrate strain. Further simulations investigate the influence of some important geometrical parameter and material characteristics of the structure. They reveal, that a change of the film thickness of the PZT layer between 0.2 and 0.8 μm has no influence on $d_{33,\mathrm{eff}}$. Also a change of the platinum layer thickness between 0.1 and 1 μm does not change the $d_{33,\mathrm{eff}}$ dependency. A strong dependency of $d_{33,\mathrm{eff}}$ can be found like it is expected from the PZT film Young's modulus. But it results only in a vertical shift of the curve and no change of its shape (see Fig. 6).

In order to investigate the effect of different substrates, we have modified the Young's modulus of the substrate in our calculations. These results are shown in Fig. 7. As can be seen, the decreasing effect on the piezoelectric coefficient lessens for stiffer substrates. Before using stiffer substrates in order to minimize the electrode size effect, one should consider that stiffer substrates might also influence the effective d_{33} of the ceramic layer. Hence, considering a certain application of the ceramic material, one should try simulate the environment of the application during the measurement. Also, for comparative research, the used electrode size and sample layer setup should be kept constant.

In Fig. 8, the following values are used to fit the calculated data to the measurements without introducing further effects to the system: Young's moduli $E_{\mathrm{cer}}=100$ GPa and $E_{\mathrm{sub}}=120$ GPa, Poisson's ratio $\nu_{\mathrm{sub}}=0.25$, piezocoefficients $d_{33}=150$ pm/V. As can be seen, it is possible to simulate the measured behavior to a certain degree. The calculations indicate a strong $d_{33,\mathrm{eff}}$ dependency for smaller electrode geometries which decreases for larger electrodes. Hence, the simulated model indicates that the measured behavior can be caused by the layered system itself and is no measurement error.

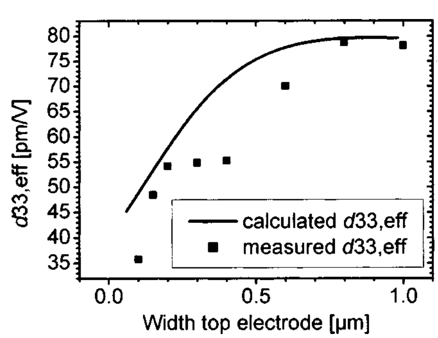

FIG. 8. Piezoelectric small-signal response of the ceramic layer in a thin film multilayer system calculated (line) by FEM in respect of different top electrode sizes and in comparison to measured values (squares).

Future refinements of the FEM simulation should include more of the effects known for thin film systems in order to receive a better quantitative agreement between the measured and the calculated strains. Up to now, the model only indicates the existence of a dependence of the electromechanical properties from sample geometry.

In conclusion, the effects of different sized top electrodes on the electric and electromechanical properties of PZT thin films have been investigated. An unexpected influence of the electrode size on the electromechanical properties was found. After ruling out methodical measurement errors, this effect was found to be generated by the mechanical properties of the multilayer system. This fact was also indicated by finite element modeling. Additionally, the stiffness of the substrate and the ceramic layer has an impact on the calculated effect. Stiffer substrates should help to minimize the effect and electrode size should be kept constant for comparative measurements.

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