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Barrier heights, polarization switching, and electrical fatigue in $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ceramics with different electrodes

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The influence of Pt, tin-doped In_2O_3 , and RuO_2 electrodes on the electrical fatigue of bulk ceramic $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) has been studied. Schottky barrier heights at the ferroelectric/electrode interfaces vary by more than one electronvolt for different electrode materials and do not depend on crystallographic orientation of the interface. Despite different barrier heights, hysteresis loops of polarization, strain, permittivity, and piezoelectric constant and the switching kinetics are identical for all electrodes. A 20% reduction in polarization after 10^6 bipolar cycles is observed for all the samples. In contrast to PZT thin films, the loss of remanent polarization with bipolar switching cycles does not significantly depend on the electrode material. © 2010 American Institute of Physics. [doi:10.1063/1.3512969]

I. INTRODUCTION

Ferroelectric materials have found their way in a broad range of applications in electromechanical systems such as actuators, piezoelectric sensors, and nonvolatile dynamic random access memories.^{1–3} Operation of ferroelectric memories depends on repeated polarization switching, which is different from unipolar cycling in normal applications of actuators. Thus bipolar fatigue is often studied on ferroelectric thin films. Electrical fatigue, i.e., the reduction in remanent polarization with increasing number of cycles, which is particularly pronounced for Pt metal electrodes under bipolar loading, is one of the prominent failure mechanisms for ferroelectric devices.

Over the past decades, various models have been proposed for the degradation phenomena, e.g., (i) domain wall pinning by electronic defects, (ii) charge-injection-induced inhibition of domains with reversed polarization, (iii) oxygen vacancy redistribution and ordering at the ferroelectric interface leading to pinning of domain walls, and (iv) local phase decomposition.^{4–7} Significant attention was paid to the role of oxygen vacancies and/or charges injected from the electrodes. It was argued that oxygen vacancies are redistributed and piled up at the ferroelectric/electrode interface through long-distance migration during cycling and then hinder the polarization switching. If the electrodes were made from conducting oxides such as $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, SrRuO_3 (SRO), LaNiO_3 , $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, or RuO_2 ,^{8–12} oxygen vacancies may be consumed by the electrode material^{13,14} thereby improving the fatigue endurance of ferroelectric capacitors. However, severe polarization reduction was also observed on epitaxial $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) films with SRO and n-type La doped SrSnO_3 electrodes recently.^{15,16} Fatigue of PZT thin films with n-type tin-doped In_2O_3 (ITO) electrodes was also reported by Rao *et al.* and Foster *et al.*^{17,18} These results

support the model that the fatigue of ferroelectric films is related to the trapping of injected charges and is predominantly an electronic phenomenon.

The electrode material and the interface properties, e.g., the Schottky barrier which defines hole or electron injection at the ferroelectric/electrode interface, is a key issue to establish highly reliable ferroelectric devices. Furthermore, the band bending caused by the different work functions of different electrode materials or thermal processing can induce asymmetric electric contacts, thus asymmetric charge injection and polarization switching.^{19–21} Despite their importance for device properties, the Schottky barrier heights at the various PZT/electrode interfaces are poorly known.

The near electrode region is also important in bulk ferroelectric materials. Jiang *et al.*^{22,23} reported that in bulk lanthanum doped PZT the adhesion between the ferroelectric and the electrode and the surface contamination are a crucial factor determining the fatigue endurance. Balke *et al.*²⁴ reported the appearance of a damaged region near the electrode after bipolar cycling in La and Fe doped PZT, and a field screening model was suggested to be responsible for bipolar fatigue. Effects of Ag and Pt electrodes on the fatigue of commercially available PZT ceramics were also compared previously.²⁵ It has been observed that Pt electrodes are much less reproducible than Ag electrodes and frequently lead to micro crack formation during cycling.

Due to the high piezoelectric coefficient, relatively large remanent polarization, small coercive field and high Curie temperature, PZT has been intensively studied as one of the most prominent ferroelectric materials. In this study, metal Pt, transparent conductive ITO, and metal oxide RuO_2 electrodes, with strongly different Schottky barrier heights at the interfaces^{26,27} have been investigated. Ferroelectric properties as polarization, strain, permittivity, and piezoelectric constant with these electrodes were analyzed. In addition,

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FIG. 1. (Color online) Energy band alignment with barrier heights at the as-grown (1.8 eV), oxidized (2.3 eV) and reduced (1.2 eV) PZT/Pt interface (a), as-grown PZT/RuO₂ interface (b), and as-grown PZT/ITO interface (c). Conduction band positions were calculated from the valence band energies by adding bulk band gap energies of the respective materials.

polarization switching was characterized as function of time and applied electric field. The fatigue behavior was investigated using bipolar cycling.

II. SCHOTTKY BARRIER HEIGHTS

The barrier heights at the different PZT/electrode interfaces, as determined by photoemission experiments which are described in detail elsewhere,^{26,27} are summarized in Fig. 1. PZT thin films prepared by pulsed laser deposition (PLD) have been used in these experiments. The surface composition of the PZT thin films used for interface studies is largely identical to those of the PZT ceramics used for the fatigue studies described below. As barrier heights are dominated by the chemical bonds at the interface, these are generally not affected by doping concentrations of a few percent.

As also observed for SrTiO₃/Pt and SnO₂/Pt interfaces,^{28,29} the barrier height at the PZT/Pt interface varies significantly with atmosphere.²⁶ For reducing conditions, the Fermi level is closer to the conduction band minimum ($E_F - E_{VB} = 2.2$ eV), while oxidizing conditions lead to a Fermi level closer to the valence band maximum ($E_F - E_{VB} = 1.1$ eV). No such variation is observed for the Schottky barriers at the PZT/RuO₂ and PZT/ITO interfaces. These are non-reactive and a unique barrier height is observed.²⁷

Barrier heights for electron or hole transport across the metal-semiconductor interface $\Phi_{B,n}$ or $\Phi_{B,p}$ are determined by the distance between Fermi level E_F and the conduction band minimum E_{CB} or valence band maximum E_{VB} at the interface, respectively. While the valence band energies are derived directly from the spectra, the conduction band positions have to be calculated from the valence band energies by adding bulk band gap energies of the materials, respectively. In Fig. 1 values of 3.4 eV and 2.7 eV have been used for PZT (Ref. 30) and ITO,^{31,32} respectively.

Although the Fermi level position at the interface varies significantly with electrode material, it never comes close to either the valence band maximum ($E_F - E_{VB} \geq 1.0$ eV) or the conduction band minimum ($E_{CB} - E_F \geq 1.3$ eV). The difference in barrier height between PZT with ITO and RuO₂ corresponds well to the different work functions of the two electrode materials. While ITO is a degenerately doped n-type semiconductor with a typical work function of ~ 4.5 eV,³³ RuO₂ is metallic with a work function of 6.1 eV.³⁴ The large

work function electrode leads to a low Fermi level at the PZT/electrode interface clearly favoring hole injection, while the low work function material leads to a higher Fermi level, favoring electron injection. However, the injection barriers derived from the photoemission experiments are ≥ 1 eV. Neither significant electron nor hole injection is, therefore, expected at not too high electric fields, although it has to be pointed out that barrier heights and charge injection at grain boundaries may be different from that at the surfaces of the grains. It is only the latter which is probed by the photoemission technique.²⁹

The ceramic PZT samples used for fatigue studies described below may have different barrier heights than the thin film samples used for the interface experiments described above. Variations in barrier heights are discussed in dependence on interface orientation for interfaces between heterovalent materials,^{35,36} or in dependence on doping level.⁶ In addition, it has been discussed that the barrier height depends on the ferroelectric polarization state.^{37,38} Interface orientation, doping level, and polarization of the PLD deposited PZT thin films are not the same as those of the ceramic samples.

An interface experiment using a ceramic PZT sample has been carried out in order to clarify whether the barrier heights of thin film and ceramic samples are the same as those of the thin films. The surface of a 1 mm thick and 10 mm diameter disk shaped ceramic PZT samples was prepared as described in Sec. III A. In order to reduce sample charging effects during photoemission measurement, the surface was first coated with a ~ 70 nm thick Pt film, leaving a 2 mm wide circular area uncoated. X-ray photoemission spectra were recorded using the same experimental setup used for interface studies of the thin film samples employing a Physical Electronics PHI 5700 spectrometer with monochromatic Al $K\alpha$ radiation. Due to small detection area of the analyzer (≤ 1 mm) spectra taken from of the uncoated area show only Pb, Zr, Ti, and O derived emissions after the sample has been cleaned by heating for 30 min at 400 °C in the vacuum system backfilled with 0.1 Pa oxygen to remove hydrocarbon adsorbates. As expected, significant sample charging occurs during measuring the uncoated surface, which could partially be compensated by use of an electron flood gun. The imperfect charge compensation is evident from the highly asymmetric shape of the emissions, which are shown at the bottom of Fig. 2.

The interface experiment was performed by repeated deposition of RuO₂ and photoemission characterization. RuO₂ deposition was carried out using reactive magnetron sputtering as described elsewhere.^{27,34} After each deposition step, the sample was adjusted in the photoemission setup centering on the Pt-free area with a microscope. All spectra reveal only emission peaks related to the PZT substrate and the RuO₂ film.

Sample charging did no more occur for RuO₂ film thickness ≥ 1.5 nm. Even without use of an electron flood gun symmetric peak shapes are obtained. A binding energy of 281.0 eV is derived for the Ru $3d_{5/2}$ component for higher film thickness, which corresponds well with stoichiometric RuO₂.^{27,34,39} This justifies that the Fermi level of the RuO₂

FIG. 2. (Color online) Photoelectron spectra recorded during stepwise deposition of RuO_2 onto a ceramic PZT sample. The spectra up to 0.5 nm coverage were recorded employing charge neutralizing by an electron flood gun. The sample geometry is sketched in the inset.

layer on top of the Pt-free PZT area can be taken as binding energy reference. Apparently the lateral electric conductivity of the RuO_2 layer is sufficient to equilibrate the Fermi level across the whole surface with the Pt layer, which is electrically connected to the sample holder.

As the Fermi level at the surface is equilibrated it is possible to derive the Schottky barrier height at the PZT/ RuO_2 interface directly from the binding energies of the PZT derived emissions. The binding energy of the Pb $4f_{7/2}$ component is constant for a RuO_2 thickness ≥ 4.5 nm and amounts to 137.5 ± 0.1 eV. This value agrees within the experimental uncertainty with the one derived during stepwise deposition of RuO_2 onto thin film PZT samples.²⁷ Hence, the barrier height at the interface between ceramic PZT and RuO_2 is, within ± 100 meV, the same as the barrier height at the interface between thin film PZT and RuO_2 , which is given in Fig. 1.

The spectra shown in Fig. 2 provide evidence that the barrier height does not depend significantly on the crystallographic orientation of the interface. Due to the Fermi level equilibration across the surface, different barrier heights would result in different binding energies of the PZT derived emissions in the photoemission experiment. Two different values for the barrier height with a difference of δE , e.g., would appear as two distinct peaks in all substrate related emissions with the same binding energy difference. The relative intensity of the two emissions then corresponds to the surface areas related with the different barrier heights. This situation is illustrated in Fig. 3. If individual peaks cannot be resolved, peak broadening (also asymmetric) may indicate a variation in the barrier height. In the absence of any peak broadening, the variation in the barrier height across the surface cannot be larger than ~ 100 meV. As the used ceramic PZT sample has a grain size of $5 \mu\text{m}$, which is much less than the area probed in the photoemission experiment, it can be expected that a large number of possible crystallographic orientations of the interface are simultaneously detected. Despite this, the Pb $4f$ and the Zr $3d$ emissions in Fig. 2 as well as the Ti $2p$ emission (not shown) are as sharp and symmetric as those measured during deposition of RuO_2

FIG. 3. (Color online) Photoemission spectra in the presence of inhomogeneous barrier heights illustrated for the example where two different interface regions A and B with different barrier heights are present. If the Fermi level across the surface is aligned, the binding energies of the substrate core levels directly correspond to the barrier height $\Phi_B = E_F - E_{VB}$. Two different barrier heights at the regions A and B will give rise to two distinct peaks A and B in the spectra of all substrate core levels. The binding energy difference $BE_A - BE_B$ directly corresponds to the difference in barrier height and the relative intensity of the peaks A and B corresponds to relative areas of the regions A and B. A distribution of barrier heights will give rise to a corresponding distribution of binding energies in all substrate core levels. The absence of additional peaks and line broadening in spectra recorded from a polycrystalline ceramic PZT sample (see Fig. 2), therefore, indicates that the barrier height does not vary along the interface.

onto thin film PZT (see Fig. 2 in Ref. 27). This is particularly evident from the deep valley between the two spin-orbit split components of the Zr $3d$ emission.

The undetectable variation in the barrier height for the ceramic PZT sample may also indicate that the barrier height does not depend on the polarization, in contrast to what has been discussed in literature.^{37,38} The used PZT sample has not been poled and also been heated two times before the interface experiment was conducted. The various grains in contact with the RuO_2 electrode should thus exhibit random polarization states as the measurement was made at room temperature, which is well below the ferroelectric transition temperature. If the barrier height depends significantly on the polarization (according to 37 and 38 the polarization modifies the barrier height by $\pm \sim 0.5$ eV), multiple peaks or peak broadening should be present in the core level spectra for random polarization. This can clearly be ruled out. However, the polarization state of the grains in contact with the RuO_2 may be affected either by the deposition or by the measurement resulting in a single rather than a random polarization state of the grains in contact with the electrode material. During deposition of RuO_2 , negative oxygen ions from the plasma discharge are accelerated toward the substrate,⁴⁰ which may adsorb on the surface and consequently lead to a change in polarization.⁴¹ The charges and currents induced by the photoemission process might also modify the surface. The performed experiment does therefore not conclusively rule out a dependence of the barrier height on polarization state. Clarification of this important issue requires additional studies.

Despite the remaining uncertainty concerning a polarization dependence of the barrier height, the interface experiment performed on the ceramic PZT sample reveals an iden-

tical barrier height than those observed for thin film PZT. Any influence of different crystallographic orientation or different doping levels of the films can be ruled out. As the effect of the deposition and/or the photoemission measurement on the polarization state would also be identical for thin film and ceramic samples, it appears safe to assume that the barrier heights shown in Fig. 1 provide reasonable measurements also for ceramic PZT samples used for the electrical studies described in the following.

III. ELECTRICAL ANALYSIS

A. Sample preparation

Commercial PZT ceramics (PIC 151, PI ceramics, Lederhose, Germany) with a composition of $\text{Pb}_{0.99}[\text{Zr}_{0.45}\text{Ti}_{0.47}(\text{Ni}_{0.33}\text{Sb}_{0.67})_{0.08}]\text{O}_3$ close to the morphotropic phase boundary were utilized. The samples were disk shaped with a diameter of 10 mm and a thickness of 1 mm. Identical material has been used by Balke *et al.*²⁵ In order to reduce the effects of surface roughness on electrical measurements, the PZT samples were polished down to 1 μm grid size. Before deposition of the electrode materials, the samples were cleaned with acetone and isopropanol in an ultrasonic bath, dried in nitrogen flow and annealed in air at 400 °C for 2 h to remove surface stress caused by polishing.

The Pt, ITO, and RuO_2 electrodes, with a thickness of 20 nm, 60 nm, and 100 nm, respectively, were deposited on both sides of PZT disks in the integrated surface analysis and preparation system DAISY-MAT (Damstadt Integrated System for Materials Research), which combines a multitechnique surface analysis system (Physical Electronics PHI 5700) and several thin film deposition chambers with an ultrahigh vacuum sample transfer.⁴² The same experimental setup and preparation procedures have been used in the interface experiments for the determination of the Schottky barrier heights. Additional Ag paste (Conrad Electronic GmbH, Hirschau, Germany), which readily dries at room temperature, was applied to the electrodes in order to improve current distribution across the electrode and to avoid mechanical damage by contact tips.

Pt electrodes were deposited by radio-frequency (rf) sputtering with a power of 5 W in pure Ar at a pressure of 0.5 Pa and a substrate to target distance of 10 cm, resulting in a deposition rate of ~ 5 nm/min. ITO was deposited by rf sputtering at substrate temperature of 400 °C using a power of 25 W, the Ar pressure is 0.5 Pa, and a distance between the substrate and target of 9 cm, resulting in a deposition rate of ~ 10 nm/min and an electrical conductivity of $\sigma \sim 5000$ S/cm.⁴³ RuO_2 was deposited by reactive dc sputtering from a 2 in. metallic Ru target, using a power of 10 W, a substrate to target distance of 10 cm, a pressure of 1 Pa, an Ar/ O_2 ratio of 92.5/7.5. The deposition rate is about 5 nm/min and the resulting films are fully oxidized.³⁴

For measuring the polarization, the samples were connected in series to a test capacitor of 13.6 μF in a Sawyer–Tower circuit. The P – E loops were evaluated with respect to the switchable polarization $2P_r$. Strain was measured simultaneously by an optical displacement sensor. Polarization and strain hysteresis loops were measured as function of dc volt-

age. In order to determine piezoelectric constant d_{33} and permittivity ϵ_{33} simultaneously, an ac voltage (amplitude of 5 V/mm and frequency 1 kHz) was superimposed on the dc voltage. The dc voltage was stepwise increased to the maximum or minimum field of ± 2 kV/mm with a step duration of ~ 5 s, reaching a 2.5 mHz frequency for the large signal hysteresis measurement. The samples were fatigued by loading bipolar sinusoidal electric fields of amplitude 2 kV/mm at 50 Hz. All samples were clamped with two soft springs during this process to avoid mechanical stress. For comparison, a commercial PIC 151 sample with Ag electrodes (fired at 720 °C) as a standard specimen (hereby noted as S) has been used.

Poling and switching experiments were performed utilizing an electrical circuit described previously.⁴⁴ The samples were at first poled to saturation by applying a dc field of $E_0 = 2$ kV/mm (about twice the coercive field strength) for 1 h assuming that the maximum saturated polarization P_s has been reached. After such a conditioning, an oppositely directed switching field E_{sw} between 1.0 to 2.0 kV/mm was applied to the sample for a definite time duration t_p varied in the range between 0.1 μs and 10^2 s. During the switching process and the subsequent short circuiting the total displacement $D_{sw}(t)$ was recorded by means of a digital oscilloscope. After each switching experiment the sample was conditioned as described above to restore its initial saturated polarization. To determine the polarization ΔP reversed during application of the field E_{sw} for the time t_p , a subsequent forward poling was performed by applying the same field E_{sw} to the conditioned sample in the same poling direction also for the time t_p . Since this sample was already polarized to saturation, the apparent displacement $D_{fp}(t)$ during forward poling contains all components of the switching experiment except for the permanently switched ferroelectric polarization ΔP . Therefore, the switched ferroelectric polarization ΔP can be calculated by subtracting the forward poling curve $D_{fp}(t)$ from the switching curve $D_{sw}(t)$ at any moment after application of the switching voltage pulse.

B. Ferroelectric properties and fatigue

The left column in Fig. 4 provides the electrical measurement results of PZT ceramics with the above analyzed electrodes. The switchable polarization $2P_r$ and coercive field E_C as measured at ± 2 kV/mm electric field are about 0.64 C/m² and 1 kV/mm, respectively. The polarization-electric field (P – E) loops of samples with different electrodes are nearly identical. Also no significant difference was found in strain-electric field and piezoelectric constant d_{33} -electric field loops. In addition, the dielectric constant ϵ_{33} as a function of electric field for PZT ceramic with Pt, RuO_2 , and ITO exhibits an almost identical behavior. However, the permittivity of the sample with the standard fired Ag electrodes shows a smaller permittivity, which may be related to diffusion of the Ag into the PZT bulk due to the high temperature (720 °C) processing of the contact. All the loops are symmetrical if centered at zero electric field, thus a symmetrical ferroelectric/electrode interface contact can be assumed. The ferroelectric properties observed for the different

FIG. 4. (Color online) Polarization P , strain S , dielectric constant ϵ_{33} , and piezoelectric constant d_{33} vs electric field of PZT bulk ceramics (PIC 151) with Pt, RuO₂, ITO, and fired Ag electrodes (s), respectively. The left/right column show measurements before/after 10^6 bipolar cycles, respectively.

electrodes are in good agreement with those reported by Balke *et al.*,²⁵ who have used identical ferroelectric material.

In order to study the effects of the electrode materials on the fatigue behavior, all the samples were cycled to 10^6 cycles under bipolar loading with electric fields of ± 2 kV/mm (see right column in Fig. 4). The $2P_r$ of PZT coated with metal electrodes decreased by 12% and 18% for fired Ag and for Pt electrodes, respectively. Again, similar reduction has been reported previously by Balke *et al.*²⁵ The samples with conductive oxide electrodes also show fatigue with a loss of remanent polarization of 22% (ITO) and 23% (RuO₂). The fatigue in PZT ceramic with ITO electrode is consistent with the results reported previously in PZT thin films coated with ITO electrodes.^{17,18} For the case of RuO₂ electrodes, fatigue in PZT ceramic contradicts those of the PZT thin films with the same electrode material.^{13,14} Although the switchable polarization decreased after repeated cycling, the results still show a saturated hysteresis loop without tilting and deformation, and the coercive field does not change during the process. This indicates that no interface layer appeared after cycling.⁴ Such layers have been observed by Balke *et al.*^{24,25} and related to microcracks formed underneath the electrode.

C. Polarization switching dynamics

Figure 5 provides the temporal dependence of the switched polarization ΔP at the initial state and after 10^6 cycles from 10^{-7} to 10^2 s at different applied electric fields.

FIG. 5. (Color online) Switched polarization ΔP vs poling time for PZT bulk ceramics (PIC 151) with Pt, RuO₂, ITO, and fired Ag (s) electrodes recorded at initial state (a) and after 10^6 cycles (b) under different applied fields as indicated.

At the initial state as shown from Fig. 5(a), the whole switchable polarization can be fully reversed by using poling pulses of 10^{-4} s at 2.0 kV/mm field, suggesting our fatigue cycling frequency of 50 Hz (corresponding to 20 ms) is sufficient to reverse the switchable polarization. The small difference between the fully reversed ΔP and $2P_r$ measured from the P - E loops may originate from the different setups. The required time for the complete switching of polarization strongly depends on the applied field. At 1.5 kV/mm the time required for full switching increases to >10 ms. Even at 1.0 kV/mm (typical E_C for PIC 151) the polarization can be totally switched within 1000 s. Before cycling, all samples show the same switching dynamics independent on electrode material.

The switchable polarization ΔP decreased from 0.69 C/m² before cycling to 0.56 C/m² after fatigue [Fig. 5(b)]. The decrease is in full accord with the hysteresis characterization (Fig. 4). For S, PZT/Pt, and PZT/RuO₂ samples, the spectra show nearly the same time dependence of polarization reversal for different electric fields. Only for the PZT/ITO sample longer switching times are required (about ten times).

D. Discussion

It has been previously suggested that the degradation in switchable polarization after cycling in thin films can be attributed to charge entrapment, domain pinning, nucleation inhibition or local phase decomposition in the near electrode region.^{4,45} Among these models the major charge defects are oxygen vacancies and/or injected charge carriers from the electrodes. The explanation for the high fatigue endurance of PZT thin films with conductive oxide electrodes, e.g., RuO₂, is based on the conception that oxygen vacancies in PZT films can diffuse into the oxide electrodes and, as a result,

the pinning of domain walls due to oxygen vacancy pileup at the interface can be alleviated. Du and Chen⁴⁶ observed that a p-Si barrier layer is more effective in improving the fatigue resistance than n-Si, which reveals that mainly injected electrons, not holes, are involved in the fatigue process. The polarization decrease in PZT thin films with ITO and n-type La doped SrSnO₃ electrodes support that probably electrons are the dominant injected carriers affecting the fatigue behavior of thin films.

The Schottky barrier heights for electrons and holes at the PZT/Pt, PZT/RuO₂, and PZT/ITO interfaces are strongly different as revealed by photoemission experiments. The barrier heights suggest a preference for either electron (ITO) or hole (RuO₂) injection for the oxide electrodes, although the barrier heights are >1 eV in any case. With Pt electrodes, the barrier height varies roughly between the limits set by the two oxide electrodes in dependence on chemical treatment.^{26,47} The variation can be induced by oxidation/reduction in the interface in different oxygen partial pressures. Considering the results mentioned above, one might expect a more pronounced fatigue with ITO electrodes.

However, despite the significant difference of barrier heights, the ferroelectric properties including hysteresis, switchable polarization, strain, dielectric and piezoelectric coefficients, and switching times are found to be largely independent on the electrode material. Furthermore, the fatigue behavior of ceramic PZT samples after 10⁶ cycles with $E = \pm 2$ kV/mm is similar for all studied electrode materials.

In contrast, Balke *et al.* have reported a significant influence of electrode preparation on fatigue for the same ferroelectric material (PIC 151). Ag and Pt electrodes have been selected for their studies due to the different work functions of these two metals. A large scatter of fatigue endurance has been observed with Pt electrodes. Balke *et al.* assigned this to formation of a “defect structure,” which sensitively depends on the sputter conditions of the Pt layer. In case strong fatigue has been observed with Pt electrodes, this is attributed by formation of cracks underneath the electrodes. Crack formation is caused by mechanically induced damage during switching cycles. This may be related to a lateral variation in contact properties, e.g., by areas with poor contact. In particular, low permittivity interlayers may be present between PZT and Pt if the PZT surface is not homogeneously cleaned. In such case, contact properties can be expected to improve with a temperature treatment. This could explain that no cracks are observed by Balke *et al.* with Ag electrodes, which have undergone such a treatment while the samples with Pt electrodes have not. This explanation is also in line with the discussion of electrode effects by Jiang *et al.*^{22,23}

The independence of fatigue on electrode material observed here for bulk ceramic PZT samples is hence most likely related to a different electrode preparation. An ultra-high vacuum magnetron sputtering system has been used for electrode preparation in this study instead of a standard sputter coater typically used for coating insulating samples to record electron microscopy images. The lower pressure in our system results in a higher energy of the deposited particles, which contributes to the removal of adsorbates on the substrate surface during deposition.

The apparent difference of electrode influence on fatigue behavior between bulk ceramic and thin film PZT might be related to the different electric field strength. For ceramic materials the electric field is typically limited to a few kilovolt per millimeter (see Fig. 4), while significantly larger fields are applied with thin films.^{16,48} As the Schottky barrier is reduced with increasing electric field,⁴⁹ carrier injection is expected to be more pronounced for thin films compared to ceramics. In the presence of dead layers, charge injection is even more pronounced as these layers have lower permittivity. Therefore, even higher electric fields are present in the near electrode region. The presented results do therefore not exclude that charge injection is a major origin of fatigue in thin film ferroelectric materials.

IV. CONCLUSION

The ferroelectric properties of PZT bulk ceramics as well as the fatigue are not noticeably influenced by the electrode material, despite significantly different Schottky barrier heights at the interfaces, which are derived from independent photoemission studies and found to be insensitive on crystallographic interface orientation. Both metallic and oxidic electrodes can be selected to obtain preference for either electron or hole injection without significantly affecting ferroelectric properties. The electrode effect on the fatigue behavior of polycrystalline PZT ceramics compared to that of thin films, which is attributed to a different magnitude of the electric field required for polarization switching.

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