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Scanning force microscopy has been used to perform a comparative nanoscale study of domain structures and switching behavior of $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films integrated into heterostructures with different electrodes. The study revealed a significant difference between polarization state of as-deposited PZT films on RuO_2 and Pt electrodes. The PZT/RuO_2 films exhibit polydomain crystallites and show almost symmetric switching behavior, while the PZT/Pt films are mainly in a single polarity state and exhibit highly asymmetric piezoelectric hysteresis loops. Formation of unswitchable polarization within the grains of submicron size as a result of fatigue process was directly observed. © *1996 American Institute of Physics.* [S0003-6951(96)05147-9]

Recent progress in the processing of high-quality ferroelectric thin films has enhanced the prospects of their application in microelectronics devices, but further work is necessary to improve the long-term reliability characteristics of film-based devices. Numerous efforts have been undertaken to eliminate the degradation effects in ferroelectric capacitors.[1] However, the majority of studies in this field has been focused on measuring and controlling integral parameters, such as switchable and stored polarization, coercive field, and transient current. Little attention has been paid to real physical processes, such as piezoelectric deformation, which occur in ferroelectric films during polarization reversal in capacitors for nonvolatile memories. Therefore, there is a need for a direct study of switching phenomena in thin films. Since the polarization state and polarization reversal are naturally linked to domain arrangements and their transformations, direct imaging of domain structures in thin films and investigation of their behavior under the applied electric field can provide a clue for general understanding of switching phenomena and the role domains play in degradation effects in ferroelectric films. Recently, it has been demonstrated that scanning force microscopy (SFM) is a useful technique for investigation of ferroelectric materials, providing high-resolution visualization of ferroelectric domains.[2–6] In the present letter we use SFM to perform a study of domain structures and switching behavior of PZT ferroelectric thin films integrated into heterostructures with different electrodes, which yield different fatigue characteristics.

A domain imaging technique, used in the present study, is based on the detection of the local vibration of the sample induced by an ac field applied between the SFM tip and the bottom electrode. This method, described in detail in previous publications,[4–6] is similar to strain observation by other scanning probe techniques.[7–9] Using the lock-in technique, the domain structure can be visualized by monitoring the first harmonic signal (piezoresponse) caused by the piezoelectric effect, since the phase of this signal depends on the sign of the piezoelectric coefficient and on the polarization direction.

SFM studies of $Pb(Zr_xTi_{1-x})O_3$ (PZT) films were performed using a commercial force microscope (Seiko Instruments SPA 300). An external voltage was applied to the film surface through the gold coated Si_3N_4 cantilever with a tip apex radius of about 20 nm. The films were imaged by applying an ac voltage with an amplitude of 1–3 V and a frequency of 10 kHz, far below the cantilever resonant frequency of 36 kHz. The topographic image of the film surface was taken simultaneously with the domain imaging. $Pb(Zr_{0.53}Ti_{0.47})O_3$ films were deposited onto electroded MgO (100) substrates by a sol–gel technique.[1] The thickness of the films was 0.18 μm. Blank bottom electrodes were produced using an ion-beam sputter-deposition method.[10] For this study, two types of electrodes, namely Pt and RuO_2 electrodes, were used to prepare samples, hereafter designated as PZT/Pt and PZT/RuO_2, respectively.

It has been well established that oxide electrodes have a significant advantage over metal electrodes. For example, Pt/PZT/Pt capacitors undergo severe polarization fatigue upon repeating switching, while RuO_2/PZT/RuO_2 capacitors exhibit excellent resistance to fatigue.[1] Other oxide electrodes (e.g., IrO_2) can also be used to minimize fatigue in PZT-based capacitors.[11] A reason for choosing materials described above for study by the SFM technique was to get new information about domain structure and its evolution at the nanometer scale which could help to clarify the fatigue mechanism in ferroelectric films.

Figure 1(a) shows a topographic image of an as-deposited PZT/RuO_2 heterostructure which reveals a crystallite structure with lateral grain sizes up to 500 nm. A corresponding piezoresponse image, where areas with opposite piezoelectric constants and polarities appear as bright and dark regions as small as 100 nm, is shown in Fig. 1(b). As can be seen from the comparison of the pattern of the piezoresponse signal with grain-boundary contours obtained from the topographic measurements [dashed white-black lines in

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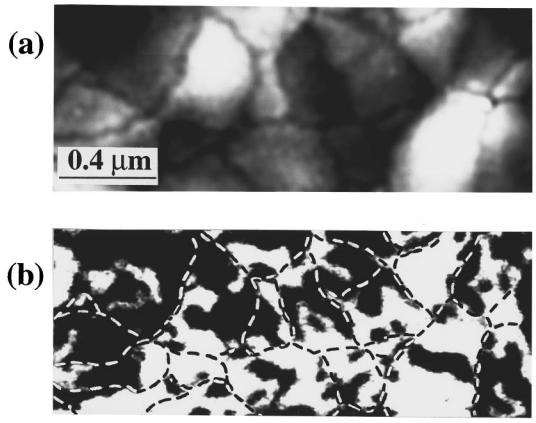

FIG. 1. Simultaneously obtained (a) topographic and (b) piezoresponse images of the PZT/RuO_2 film. White and black regions on the piezoresponse image correspond to negative and positive domains, respectively. Dashed black-white lines in (b) represent grain-boundary contours obtained from the topographic image (a).

Fig. 1(b)], large grains in the PZT/RuO_2 film are randomly split into domains of opposite polarities and there is almost no correlation between domain and crystallite structures. This is in contrast to the results obtained by Franke *et al.*[4] In some areas, the adjacent parts of two neighboring grains are occupied by one domain, while in other regions grain boundaries separate two oppositely polarized crystallites.

To further characterize the PZT/RuO_2 film at the nanometer scale, the piezoresponse signal was measured as a function of a dc poling voltage for domains of both polarities (Fig. 2). The poling voltage was applied for 1 s to some selected points on the surface. Immediately after turning it off, a small ac voltage was applied to measure a local piezoresponse. It can be seen that a voltage dependence of the piezoresponse signal shows typical ferroelectric hysteresis behavior. Since the piezoresponse signal from the white domain changes its sign under the positive voltage (''+'' applied to the tip), it was concluded that the white regions in the piezoresponse image correspond to negative domains (polarization up) while positive domains (polarization down) are represented by the black regions. As can be seen from Fig. 2(a), the hysteresis loop for the negative domain is almost symmetric, but there is a voltage offset for the positive domain [Fig. 2(b)]. This difference can be explained by asymmetry of the PZT/RuO_2 heterostructure which creates an asymmetric distribution of interfacial traps for charge carriers.

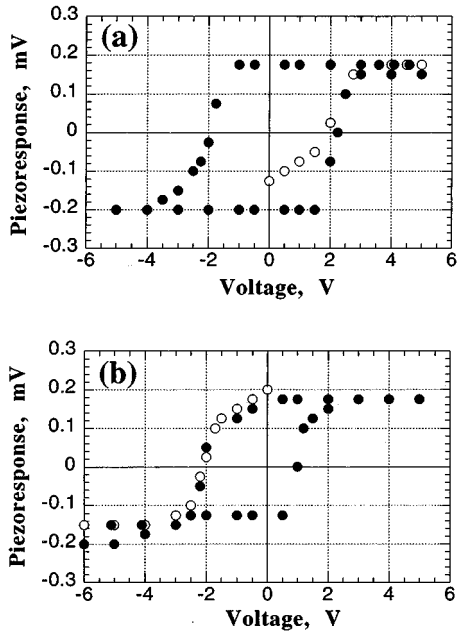

FIG. 2. Piezoresponse hysteresis loops for (a) negative and (b) positive domains in the PZT/RuO_2 film. Open circles illustrate initial parts of the hysteresis loops.

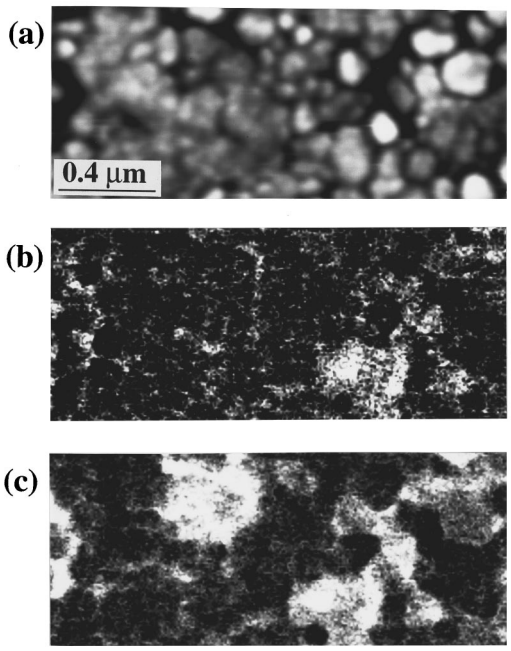

FIG. 3. Simultaneously obtained (a) topographic and (b) piezoresponse images of the as-deposited PZT/Pt film. (c) A piezoresponse image of the same area after it was scanned for about 1 h with the tip held under an applied ac voltage of 8 V (peak to peak). The coercive voltage for the corresponding Pt/PZT/Pt capacitor is 1.5 V.

Quite a different situation has been found in the as-deposited PZT/Pt heterostructure after acquiring its piezoresponse image (Fig. 3). In contrast to the PZT/RuO_2 case, the major part of the PZT/Pt film is in a single polarity state although there are few crystallites of opposite polarity (it should be noted that the piezoresponse signal from these crystallites is very weak). No crystallites in the polydomain state have been found. A hysteresis loop, taken from the black region in Fig. 3(b), is shown in Fig. 4(a). As can be seen, the loop is asymmetric and shifted upward and toward the negative direction of the voltage axis, suggesting that the major part of the as-deposited PZT/Pt film is polarized in a positive direction (polarization down), probably due to the highly [001]-oriented Pt layer, and that it has a positive bias field. Therefore, the asymmetry of PZT/Pt heterostructure affects not only the charge distribution but also the polarization state of the PZT layer, which can cause an initial imprint of a Pt/PZT/Pt capacitor.

To induce repeated polarization switching and to simulate the fatigue process, the film was scanned for about 1 h with the tip held under the applied ac voltage with amplitude higher than the coercive voltage. Such scanning was effec-

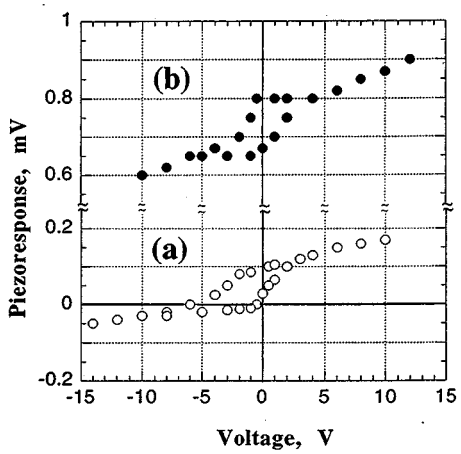

FIG. 4. Piezoresponse hysteresis loops for (a) virgin and (b) fatigued (6×10^3 switching pulses) PZT/Pt heterostructures.

tively equivalent to the application of about 6×10^3 switching pulses to each point on the film surface. Figure 3(c) shows a considerable change in the piezoresponse pattern of the scanned area. Some positively poled crystallites have become repolarized into a negative state as a result of the scanning. The scanning also caused a significant shift of the hysteresis loop in the vertical direction [Fig. 4(b)]. Some of the crystallites became so well polarized that they could not be switched by applying a high dc voltage up to 15 V. Figure 5 shows the piezoresponse image of the PZT/Pt film where a negative 15 V dc voltage was applied through the scanning tip to a square of 1×1 μm^2 area. Nevertheless, some of the crystallites apparently have not been switched and still exhibit a positive piezoresponse signal. This result, which can be explained by strong domain pinning in these crystallites, is direct experimental proof that repeated switching results in formation of unswitchable polarization, which, in turn, leads

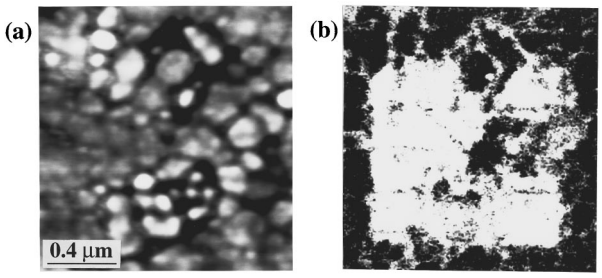

FIG. 5. Simultaneously obtained (a) topographic and (b) piezoresponse images of the fatigued PZT/Pt heterostructure. The bright square of 1×1 μm^2, produced by moving the SFM tip while applying a negative 15 V dc voltage, represents a negatively polarized region. Unswitchable crystallites appear as dark areas inside the white square region.

to the degradation of switching characteristics. Pinning and depinning of ferroelectric domains were discussed in previous publications related to fatigue in KNO_3 films,[12] where it was suggested that both defect pinning and space charge effects could play a role in fatigue of ferroelectric capacitors. Since only a slight decay of switchable polarization is usually observed after 10^3–10^4 switching pulses in Pt/PZT/Pt capacitors,[1] it is not surprising that domain pinning was observed in just a few crystallites. It should be also noted that our results are in fairly good agreement with recently reported results on piezoelectric fatigue in PZT films by means of laser interferometry, where a vertical shift of piezoelectric hysteresis loops and a buildup of the fixed polarization were observed.[13]

In conclusion, our study revealed significant differences between domain structures and polarization states of as-deposited PZT/RuO_2 and PZT/Pt heterostructures, which have been observed for the first time at the nanometer scale. The PZT/RuO_2 films exhibit crystallites which are randomly split into domains of opposite polarities, and show almost symmetric switching behavior. Contrary to the PZT/RuO_2 films, the PZT/Pt films are mainly in a single polarity state and exhibit highly asymmetric piezoelectric hysteresis loops. Formation of unswitchable polarization within the grains of submicron size as a result of fatigue process was experimentally observed. The obtained results are significant in relation to understanding the mechanism of fatigue phenomena in PZT-based capacitors.

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