Electric fatigue in Pb(Nb,Zr,Sn,Ti)O₃ thin films grown by a sol–gel process

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Antiferroelectric Pb(Nb,Zr,Sn,Ti)O₃ (PNZST) thin films were deposited via a sol–gel process on LaNiO₃-buffered Pt/Ti/SiO₂/Si substrates. The highly (100)-oriented LaNiO₃ buffer layer facilitated the formation of high-quality PNZST films with a strong (100) preferred orientation. These films showed improved electric fatigue properties than those grown on Pt/Ti/SiO₂/Si substrates. With increasing cycling field, the remanent polarization increases but the saturated polarization decreases. Fatigue properties of PNZST antiferroelectric thin films might be closely related to the nonuniform strain buildup due to switching that tends to stabilize the ferroelectric phase. © 2003 American Institute of Physics. [DOI: 10.1063/1.1594843]

Antiferroelectric (AFE) materials have received attention due to their potential usage as microactuators, digital memories, as well as in high-energy storage capacitors. Thin films of both ferroelectric and antiferroelectric materials are of particular interest because of their relevant applications in connection with microelectronic devices. Devices that are operated with an ac field over long cycles must possess acceptable electric fatigue performance to ensure the long-term reliability. Fatigue characteristics have not been examined in much detail in antiferroelectric PbZrO₃, (Pb,Ln)(Zr,Sn,Ti)O₃, and Pb(Nb,Zr,Sn,Ti)O₃ thin films.

A nominal composition of Pb₀.₉₉₁Nb₀.₀₂(Zr₀.₈₅Sn₀.₁₃Ti₀.₀₂)₀.₉₈O₃ (PNZST) is formulated to indicate both the B-site mixing of four elements (Nb, Zr, Sn, and Ti), and the charge balance between the A and B sites. It is a composition close to the morphotropic boundary separating the orthorhombic AFE phase from the rhombohedral ferroelectric (FE) phase. Details of the sol–gel process for PNZST thin films can be found in a recent article by Zhai et al. The thickness of LaNiO₃ buffer layer was added at the end before the films went through a final heat treatment were repeated several times to obtain the desired thickness. A capping layer of 0.8 M PbO precursor solutions was added at the end before the films went through a final anneal at 700 °C for 30 min in air. The PbO capping layer prevented the excessive Pb evaporation, thus enabling a complete crystallization into the perovskite phase. Gold electrode pads of 200 × 200 μm² were made on top of the PNZST films by dc sputtering. Fatigue properties were measured using a Radiant Technologies Precision Pro ferroelectric tester. Polarization (P) versus electrical-field (E) measurements were performed at 1 kHz frequency. The phase and preferred orientation of the PNZST were studied by x-ray diffraction (XRD) techniques using a SIEMENS D-500 powder x-ray diffractometer. Film thickness was determined using scanning electron microscopy.

Figure 1 shows two typical XRD patterns of the PNZST films of a similar thickness deposited on (Fig. 1(a)) the LaNiO₃/Pt/Ti/SiO₂/Si substrates, respectively. For films grown on Pt/Ti/SiO₂/Si substrates, the perovskite phase was obtained at about 600 °C and had no obvious preferred orientation. In contrast films deposited on LaNiO₃/Pt/Ti/SiO₂/Si substrates showed highly oriented (100) fiber texture after annealing as low as 500 °C. It is apparent that LNO forms a template facilitating grain-on-grain growth of the overlying PNZST films. No observable impurity phases were found in either case. The PNZST thin films deposited on LaNiO₃/Pt/Ti/SiO₂/Si substrates can be crystallized at a lower annealing temperature.

Figure 2 shows a group of hysteresis loops of PNZST thin films grown on two types of substrates. Data were taken at different voltages and the switching fields from the AFE to the FE were 280 kV/cm and 440 kV/cm with the LNO-buffered substrate samples showing a higher switching electric field.

Fatigue properties of PNZST thin films (720 nm thick) on LNO/Pt/Ti/SiO₂/Si substrates are shown in Fig. 3 with the applied ac electric field of 230, 340, 460, and 570 kV/cm. The ac frequency was kept at 100 kHz. P* is the switched polarization (the measured polarization value at the top of the first pulse); P* is the switched remanent polarization (the

FIG. 1. XRD patterns of PNZST thin films deposition on (a) Pt/Ti/SiO₂/Si and (b) LNO/Pt/Ti/SiO₂/Si substrates. Both were annealed at 700 °C for 30 min in air.
measured polarization value at 0 V after the first pulse); \( P^\wedge \) is the nonswitched polarization (the measured polarization value at the top of the second pulse); and \( P_{r}^\wedge \) is the non-switched remanent polarization (the measured polarization value at 0 V after the second pulse).

Below the AFE–FE switching field, films showed fatigue-free properties. With increasing cycling field beyond the switching limit, the remanent polarization increases but the saturated polarization decreases. The hysteresis loop changes from a square shape in the virgin state to a diffused one in the fatigued state (see insets in Fig. 3). The induced saturated polarization decreases and the transition fields are diffused after fatigue. Those behaviors might be understood on the basis of nonuniform strain fields. When the grains in thin films deform due to polarization switching under the applied electric field, they deform differently because of the dielectric and electromechanical anisotropy of individual grains. Each grain containing AFE/FE domains experiences a different degree of expansion/contraction, depending on the orientation of adjacent grains and the configuration of domains therein. Therefore, one can expect to see the internal stress buildup after repetitive cycles of switching because of the increasing population of retained FE phase as evidenced by the increasing remanent polarization in Fig. 3. Some regions may be subject to tensile stresses while other regions may be subject to compressive stresses. These internal stresses could modify the transition field of different regions. Thus, the AFE–FE switching field, or its reverse field, would become more diffused. The ending result would be that in
some regions the strain field buildup becomes sufficiently large so that the field-induced FE state may no longer able to switch back, therefore giving rise to the observed reduction in induced saturated polarization and the increased remanent polarization. Under a high driving electric field, current injection from the electrode and space charge within the thin film may also modify the local electric fields of the thin film, resulting in the observed fatigue effects.

Recent studies demonstrated that non-180° domain-wall mobility is restricted in thin films.\textsuperscript{11,12} Therefore, the argument that fatigue is more critical in FE materials because they switch by non-180° domain-wall motion is not necessarily applicable to thin films. The field-induced FE phase is stable only under a high field and, at low fields, FE returns to the AFE state. The AFE–FE transition includes not only the structural phase transformation but also the couplings among domains. The AFE material is characterized by rows of dipoles with the dipole moment of adjacent rows equal but antiparallel to each other so that in equilibrium there is no net spontaneous polarization. The increase of the switchable remanent polarization ($P_r^s$) in antiferroelectric PNZST thin films is mainly due to some dipoles that cannot return to the initial state of antiparallel configuration after repetitive switching cycles.

Figures 4(a) and 4(b) show the $P-E$ curves as a function of switching cycles measured by applying a square wave form up to 330 kV/cm (on Pt/Ti/SiO$_2$/Si) and 460 kV/cm (on LNO/Pt/Ti/SiO$_2$/Si) at 100 kHz, respectively. The major difference appears to be the change of magnitude of the saturated polarization. It is obvious to see the decrease of saturated polarization with increasing switching cycles in Fig. 4(a). Films deposited on Pt/Ti/SiO$_2$/Si substrates show more severe polarization degradation. It has been reported that the polarization fatigue in FE films on Pt electrodes is mainly originated from the accumulation of oxygen vacancies and domain-wall pinning.\textsuperscript{13} Using oxide bottom electrodes, such as LNO in this study which act as a sink for oxygen vacancies, it can greatly improve fatigue properties.\textsuperscript{14} It is generally argued that the oxide electrode may help control charged defects at the FE/electrode interface. In addition, the oxide electrode may provide a better work function match to the FE material. The different surface can yield a different amount of charge injection because of the varying electric-field concentration at the interfaces. The injected charges can interact with regions containing discontinuous polarization, become trapped there and stabilize the regions. This mechanism can also contribute to the observed electric fatigue. The better fatigue character of the (100)-oriented PNZST thin films grown on LNO/Pt/Ti/SiO$_2$/Si substrates may be partly attributed to the relatively lower internal field stress induced during switching and the small number of oxygen vacancies at the FE–LNO electrode interface.

In conclusion, PNZST AFE thin films deposited on the LaNiO$_3$-buffered Pt/Ti/SiO$_2$/Si substrates displayed improved electric fatigue properties as compared with films grown on Pt/Ti/SiO$_2$/Si. Fatigue properties of PNZST AFE thin films might be closely related to the nonuniform strain buildup due to switching that tends to stabilize the FE phase. It is believed that the use of an oxide electrode combined with highly (100)-oriented films gives rise to the improved fatigue performance of PNZST antiferroelectric thin films grown on LNO-buffered substrates. These behaviors might be closely related to the relatively low internal stress and the accumulation of oxygen vacancies and domain-wall pinning due to the LNO electrode layer.

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