THE THRESHOLD STRESS OF 90 ºDOMAIN SWITCHING IN THE MISFIT STRAIN-EXTERNAL STRESS PHASE DIAGRAM

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Summary The different mechanical compressive forces were applied on the selected areas of $Pb(Zr_{0.52}Ti_{0.48})O_3$ ferroelectric thin film by the tip of piezoelectric force microscopy, and 90º polarization switching was observed on the piezo-phase images. Based on nonlinear thermodynamic theory, we describe the dense domain states of single grain to obtain the misfit strain-external stress phase diagram, and it demonstrates the threshold stress is -1.07GPa for the force-generated 90º domain switching at misfit strain 0.001.

INTRODUCTION

During the last decade, piezo-force microscopy (PFM) was used to record the piezoelectric phase images under the external mechanical stress field or electric field [1, 2]. Recently, a thermodynamic theory is developed for dense domain states in epitaxial ferroelectric thin films [3]. Moreover, the stability of the polarization states under the external force is an important index in micro-electromechanical systems. However, relatively few of the relations between the force-generated switching, misfit strain, and polarization state are available in the literature. It is worth mentioning that we understand the effects of external stress field and residual strain on the polarization state, and the explanation on the force-generated domain switching by the misfit strain-external stress phase diagram will offer a useful guideline to the design of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) ferroelectric thin film devices.

EXPERIMENTAL

PZT thin film on Si substrate was prepared by pulse laser deposition. X-ray diffraction pattern (see Fig. 1(a)) shows single-phase perovskite peaks and (110) peak indicating [110] preferential orientation of PZT crystals and no pyrochlore phase. The polarization-electric field hysteresis loop of PZT thin film was given in the inset as Fig. 1(b), and P_r value is $100\mu c/cm^2$. Generally, the external stress field was applied on the whole scan region by the tip of PFM to record the piezo-phase image [4], however only the part of region was exerted the force on the valid single grains in order to observe the polarization in the grains clearly in this study. The piezo-phase images are 800×800 nm^2 for the large scan area as shown in Figs.2 (a)-(c) and 500×500 nm^2 for the small scan area in Figs.2 (d)-(f), and the applied force regions marked by the black dashed lines are corresponding to 400×800 nm^2 and 200×500 nm^2. The bright and dark contrasts correspond to the out-plane polarization vectors (*c* phase), and grey contrast represents in-plane polarization (*aa** phase or *a* phase) or the polarization vector at some angle to the film's plane (*ca* phase or *r* phase) [5]. Within these grains, the dark and bright contrasts are gradually changed into grey. Especially, the single grains marked by black loop in Figs. 2(d)-(f) displays the typical 90º domain switching. The multicolor contrasts of the grain for the external force 17 nN shows a polydomain state in Fig. 2(d), and the dark and bright contrasts in the grain are gradually changed into grey till the external force 165 nN as shown as Fig. 2(e). At the external force 330 nN, the contrasts finally become grey in Fig. 2(f), and it indicates that 90 ºdomain switching occurs. Obviously, all single grains marked are of the same variation with the increase of external force, therefore the single grain marked by black loop can be taken as the typical object of modeling as follow.

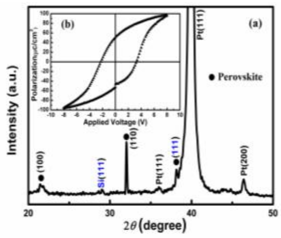

Fig. 1 XRD pattern (a) and P-E hysteresis loop (b) of PZT thin film.

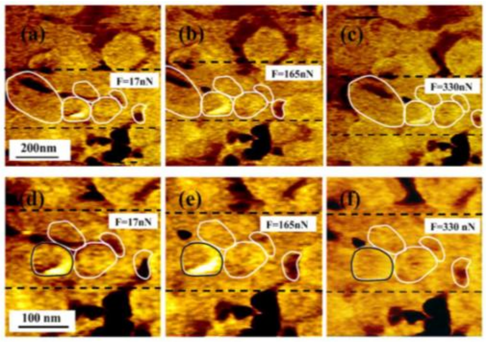

Fig. 2 The phase images at different external forces of 17nN (a), 165nN (b), 330nN (c) in scan area 800×800nm^2 and 17nN (d), 165nN (e), 330nN (f) in scan area 500×500nm^2.

MODELING

Since the polarization and lattice strains vary from one domain to another in a polydomain film, we cannot use the standard Gibbs function for the determination of polydomain states in a single grain. In this case the modified thermodynamic potential of the Helmholtz free energy function $\tilde{F}$ should be used [3]

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$$\tilde{F} = a_1(P_1^2+P_2^2+P_3^2)+a_{11}(P_1^4+P_2^4+P_3^4)+a_{12}(P_1^2P_3^2+P_2^2P_3^2+P_1^2P_2^2)+a_{111}(P_1^6+P_2^6+P_3^6)+a_{112}[P_1^4(P_2^2+P_3^2)+P_3^4(P_1^2+P_2^2)+P_2^4(P_1^2+P_3^2)]$$
$$+a_{123}P_1^2P_2^2P_3^3+\frac{1}{2}s_{11}(\sigma_1^2+\sigma_2^2+\sigma_3^2)+s_{12}(\sigma_1\sigma_2+\sigma_1\sigma_3+\sigma_2\sigma_3)+\frac{1}{2}s_{44}(\sigma_4^2+\sigma_5^2+\sigma_6^2)$$

where σ_3 is the external mechanical stress normal to the film surface. The domain structure of a single grain can be approximately assumed as the monocrystalline dense domain. The polydomain states can be composed of alternating domains of two types. According to the previous results [3], the possible phases are the paraelectric phase, the *c*, *a* and *aa* phases, and the *c/a/c/a*, *c/ca/c/ca*, $a_1/a_2/a_1/a_2$, $r_1/r_2/r_1/r_2$ and *ca*/aa*/ca*/aa** polydomain states during the polarization switching in the single grain of PZT thin film under the external stress. For periodic domain structures [3], the mean density $<\tilde{F}>$ can be described from the relation $<\tilde{F}>=\phi\tilde{F}'+(1-\phi)\tilde{F}''$, where $\tilde{F}'$ and $\tilde{F}''$ are the characteristic energy densities in the inner regions of domains of the first and second type. Using the boundary conditions [3], the minimization of $<\tilde{F}>(P_i', P_i'', \phi)$ can be rewritten as the form $<\tilde{F}>(S_m, \sigma_3)$, which is determined as a function of the misfit strain S_m and σ_3. The dense domain states of the single grain under external stress can be obtained.

RESULTS AND DISCUSSION

The in-plane strain of thin film was approximately regarded as the misfit strain and deduced from constitutive equations considering piezoelectric effect [6]. In this paper, the equal-biaxial in-plane strain of PZT thin film is evaluated as 0.001. After the simplification of uniform stress distribution [6], the misfit strain-external stress phase diagram and the external stress-polarization components curve at the fixed misfit strain 0.001 are given in Figs. 3(a)-(b). In Fig. 3(a), there are two polydomain states (*c*/*ca*/*c*/*ca* and *ca**/*aa**/*ca**/*aa**) and two single domain states(c phase and aa phase). When the tensile stress is above 0.40GPa, PZT thin film is in the *c* phase. With the increase of the compressive stress, the decreasing out-of-plane polarization component causes the *c/ca/c/ca* turn into the *ca*/aa*/ca*/aa** (in which *ca** phase corresponds to *a* distorted *ca* one and *aa** phase corresponds to a distorted *aa* one). Comparing S_m with the values of abscissa axis in Fig. 3(a), we can obtain that the threshold stress is -1.07GPa for $S_m = 0.001$, corresponding to the phase transition from heterophase *ca*/aa*/ca*/aa** to *aa* phase, and it is in agreement with the experimental observation on the external compressive force 330 nN (-1.65GPa), as shown in Fig. 2(f). At fixed misfit strain $S_m = 0.001$ the external stress-polarization components curve is shown in Fig. 3(b). It shows that the increasing external force leads to a drastic change of the polarization components. At the compressive stress -1.07 GPa, the polarization components change from P_1^{aa*} and P_2^{aa*} to P_2^{ca*} and P_3^{ca*}, corresponding to the phase transition from heterophase *ca*/aa*/ca*/aa** to *aa* phase.

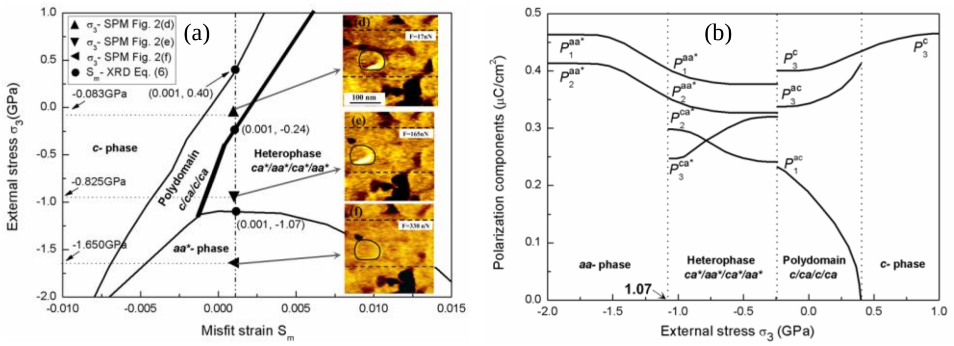

FIG. 3 The external stress-misfit strain phase diagram (the first- and second- order phase transitions are shown by thick and thin lines, respectively) (a), and the external stress-polarization components curve (b) at *T*=25 ℃.

CONCLUSIONS

The compressive forces were applied on the selected areas of PZT thin film, and the change of opposite color contrasts was observed from dark and bright to grey. We theoretically obtain the misfit strain-external stress phase diagram and the external stress-polarization components curve are simulated at the simplification of uniform stress distribution for the selected single grain. The external stress at fixed misfit strain is -1.07GPa for the phase transition from heterophase *ca**/*aa**/*ca**/*aa** to *aa* phase, and it is corresponding to the threshold external stress for force-generated 90 º domain switching observed by the piezo-phase images.

References

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