Peculiar ferroelectric and dielectric properties of quasiperiodic PbZr$_{0.4}$Ti$_{0.6}$O$_3$ multilayers

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**Abstract.** Based on phase separation, quasiperiodic PbZr$_{0.4}$Ti$_{0.6}$O$_3$ (PZT) multilayers with alternating PZT and porous-PZT layers were fabricated by using a single precursor, and the ferroelectric and dielectric behaviours of the PZT multilayers were investigated. The PZT multilayers have an averaged remanent polarization of 42.3 $\mu$C cm$^{-2}$ and an average coercive field of 43 kV cm$^{-1}$. Two distinct dielectric relaxation phenomena were observed in the frequency range from 100 Hz to 1 MHz: the one at lower frequency is attributed to space charge polarization, while the one at higher frequency, with an activation energy of 0.49 eV, is expected to be associated with dipolar defect complexes related to oxygen vacancies.

**Contents**

1. Introduction 2
2. Experiment 2
3. Results and discussion 2
Acknowledgments 6
References 6

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1. Introduction

Lead zirconate titanate PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) thin film is a ferroelectric material with various functions desirable for integrated optoelectronics. PZT has interesting dielectric, ferroelectric, piezoelectric, and pyroelectric characteristics, as well as high electro-optical coefficient [1]–[5]. We had reported previously that incorporating polyvinylpyrrolidone (PVP) into coating solution allows preparation of quasiperiodic PZT multilayers (QPM) in which the building block is a distinct PZT/porous-PZT bilayer formed in a single spin-casting/annealing step and the formation of the bilayer is governed by phase segregation. The prepared QPM exhibits more than 90% optical reflectivity and no less than 20 nm photonic stop-band width at a given wavelength [6, 7]. In this study, we demonstrate that, in addition to the superior optical property, a good dielectric and ferroelectric performance can also be achieved in the QPM fabricated based on the phase separation. Possible mechanisms for the enhancement of the dielectric and ferroelectric properties in QPM are discussed. Very interestingly, two distinct dielectric relaxation processes were observed in the Pt/QPM/LaNiO$_3$ capacitor structure. The one at lower frequency is attributed to electrode polarization (space charge polarization) while the other at higher frequency, with the activation energy of 0.49 eV, is expected to be associated with oxygen vacancy-related defect dipoles. To the best of our knowledge, the high frequency dielectric relaxation has been observed for the first time on PZT materials.

2. Experiment

The details of the procedure of the precursor solution preparation and the QPM deposition have been described and the optical properties of the QPM have been investigated in [6, 7]. In order to improve lattice matching between PZT films (a-axis lattice constant of bulk PZT material $\sim$3.982 Å) and the silicon substrate, a 200 nm conductive LaNiO$_3$ buffer layer (lattice constant 3.84 Å) was deposited on a silicon substrate having a low electric resistivity ($\rho$ < 0.01 $\Omega$ cm). The conductive buffer layer was also used as an electrode in the electrical measurements [8, 9]. The QPM was then grown on the LNO/Si substrate. The sample examined in this study consists of 24 bilayers of PZT/porous-PZT with a total thickness of 2.1 $\mu$m determined by scanning electron microscopy. The thickness of each bilayer is 90 nm. Pt electrodes were fabricated by sputtering deposition onto the top of the QPM.

3. Results and discussion

All the electrical measurements were carried out on the Pt/QPM/LNO capacitors. The ferroelectric measurements of the PZT QPM film were carried out using a RT66 2000 ferroelectric test system with a triangular wave at 0.5 KHz, with the top Pt electrode connected positively. Figure 1 shows characteristic polarization (P–E) curves of the QPM obtained at room temperature with a maximum applied voltage of 40, 80 and 100 V. The polarization of the QPM appears to saturate as the applied voltage increases to above 80 V. The averaged remanent polarization and the averaged coercive field are 42.3 $\mu$C cm$^{-2}$ and 43 kV cm$^{-1}$, respectively, which are derived from the polarization curves measured at an applied electric field of 500 kV cm$^{-1}$.
Figure 1. Ferroelectric hysteresis loops of the QPM film measured at room temperature. The data were taken at the maximum driving voltages of 40, 80 and 100 V, respectively.

Compared with the single-phased PZT films grown on the same substrates, [10]–[12] the QPM sample exhibits a larger average remanent polarization and a lower coercive field. To check whether the large remanent polarization $P_r$ is primarily contributed by a leakage current, we perform a leakage current measurement on the QPM. Under a DC bias voltage of 100 V, the values of leakage current, resistance and resistivity of the QPM capacitor are $3.52 \text{nA}$, $1.328 \times 10^{10} \Omega$ and $2.788 \times 10^{10} \Omega \text{cm}$, respectively, suggesting that the QPM is a good electric isolator, and the contribution of leakage current to the polarization is negligible (the slender P–E loops also provide strong evidence).

Such a large $P_r$ was reported in a recent study on a 300 nm PZT film epitaxially grown on an iridium/magnesium oxide substrate [13]. x-ray diffraction (XRD) data measured on the film reveal a nearly perfect alignment of ferroelectric domains in the direction perpendicular to the substrate and such an alignment is attributed to the release of compressive stress in the thin film. More recently, enhanced ferroelectric polarization with a larger magnitude was observed in a pseudo-epitaxial PZT thin film fabricated on Si substrate by a pulsed-laser deposition process [14]. It is shown that $P_r$ depends on the stress in the film and, for PZT, $P_r$ decreases with the tensile stress in the films [15, 16]. For a polycrystalline PZT film deposited on silicon substrate, larger stress usually exists due to the mismatch in thermal expansion coefficient between Si and PZT, which substantially lowers $P_r$. Detailed microscopic analysis shows granular morphology with nano-sized pores distributed across the polycrystalline film, implying that the relaxation of the tensile stress could result in an enhancement of $P_r$ [14]. It is very likely that the similar mechanism plays a role in producing the large remanent polarization in our QPM samples. Here, in our case, the large number of nano-sized pores in the porous PZT layer and a larger film thickness ($\sim 2 \mu m$) lend itself to release the tensile stress, leading to the enhancement of $P_r$ in the QPM. As presented in figure 2(a), the (XRD) pattern shows that the QPM has a polycrystalline structure with a single perovskite phase. The QPM lattice constant $a \sim 4.048 \text{Å}$ obtained from the XRD data is slightly larger than 3.982 Å of bulk PZT with the same composition (the relative variation <2%), revealing that the examined QPM is still under tensile strain.
An interesting feature exhibited in all of the experimental $P-E$ loops is a negative voltage offset along the electric field axis, resembling that observed by Pike et al [16] in a similar system. The voltage offset was explained as due to a process-induced accumulation of oxygen vacancies at the interface of film-electrode and the trapping of electrons at the interface. To find out if a similar mechanism is responsible for the voltage offset observed in the QPM samples, Auger electron spectroscopic measurement, followed by Ar ion etching, is repeatedly performed on one of the QPM samples. The obtained depth profile of atomic concentration percentage (ACP) shown in figure 2(b) shows changes in the composition within 15 nm below the top surface of the film. Thus there could be a positively charged layer at the film-electrode interfacial region which is responsible for the shift of the hysteresis loop towards the negative electric field direction. The (ACP) measurement shows that, away from surface, our sample has a Zr/Ti ratio of 38% : 62%, rather than nominal 40% : 60%. The deviation is mainly due to the errors in weighting the source materials during the preparation of the precursor. Figure 2 shows that Pb concentration near surface is higher than the rest of the film. The phenomenon is also found on other samples, so that it is most likely related to our sample preparation procedure. The reason for higher Pb concentration near surface is currently unclear.

The dielectric permittivity of the QPM was measured on an HP4194A impedance analyser in a frequency range of $10^2$–$10^6$ Hz and over a temperature range of 300–560 K under a small ac signal of 0.5 V. The sample temperature was controlled by a temperature variation stage equipped with micro-probes (MMR Technologies, Inc.). As seen from figure 3(a), the real part $\varepsilon'$ of the dielectric permittivity of the QPM increases with temperature and exhibits a huge dielectric constant ($\varepsilon' > 2300$) at low frequency limit, while $\varepsilon'$ decreases rapidly with increasing frequency and exhibits a strong dielectric dispersion. A close examination to the $\varepsilon'$-frequency spectra in figure 3(a) finds that $\varepsilon'$ displays two sharp rises, corresponding to two different dielectric relaxation processes.

Figure 3(b) shows the frequency dependence of dissipation factor at several temperatures. Two broad dielectric loss peaks are observed clearly in the temperature range of 340–460 K. Below 500 K, it is rather difficult to determine the position and the magnitude of the low-frequency
Figure 3. (a) The real part $\varepsilon'$ of dielectric permittivity. (b) The dissipation factor for QPM.

Figure 4. $\ln f_p$ versus $1000/T$ plot, where $f_p$ is the frequency of the high-frequency peak in dissipation factor curve.

loss peak due to the overlap of the lower-frequency and the high-frequency peaks. Above 500 K, the intensity of the low-frequency loss peak increases and the peak position shifts toward lower frequency gradually. The two peaks then become well separated. In order to understand the underline physics, a 10 V DC bias was applied on the Pt/QPM/LNO capacitor and it was found that the DC bias causes $\varepsilon'$ in the frequency range of $100 \text{ Hz} \leq f < 10 \text{ KHz}$ to decrease evidently. This indicates that the low-frequency dielectric relaxation observed in QPM possesses a typical feature of electrode polarization or space charge polarization [17, 18]. The high-frequency peak shifts toward higher frequencies as temperature increases. Figure 4 plots the frequency $f_p$ of the peak as a function of $1/T$ that shows an Arrhenius characteristic. A least-squares fit to the data gives a thermal activation energy $E_a = 0.49 \pm 0.01$ eV.

Ang and Yu [19] and Zhang et al [20] have shown that the intrinsic dielectric constants for PZT ceramics or thin films are in the order of 100. The measured giant dielectric permittivity in the QPM must be an extrinsic effect in origin. The extrinsic dielectric response may be caused by
electrode polarization and/or space charge polarization, domain-wall motion polarization, and grain boundary and interface polarization (barrier layer capacitance effect, BLC) [19], [21]–[24]. The low-frequency giant $\varepsilon'$ in our case, arises predominantly from the electrode polarization, given the fact that it is sensitively dependent on applied bias and its peak position shifts to lower frequency with temperature. In the presence of high concentration of oxygen vacancies near the top surface of the QPM, a Schottky barrier could form between Pt-electrode and PZT film [25]. On the other hand, there are numerous interfaces between dense PZT and porous PZT layers in the QPM. Thus the BLC could make significant contribution to the low-frequency dielectric dispersion of the QPM. The combination of the several polarization mechanisms leads to the wide distribution of the relaxation time.

At present, the origin of the high frequency loss peak is undoubtedly not clear. Since $f_p$ as a function of $1/T$ of the high-frequency loss peak displays an Arrhenius behaviour, very likely the peak is related to atomic defects in the system. Conductivity study on PZT films gives a charge trap energy of 0.5 eV [26]. A study on leakage current in PZT reveals ionization energy of 0.5 eV for Ti$^{4+}$ [25]. The two processes having the same activation energy are expected, since the ionization of a Ti$^{4+}$ is usually accompanied by creating an oxygen vacancy. As described above, Auger measurement shows a defected layer in the region near the top surface of the QPM. As a result, the oxygen vacancies may accumulate in the interfacial region between pores and dense PZT. Based on our measured thermal activation energy of 0.49 eV, we expect that the high frequency dielectric relaxation may be related to the microscopic defects, such as doubly positive oxygen vacancies $(V_O)^{2+}$, dipolar defect associations of $(V_O)^{2+}-(V_{pb})^{2-}$, and/or other dipolar complexes [27, 28]. It should be noted that this phenomenon might not be observable if the concentration of oxygen vacancy in PZT films is not high enough.

Recently, Roytburd et al [29] had theoretically discussed in detail the effects of electrostatic coupling between the neighbouring layers, stress and compositional inhomogeneity on the ferroelectric and dielectric properties of the ferroelectric–ferroelectric or ferroelectric–paraelectric bilayers and multilayers [29, 30]. To gain insight into the peculiar dielectric and ferroelectric behaviours of the overall QPM, the roles of above-mentioned factors in the QPM should be considered. However, it is very difficult to establish a concise picture that models the QPM and gives a satisfactory explanation to the experimental observations due to the complex sample structure and blurry interface between dense-PZT and porous-PZT. Much more study needs to be done for a full understanding of the observed phenomena in the QPM.

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New Journal of Physics 8 (2006) 316 (http://www.njp.org/)
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