Leakage current and relaxation characteristics of highly (111)-oriented lead calcium titanate thin films

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Highly (111)-oriented $(Pb_{0.76}Ca_{0.24})TiO_3$ (PCT) thin films were grown on $Pt/Ti/SiO_2/Si$ substrates by a sol–gel process. The Au/PCT/Pt metal–insulator–metal film capacitor showed well-saturated hysteresis loops at an applied field of 800 kV/cm with remanent polarization (P_r) and coercive electric field (E_c) values of 18.2 $\mu C/cm^2$ and 210 kV/cm, respectively. The leakage current depended on the voltage polarity. At low electrical field and with Pt electrode biased negatively, the Pt/PCT interface exhibits a Schottky emission characteristics. The Au/PCT interface forms an ohmic contact. The conduction current when the Au electrode is biased negatively shows a space-charge-limited behavior. The dielectric relaxation current behavior of Au/PCT/Pt capacitor obeys the well-known Curie–von Schweidler law at low electric field. At higher fields, the currents have contributions to both dielectric relaxation current and leakage current. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1611627]

I. INTRODUCTION

Much attention has been paid to the application of ferroelectric thin films, such as $PbTiO_3$, $Pb(Zr,Ti)O_3$ and $(Ba,Sr)TiO_3$ because of their piezoelectric, dielectric, electro-optical, and pyroelectric properties. Lead calcium titanate $(Pb,Ca)TiO_3$ (PCT) is a promising candidate for piezoelectric and pyroelectric sensor materials.[1] PCT ceramics have been extensively investigated in view of high-frequency transducer and hydrophone applications.[2,3] PCT films are better than $PbTiO_3$ films in pyroelectric infrared detector performance[4] and porous PCT films have high figure-of-merit for pyroelectric applications.[5] Recent investigations have shown that the piezoelectric properties of $(Pb,Ca)TiO_3$ films with 24-mol % Ca are close to those of corresponding bulk ceramics.[6–8] PCT thin films have decreased tetragonality and can maintain good ferroelectric, piezoelectric, and pyroelectric properties.[5–9] However, the leakage current characteristics of PCT thin films on Pt-coated silicon have not been studied extensively. In this work, the relaxation and leakage current mechanism of highly (111)-oriented $(Pb_{0.76}Ca_{0.24})TiO_3$ (PCT) thin films on $Pt/Ti/SiO_2/Si$ substrates are reported.

II. EXPERIMENT

Ferroelectric $(Pb_{0.76}Ca_{0.24})TiO_3$ thin films were prepared by a sol–gel method with a spin-coating process. Details of the sol–gel process and its use for the deposition of the ferroelectric thin films may be found elsewhere.[8] The 0.2-M/L PCT coating solution was deposited onto $Pt/Ti/SiO_2/Si$ substrates by spin coating at 3600 rpm for 30 s. After each spin-coating process, the samples were heat-treated at 300 °C for 10 min in an air atmosphere by using a hot plate. This step was repeated several times to obtain the desired film

thickness. The PCT films on $Pt/Ti/SiO_2/Si$ substrates were annealed at 600 °C for 10 min by rapid thermal annealing (RTA) in oxygen atmosphere. The heating rate was 100 °C/s. The thickness of the highly (111)-oriented PCT films with four layers on $Pt(111)/Ti/SiO_2/Si(100)$ substrates, as measured by a spectroscopic ellipsometer (ISA Obin-Yvon, UVISEL/460, France), was 200 nm. The surface roughness was 1.2 nm.

The crystalline phase of the PCT film was determined by x-ray diffraction (XRD) (Philips PW3710, Cu K_α). To investigate the electrical properties of the PCT thin films, top electrodes of gold (Au) of 0.2-mm diameter were prepared on the PCT films through a shadow mask in a vacuum rf-magnetron sputtering system. The polarization–electric-field ($P-E$) hysteresis loop was obtained using a TF Analyzer 2000 (aixACCT, Aachen, Germany) system with a 1-kHz sinusoidal input signal. The $I-V$ characteristics of the Au/PCT/Pt capacitor under different applied fields and with the Pt electrode under either positive or negative bias voltages were measured at room temperature by a Keithley 6517A programmable electrometer. A dc voltage was then applied to the thin film with the positive or negative potential connected to the Pt and maintained for 3 s, and the dielectric relaxation current versus time characteristics of the Au/PCT/Pt capacitor were measured after removal of the dc field.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the PCT thin film with a thickness of 200 nm. Inset shows the splitting of the (101)/(110) doublet. It can be seen that the (001), (100), (101), (110), (111), (002), (200), (112), and (211) peaks were detected for the PCT film on $Pt/Ti/SiO_2/Si$ substrate. A highly (111) oriented perovskite PCT film was formed. As indicated by the splitting of the (001)/(100), (101)/(110), (002)/(200), and (112)/(211) doublets, which suggests the
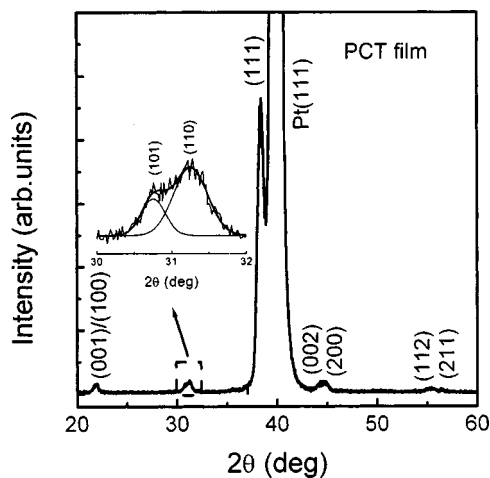
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FIG. 1. XRD pattern of the PCT film on a Pt/Ti/SiO$_2$/Si substrate. Each layer of the sample was heat-treated at 300 °C for 10 min in air using a hot plate, and the film was annealed at 600 °C for 10 min by RTA in oxygen atmosphere. Inset shows the splitting of the (101)/(110) doublet.
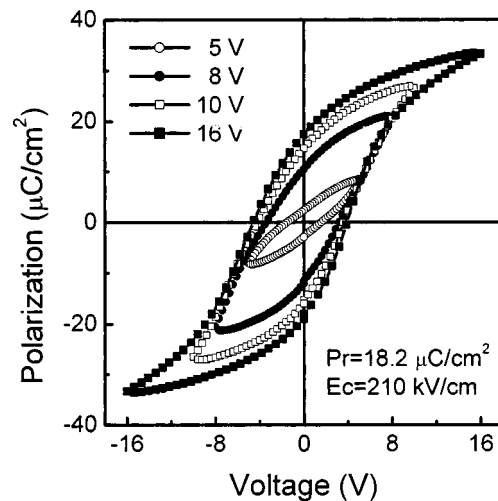

FIG. 2. Typical hysteresis loops for the highly (111)-oriented PCT thin film on a Pt/Ti/SiO$_2$/Si substrate annealed at 600 °C for 10 min in oxygen atmosphere by RTA.

presence of the tetragonal structure in the crystallized films. Tani *et al.*[10] suggested that whenever the Ti from the adhesion layer formed Pt$_3$Ti on the surface, a (111) perovskite texture was obtained. Pt$_3$Ti is believed to alter the surface energy and lattice spacing so as to promote crystallization of (111) perovskite phase due to its B-site cation position matching and lattice matching with the cubic Pt$_3$Ti structure. Gonzalez *et al.*[11] also reported that PCT thin films crystallized with (111) texture as induced by the Pt$_3$Ti(111). In this Pt$_3$Ti cubic structure, the Ti–Ti distance in the (111) plane is 5.55 Å. For the Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ perovskite, the Ti–Ti distance in the (111) plane is 5.52 Å. Thus, the nuclei have a preferred (111) orientation owing to the cubic Pt$_3$Pb is acting as a lattice-matching buffer layer between the Pt and PCT. When the film has this perovskite seeding layer, the activation energy for the crystallization of the films decreases. If the film is then subjected to a higher temperature heat treatment, the (111) nuclei will grow and strong (111) texture develops.

Figure 2 shows a typical $P–E$ hysteresis loops for the PCT film on a Pt/Ti/SiO$_2$/Si(100) substrate. The remanent polarization (P_r) and the coercive electric field (E_c) obtained from the $P–E$ hysteresis loops, are 18.2 μC/cm^2 and 210 kV/cm, respectively, for an applied electric field of 800 kV/cm. It shows that the highly (111)-oriented PCT film on Pt/Ti/SiO$_2$/Si substrate prepared by the sol–gel processing have good ferroelectric properties. A low P_r of 6 μC/cm^2 has been reported for PCT(24) films on Pt-coated silicon substrate.[7] A high P_r value of 41 μC/cm^2 was reported for c-axis oriented PCT(30) films on Pt-coated MgO substrates using multiple-cathode sputtering, and the E_c is about 400 kV/cm.[12]

From Fig. 2, it is seen that the symmetry center of the $P–E$ hysteresis loop shifts in a direction of negative voltage. The negative and positive coercive voltages (V_c) are −4.41 and 3.97 V, respectively. The imprint voltage, defined as $[+V_c+(−V_c)]/2$, is estimated to be −0.22 V. Warren *et al.*[13] suggested that the voltage shift arose from the trap-

ping of electrons at defect sites near the film/electrode interface. The trapped electrons then stabilized the existing domain configuration against switching. Another origin of the voltage shift is related to the magnitude of polarization.[14] The polarization constitutes an electrostatic potential well that attracts the electronic charge carriers, where they are trapped at near interfacial defect sites. A larger remanent polarization represents a deeper potential well, and consequently the trapping of charge carriers is more effective. So, the voltage shift is related to the top and bottom electrodes difference, the magnitude of polarization and/or the contribution of defect-dipole complexes.

Figure 3 shows the current density as a function of voltage when the Pt electrode is negatively and positively biased in the voltage range of −5 to 5 V. The leakage current density was lower than 1×10^{-7} A/cm^2 over the voltage range of 0 to ±5 V, indicating that the film has good insulating property. The leakage current when the Pt electrode was under a positive bias voltage was a little higher than when the
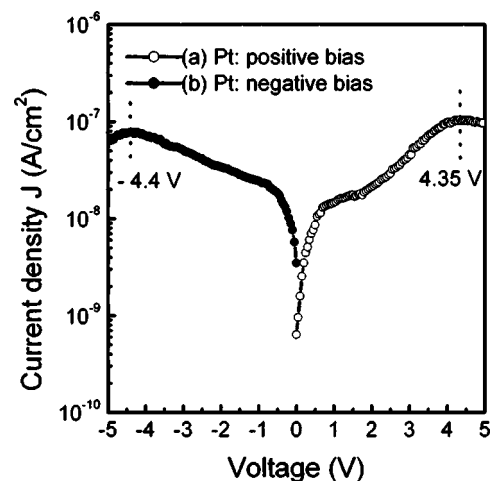

FIG. 3. Leakage current density vs. voltage characteristic for the Au/PCT/Pt thin-film capacitor.
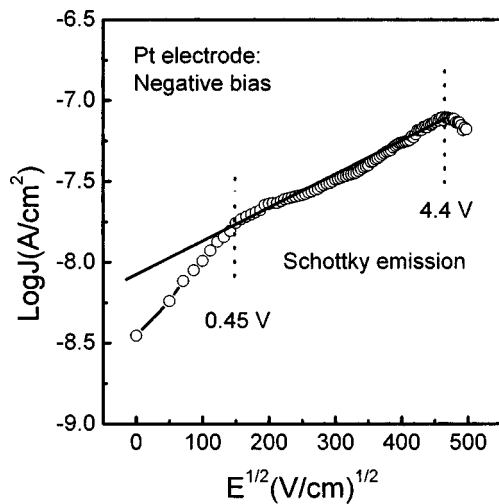
FIG. 4. Log J vs. $E^{1/2}$ plot when the Pt bottom electrode of the Au/PCT/Pt thin-film capacitor was under a negative bias.

FIG. 5. Log J vs. log E plot when the Au electrode of the Au/PCT/Pt thin-film capacitor was under a negative bias.

Pt electrode was under a negative bias voltage. In fact, the leakage currents in two opposite directions were limited by the interfaces between the film and the Pt or Au electrodes,[15,16] respectively. The positive leakage current was limited by the interface between the Pt bottom electrode and the PCT film (the bottom interface), while the negative leakage current was limited by the interface between the Au top electrode and the PCT film (the top interface). When the applied bias voltage was higher (or lower) than 4.35 V (-4.40 V), the leakage current density decreases with increased bias voltage (see Fig. 3). From Fig. 2, we can see that this value is close to the coercive voltage (-4.41 and 3.97 V) which indicates that the polarization reversal induces the change in leakage current.

The leakage current depends on the bias polarity. As a result, the conduction mechanism should be electrode limited for at least one of the metal–insulator junctions. The Schottky emission can be expressed as $\log J$ (where J is the leakage current density) being proportional to the square root of applied electrical field (E).[17,18] The space-charge-limited current (SCLC) can be expressed as $\log J$ being proportional to $\log E$.[18] Figure 4 shows the plot of $\log J$ versus electrical field $(E)^{1/2}$ with the Pt electrode biased with negative voltage for the Au/PCT/Pt thin-film capacitor. The leakage current shows a Schottky emission behavior. The PCT/Pt interface forms a Schottky barrier under an electric field range from 22.5 to 220 kV/cm.

Figure 5 shows the plot of $\log J$ versus $\log E$ with the Au electrode negatively biased for the Au/PCT/Pt thin-film capacitor. The slope is close to 1 in the low electric field (<35 kV/cm) region. The Au/PCT contact is thus ohmic at low electric field. At an electric field range from 35 to 105 kV/cm, for the Au electrode biased at negative voltage (not shown), as well as for a Pt electrode biased at negative voltage (with the $\log J$ versus $E^{0.5}$ plot shown in Fig. 4), both agree well with the Schottky emission characteristics. At higher bias voltages above 2.1 V, the $\log J$ versus $\log E$ plot shows a slope close to 2.6, which agrees well with the SCLC theory.[18] From Figs. 2–5, it can be seen that the trap-filled
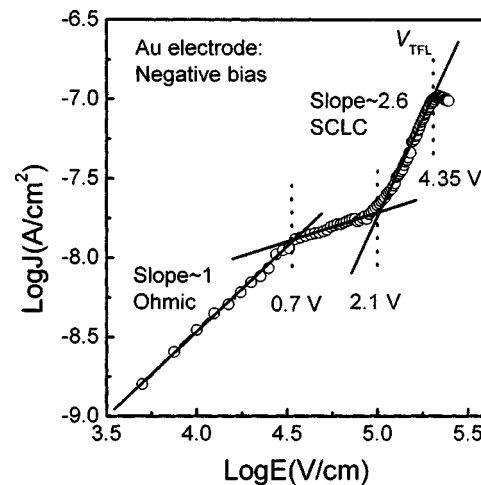
limit voltage (V_{TFL}) is 4.35 V, which is close to the average value of the coercive electric voltages (~ 4.2 V).

Figure 6 shows the current–time characteristics for dielectric relaxation current after different voltages have been applied to the bottom Pt electrodes. The relaxation current measured at low field (150 and 250 kV/cm) indicates the contribution of pure dielectric relaxation current. The current–time decay obeys the well-known Curie–Von Schweidler law,[19] $J = J_0 + J_s t^{-n}$ where J_s is the steady-state current density, n equal to the slope of the log–log plot, and t is time. The exponents, n, are found to be 0.52 and 0.65 for this film, respectively, at 150 and 250 kV/cm. The three possible mechanisms for the Curie–Von Schweidler law are well-known as space-charge trapping, relaxation time distribution, and electrical charge hopping.[20] As positive potential was applied to the Pt bottom electrode at low field, it indicates the contribution of pure relaxation current. At a higher field (300 kV/cm), the current has contributions from both pure dielectric relaxation current and leakage current,[21] the leakage current is affected by oxygen vacancy concentration and the magnitude of polarization.
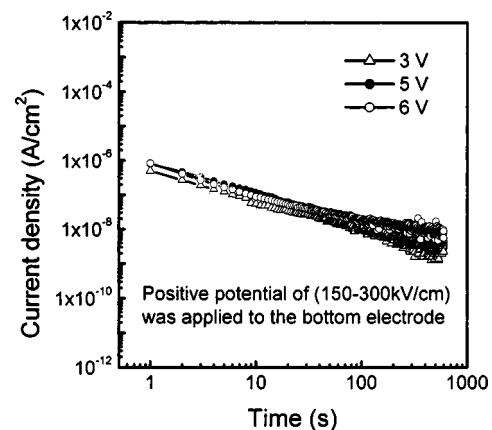

FIG. 6. Dielectric relaxation current of the Au/PCT/Pt capacitor with different positive bias voltages applied to the Pt bottom electrode.
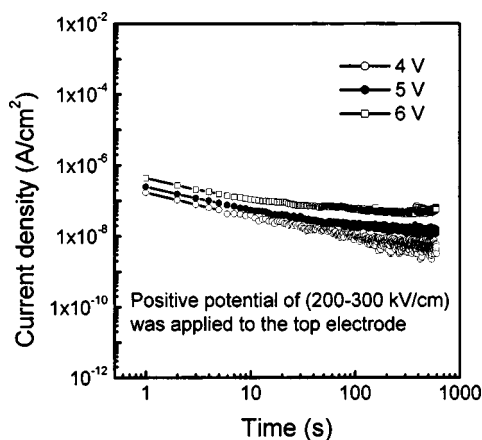
FIG. 7. Dielectric relaxation current of the Au/PCT/Pt capacitor with different positive bias voltages applied to the Au top electrode.

Figure 7 shows the current–time characteristics for dielectric relaxation current at different voltages with positive voltage applied to the Au top electrode. The relaxation currents measured at low field (200 kV/cm) indicates the contribution of pure dielectric relaxation current. At higher fields (250 and 300 kV/cm), the current has contributions from both dielectric relaxation current and leakage current. From the results, the leakage currents include effects of oxygen vacancy concentration, the magnitude of polarization, space charge trapping, electrical charge hopping, and/or the contribution of defect-dipole complexes.

IV. CONCLUSIONS

The highly (111)-oriented PCT film studied in this work has a remanent polarization and coercive electric field of 18.2 $\mu C/cm^2$ and 210 kV/cm, respectively. The leakage current density of the highly (111)-oriented PCT film was less than 1×10^{-7} A/cm^2. The leakage current depended on the polarity of the applied voltage. At low electrical field and with the Pt electrode biased negatively, the Pt/PCT interface forms a Schottky barrier, while the Au/PCT interface forms an ohmic contact. The conduction current when the Au electrode is biased negatively shows space-charge-limited behavior. The dielectric relaxation current behavior of the Au/PCT/Pt capacitor obeys the well-known Curie–Von Schweidler law at low electric field. The leakage currents include the effect of oxygen vacancy concentration, the magnitude of polarization, space charge trapping, electrical charge hopping, and/or the contribution of defect-dipole complexes.

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