Structural and Electrical Investigations of Pulse-Laser-Deposited (Pb,Sr)TiO$_3$ Films at Various Oxygen Partial Pressures

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Pulsed-laser deposited (Pb,Sr)TiO$_3$ (PSrT) films on Pt/SiO$_2$/Si substrate deposited at various oxygen partial pressures ($P_{O_2}$), ranging from 50 to 200 mTorr, were investigated in this work. PSrT films exhibit (100) preferred orientation at lower $P_{O_2}$ and then transit to (110) preferred orientation above 100 mTorr. The paraelectricity/ferroelectricity transition and dielectric constant of PSrT films are associated with the preferred orientation and oxygen concentration at various $P_{O_2}$. Furthermore, films deposited at higher $P_{O_2}$ exhibit higher breakdown field and smaller leakage current density as a consequence of fewer oxygen vacancies. Except for the case of films deposited at 200 mTorr, the conduction mechanism is identified as Schottky emission/Poole–Frenkel emission at low/high electric fields.

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PbTiO$_3$ (PTO) film has been considered for applications in non-volatile random access memory (NVRAM), but many drawbacks of this film must be improved, such as high coercive field, high crystallization temperature, and poor microstructure. The (Pb,Sr)TiO$_3$ (PSrT) is composed of the solid solutions: PbTiO$_3$ (PTO) and the SrTiO$_3$ (STO). PTO and STO films, at room temperature, behave in a tetragonal structure (ferroelectric phase) and a cubic structure (paraelectric phase), respectively, because PTO has the Curie temperature ($T_c$) at 490°C and STO has the $T_c$ at ~220°C. The effects of lead substituted by strontium (Sr) in the PTO film decrease the crystallization temperature and offer good control of the dielectric properties at room temperature. Therefore, PSrT is suitable for memory, sensor, frequency tuning devices, and electric properties of ferroelectric devices.

The PLD process consists of three steps: (i) vaporization of a target material by laser beam, (ii) transport and interaction of a vapor plume with a background ambient, and (iii) condensation of the ablated material onto a substrate where a thin film nucleates and grows. Hence, the structural and electrical characteristics of the PLD ferroelectric films are strongly affected by processing parameters such as substrate temperature, laser energy fluence (laser power density), and oxygen ambience.

To our knowledge, much less is known about the ambient oxygen effect on PLD ferroelectric films and only a few works studied the properties of PLD PSrT films prepared on Pt/SiO$_2$ substrate. Therefore, this study investigates the influence of oxygen partial pressure on structural and electrical characteristics of PSrT films deposited by low-temperature PLD. Moreover, the relationship between the texture and the corresponding ferroelectricity of PLD-PSrT films is also addressed.

**Experimental**

p-Type silicon wafers with (100) orientation were employed as the substrate in this study. A 100 nm thick SiO$_2$ was grown after the initial RCA cleaning process. The platinum (Pt) film, 100 nm thick, was sputtered onto SiO$_2$/Si as the bottom electrode and followed by annealing at 450°C for 30 min in N$_2$ ambient. Thin PSrT films (200 nm thick) were deposited on Pt/SiO$_2$/Si substrate electrodes with a KrF ($\lambda = 248$ nm) pulsed laser deposition system (Excimer Laser LPX 210i, Lambda Physik). A set of optical lenses was used to focus the excimer laser beam onto the (Pb$_{0.6}$Sr$_{0.4}$)TiO$_3$ target in vacuum. The PSrT target was prepared with a conventional ceramic fabrication process. The vacuum chamber was pumped down to a base pressure of 0.1 mTorr and then refilled with O$_2$ as the working gas. The vaporized species of the target was transferred and deposited on the substrate heated by a thermal heater. The target-to-substrate distance was 4 cm. The deposition temperature was fixed at a relatively low substrate temperature of 400°C, calibrated at the wafer upper surface. The oxygen partial pressure ($P_{O_2}$) was varied from 50 to 200 mTorr. The laser pulsed rate and the average energy fluence were 5 Hz and 1.55 J/cm$^2$ per pulse, respectively.

The surface roughness of PSrT films was inspected by atomic force microscopy (AFM; DI Nano-Scope III, Digital Instruments Co.). Auger electron spectroscopy (AES; Auger 670 PHI Xi, Physical Electronics) was used to analyze the element depth profile. The crystallinity of the film was analyzed by X-ray diffractometer (D5000, Siemens Co., using Cu K$_\alpha$, $\lambda \approx 0.154$ nm). Cross-sectional transmission electron microscopy (TEM) samples were prepared by standard sample preparation techniques with tripod polishing and ion milling using the Gatan PIPS system operated at 3 kV. The TEM experiments were carried out on a JEM-2000FX (JEOL, Ltd.) operated at 200 kV.

After the physical examination, the Pt top electrode, with a thickness of 100 nm and a diameter 75 $\mu$m, was deposited by sputtering and patterned by a shadow mask process to form a metal/ferroelectric/metal (MFM) capacitor structure. The noble metal platinum, with low resistivity, is considered as the electrode of
Pt/PSrT/Pt capacitors because of its low power consumption and RC delay. An automatic measurement system that combines an IBM PC/AT, semiconductor parameter analyzer (4156C, Agilent Technologies) and a probe station was used to measure the leakage current ($I-V$ characteristics) and breakdown properties. A capacitance-voltage ($C-V$) analyzer (Package 82 system C-V 590, Keithley Co.) was also used to measure $C-V$ curves at 100 kHz, and the dielectric constant was extracted from the $C-V$ measurement.

Results and Discussion

Physical properties of PSrT films.— PLD PSrT films were prepared at various oxygen partial pressures ($P_{O_2}$). Figure 1a shows AFM images of PLD PSrT films deposited on Pt/SiO$_2$/Si(100) wafers and indicates the surface morphology is a function of $P_{O_2}$ associated with increasing collisions between ejected species and the ambient gas. For numerical analysis, Fig. 1b gives the normalized root-mean-square roughness ($R_{rms}$), revealing that the maximum $R_{rms}$ and minimum $R_{rms}$ are 7.41 and 4.66 nm as $P_{O_2}$ equals 50 and 80 mTorr, respectively, and then $R_{rms}$ increases very slightly as $P_{O_2}$ increases. In short, films deposited at a higher $P_{O_2}$ have smoother surface morphology. Figure 2 presents the intensity of the oxygen element in the AES depth profiles and indicates higher oxygen concentration for films deposited at higher $P_{O_2}$.

Figure 3a displays the X-ray diffraction (XRD) spectra of PSrT films deposited at various $P_{O_2}$ on Pt/SiO$_2$/Si(100) wafers. All of these spectra exhibit the diffraction peaks of (Pb$_{1-x}$Sr$_x$)TiO$_3$ perovskite phases. The crystalline PSrT films are observed at such low temperature (400°C) because (i) the addition of strontium (Sr) induces a lower crystallization temperature of PSrT than that of PZT, and (ii) the PLD technique can preserves the crystalline phases and stoichiometric ratio of the target material at low substrate temperature. Furthermore, the intensity of the (100) and (110) diffraction peaks varies significantly as the oxygen partial pressure...
Electrical characteristics of PSrT films.— Figure 5a plots the capacitance vs electric field (C-E) characteristics of the PSrT films deposited at various $P_{O_2}$ and presents the typical C-E hysteresis characteristics of ferroelectric materials.

The capacitance shows a maximum value at negative bias corresponding to the coercive field ($E_c$) of the hysteresis loop as the applied field sweeps from $+200$ to $-200$ kV/cm. The maximum capacitance appears at positive $E_c$ when the applied field sweeps in the opposite direction. The four C-E curves are not symmetric, probably because of the difference in the configuration of electrodes used in the measurement, because the bottom electrode has a large area and the other, defined by a shadow mask, is small. Furthermore, the C-E hysteresis loop expands from $P_{O_2} = 50$ mTorr to $100$ mTorr and then shrinks as $P_{O_2}$ is higher than $100$ mTorr, suggesting that the ferroelectricity of PSrT films is suppressed at higher $P_{O_2}$ (200 mTorr). The ferroelectricity of ferroelectric material could be obtained analytically by calculating the polarization $P$ from the relative permittivity ($\varepsilon_{r}$) vs electric field ($E$) using the following formula

$$P = \varepsilon_0 \times \int (\varepsilon_{r} - 1) dE$$

where $\varepsilon_0$ is the vacuum permittivity and $\varepsilon_{r}$ is obtained from C-V relations. The zero-field capacitance, used in the dielectric constant calculation as shown in Fig. 5b, depends considerably on the $P_{O_2}$. The polarization of the lead-titanate-based crystal is maximum in the [100] direction, so the polarizations of the films enhanced with the preferred (110) orientation are weaker than those of the films with the preferred (100) orientation. Furthermore, the tetragonality ($c/a$), i.e., the ratio of $c$ axis/$a$ axis lattice constant obtained by electron diffraction patterns (not shown in this work) of the PSrT films deposited at $50$ mTorr and $200$ mTorr are $1.033$ and $1$. 

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**Figure 2.** (Color online) Intensity of oxygen element in AES depth profiles of PSrT films deposited at various oxygen partial pressures on Pt/SiO$_2$/Si(100) wafers.

**Figure 3.** (Color online) X-ray diffraction analyses of PSrT films deposited at various oxygen partial pressures on Pt/SiO$_2$/Si(100) wafers: (a) diffraction spectra and (b) texture characteristics.
The larger tetragonality for films deposited at lower $P_{O_2}$ may be attributed to the oxygen deficiency. Because the ferroelectric dipole originates from ionic displacement in the $c$-axis direction, large spontaneous polarization is obtained with the elongated $c$ axis, the larger tetragonality. However, the lower $P_{O_2}$-deposited film (the most oxygen deficient) exhibits larger leakage current density (addressed later), which usually degrades the dielectric constant. In other words, the dielectric and ferroelectric properties of PSrT films are the combined effects of the preferred-orientation and oxygen content. Thus, the PSrT film deposited at 100 mTorr exhibits the maximum dielectric constant of 642, which is connected with the enhanced $(100)$ preferred orientation (Fig. 3b) and the higher oxygen concentration (Fig. 2).

Figure 6 shows that the time-zero dielectric breakdown (TZDB) accordingly. The larger tetragonality for films deposited at lower $P_{O_2}$ may be attributed to the oxygen deficiency. Because the ferroelectric dipole originates from ionic displacement in the $c$-axis direction, large spontaneous polarization is obtained with the elongated $c$ axis, the larger tetragonality. However, the lower $P_{O_2}$-deposited film (the most oxygen deficient) exhibits larger leakage current density (addressed later), which usually degrades the dielectric constant. In other words, the dielectric and ferroelectric properties of PSrT films are the combined effects of the preferred-orientation and oxygen content. Thus, the PSrT film deposited at 100 mTorr exhibits the maximum dielectric constant of 642, which is connected with the enhanced $(100)$ preferred orientation (Fig. 3b) and the higher oxygen concentration (Fig. 2).

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of the Pt/PSrT/Pt capacitor is enhanced as $P_{O_2}$ increases. TZDB is influenced by grain size and oxygen stoichiometry of the films because of a large potential drop across the high-resistivity grain boundary, and because the space charge of oxygen vacancies (OVs) causes resistance degradation as expressed by the following reaction\textsuperscript{22-25}

$$O_\circ \leftrightarrow V_\circ + 2e^- + \frac{1}{2}O_2.$$ \hspace{1cm} [3]

where $O_\circ$, $V_\circ$, and $e^-$ represent the oxygen ion on its normal site, the oxygen vacancy, and the electron, respectively. The PSrT films deposited at higher $P_{O_2}$ exhibit a higher breakdown field, due presumably to the fewer OVs (i.e., higher oxygen concentration shown in Fig. 2).

Table I summarizes the physical properties and electrical characteristics of PLD PSrT films deposited at various oxygen partial pressures on Pt/SiO$_2$/Si(100) wafers. It can be seen that the leakage current density increases at $+100$ kV/cm decreases as $P_{O_2}$ increases. The PSrT films deposited at higher $P_{O_2}$ have more OVs and rougher surface than those deposited at lower $P_{O_2}$.

Table I. Summarized characteristics of PLD PSrT films deposited at various oxygen partial pressures on Pt/SiO$_2$/Si(100) wafers.

<table>
<thead>
<tr>
<th>Oxygen partial pressure ($P_{O_2}$, mTorr)</th>
<th>50</th>
<th>80</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS roughness ($R_{RMS}$, nm)</td>
<td>7.41</td>
<td>4.66</td>
<td>4.68</td>
<td>5.04</td>
</tr>
<tr>
<td>$X_{OV}$ Relative proportion (%)</td>
<td>51.5</td>
<td>55.8</td>
<td>54.3</td>
<td>7.9</td>
</tr>
<tr>
<td>TZDB field (kV/cm)</td>
<td>721</td>
<td>976</td>
<td>1042</td>
<td>1117</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>279</td>
<td>536</td>
<td>642</td>
<td>180</td>
</tr>
<tr>
<td>Current density (μA/cm$^2$)</td>
<td>0.812</td>
<td>0.416</td>
<td>0.187</td>
<td>0.119</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Evaluated from AFM analysis.

\textsuperscript{b} Evaluated from XRD spectra.

\textsuperscript{c} Evaluated from C-E curves at zero field.

\textsuperscript{d} Evaluated from J-E curves at +100 kV/cm.

Later in the text, the leakage current data are interpreted as Schottky emission (SE) at lower electric fields and Poole–Frenkel emission (PF) at higher electric fields, which are used to analyze the interface-limited and bulk-limited characteristics of Pt/PSrT/Pt capacitors, respectively.\textsuperscript{22-25}

The SE behavior is expressed as

$$\text{SE:log}(J/SE(T^2)) = -q[\varphi_i - (qE/4\pi e_{PSrT})^{1/2}](k/T\ln 10) + \log(A^*)$$ \hspace{1cm} [4]

where $A^*$ is the effective Richardson’s constant, $\varphi_i$ is the potential barrier height at the interface, $e_d$ is the dynamic dielectric constant of the ferroelectric material in the infrared region, $q$ is the unit charge, $k$ is Boltzmann’s constant, $T$ is current density, $T$ is absolute temperature, and $E$ is the external electric field. The conduction current follows SE behavior, and then a log$(J/SE)$ vs $E^{1/2}$ plot should be linear. Similarly, a log$(J/PF)$ vs $E^{1/2}$ plot can be made for PF. Figure 7a presents the SE plot of Pt/PSrT/Pt capacitors deposited at various $P_{O_2}$ and the dashed lines represent the fitted results. The inhibited leakage current of PSrT films deposited at higher $P_{O_2}$ is correlated with the lower Schottky barrier, fewer interface states and fewer space charges (charged OVs) due to the smoother surface morphology (Fig. 1) and fewer OVs. The result is consistent with the breakdown field of TZDB (Fig. 6). As seen in Fig. 7a, this indicates that films deposited at 200 mTorr exhibit SE conduction only (without a transition of conduction). Figures 7b and c draw the electron energy band at the interface of substrate electrodes and reveals PSrT films act as n-type semiconductors due to the generation of OVs in ABO$_3$ perovskites.\textsuperscript{22-25}

In the case with lower $P_{O_2}$, more interface states result in more charge accumulation and severe image-force effects at the edge of the electrodes, leading to the decrease ($\Delta\varphi$) of Schottky barrier height.\textsuperscript{27-28} In the case with higher $P_{O_2}$, the increase of $P_{O_2}$ yields fewer interface states and a higher Schottky barrier, resulting in a small leakage current.

Figure 8a shows the PF plot using the same experimental I-V data, given by the following equation, indicating that the curves follow PF behavior when the bias exceeds +130 kV/cm and trapping states exist for PLD-PSrT films deposited at 50–100 mTorr.

$$\text{PF:log}(J/PF(E)) = -q[\varphi_i - (qE/\pi e_{PSrT})^{1/2}](k/T\ln 10) + \log(B)$$ \hspace{1cm} [5]

where $B$ is a constant, and $\varphi_i$ is the trapped energy level. In contrast, the leakage current of PSrT films deposited at $P_{O_2} = 200$ mTorr is not governed by PF. Figure 8b reveals that PSrT films deposited at lower $P_{O_2}$ have more OVs and rougher surface than those deposited at higher $P_{O_2}$, yielding more interfacial states as stated in Fig. 7b and more trapping states inside PSrT films. Thus, the magnitude of leakage current is governed by the balance between the injected electron current and the trapping/detrapping rate. The field-assisted emission of trapped charged carriers follows PF emission rate, revealing bulk-limited conduction as the dominant mechanism for the lower $P_{O_2}$ case. In contrast, Fig. 8c indicates that higher $P_{O_2}$ yields fewer interfacial states with the higher barrier and fewer trapping

\[ \text{Figure 7. (Color online) (a) Experimental and fitted log } (J/SE) \text{ vs } E^{1/2} \text{ (Schottky emission) plots, and the electron energy band at the interface of substrate electrodes for PSrT films deposited at (b) lower } P_{O_2} \text{ and (c) higher } P_{O_2}. \]
fewer oxygen vacancies (OVs). It is also seen that the leakage current density biased at +100 kV/cm decreases as a function of $P_{O_2}$. The leakage current analysis of Pt/PSrT/Pt capacitors reveals SE/PF (Schottky emission/Poole–Frenkel emission) at low/high applied field, except the PSrT films deposited at $P_{O_2} = 200$ mTorr only reveal SE behavior at the applied field range. The increased $P_{O_2}$ yields fewer interface states and a higher Schottky barrier and fewer trapping states inside PSrT films. Furthermore, the conduction mechanism of PLD PSrT films changes from bulk-limited (PF) to interface-limited (SE) as $P_{O_2}$ increases. PLD PSrT films, deposited at oxygen partial pressures from 50 to 200 mTorr, have been demonstrated with dense surface morphologies, good crystallinity, single-crystal grains in column-like granular structure, and excellent electrical properties. Hence, the PLD PSrT film is a promising material for integration in integrated-circuit-compatible process.

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