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Electrical properties of paraelectric (Pb,La)(Nb,Ti)O_3 thin films for dynamic random access memory devices

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Paraelectric (Pb,La)(Nb,Ti)O_3 (PLNT) thin films were deposited by the sol-gel method on (111)Pt/Ti/SiO_2/Si substrates at temperatures as low as 600 °C for the use of ULSI (ultralarge scale integration) DRAM (dynamic random access memory) capacitors. Films exhibited a regular polycrystalline cubic perovskite phase and showed the presence of paraelectricity in terms of hysteresis of capacitance–voltage ($C-V$) and polarization–electric field ($P-E$) characteristics in metal–insulator–metal (MIM) capacitors. The dielectric constants of the films are 611 for a 200 nm thick film and 619 for a 300 nm thick film in a frequency of 100 kHz. The charge storage density obtained from the polarization measurement for a 200 nm thick film was about 50 fC/μm^2, while a leakage current density of 70 nA/cm^2 was observed at an applied field of 100 kV/cm. These values qualify the PLNT thin films for an alternate storage node dielectric in DRAM capacitors. © *1996 American Institute of Physics.* [S0003-6951(96)04306-5]

As device dimensions are scaled down, ferroelectric thin films compared with other conventional storage node dielectrics have become extremely important due to their suitability in developing ULSI (ultralarge scale integration) DRAM (dynamic random access memory) storage capacitors.[1,2] Recently, trends[3,4] for replacing the trench and stack capacitors in DRAM with a planar capacitor configuration prompted the need for the development of high dielectric constant materials ($\varepsilon_r > 100$) with reliably low leakage current density ($J < 10^{-7}$ A/cm^2) and high dielectric breakdown strength ($E_B > 10^6$ V/cm). For this purpose, several ferroelectric compositions such as Pb(Zr,Ti)O_3, (Pb,La)(Zr,Ti)O_3, $SrTiO_3$, and (Ba,Sr)TiO_3 have been investigated because of their high charge storage density ($Q_c = \Delta P = P_{\max} - P_r$, where $P_{\max}$ is maximum polarization and P_r is remanent polarization in ferroelectric hysteresis curve) and the high dielectric constant. However, the polarization hysteresis normally observed in ferroelectric composition is not necessary. Since nonswitching cubic paraelectric materials in principle have greater potential for DRAM application, the key to their production is to turn a Pb-based ferroelectric perovskite into a paraelectric phase of cubic perovskite structure by chemical modification.[3] The perovskite-structured (Pb,La)TiO_3 (PLT) solid-solution system provides an interesting example of a compositional series for which a changeover from conventional to diffuse ferroelectric phase transition is observed, and undergoes the phase transition from a centrosymmetric cubic ($m3m$) paraelectric to a tetragonal ($4mm$) ferroelectric phase by varying the La content. Few attempts are evident in the literature to develop PLT thin films.[3,5]

In the present letter, thin films of ($Pb_{0.72}$,$La_{0.28}$)TiO_3 were selected since the composition was near the morphotropic phase boundary (MPB) in which physical parameters such as dielectric constant, piezoelectric constant, electro-optic coefficient, and so on reach maximum value.[6] We report on the sol-gel growth and the electrical properties of 5 mol % Nb modified ($Pb_{0.72}$,$La_{0.28}$)TiO_3 (PLNT) thin films, while examining its suitability to DRAM device development.

PLNT thin films were fabricated using 0.4 M alkoxide-derived solution that was prepared from lead (II) acetate trihydrate, lanthanum (III) acetate hydrate, niobium (V) ethoxide, and titanium (IV) isoproxide as precursors. 2-methoxyethanol was used as a solvent. 5 mol % excess PbO over the stoichiometric amount was introduced in the PLNT batch composition, to compensate for the loss of lead during heat treatment. In order to prevent cracking and to improve surface smoothness of the film, nitric acid and ethylene glycol were used as catalyst. All the operations were carried out in N_2 gas. The films were deposited on (111)Pt(100 nm)/Ti(80 nm)/SiO_2(100 nm)/Si(100) substrates by spin coating using a photoresist spinner operated at 3000 rpm for 60 s. The films were pyrolyzed in air at 350 °C for 5 min to remove solvent and other organics, and the deposition-pyrolysis cycle was repeated until the desired thickness was obtained. Finally, all the films were annealed in air using a conventional furnace at 600 °C for 30 min to obtain the cubic perovskite phase. PLNT thin films were confirmed to be a cubic perovskite phase by x-ray diffraction. In order to make metal–insulator–metal (MIM) capacitors, 300 nm thick Au films were deposited on PLNT films by thermal evaporation. After deposition, the Au films were chemically etched, using photolithography, to form a circle top electrode of area 2.8×10^{-3} cm^2. The dielectric behavior of PLNT films was measured using a computer-controlled impedance analyzer (HP4194A).

The surface morphology, crystalline size, and thickness of PLNT thin films have been observed using scanning electron microscopy (SEM). The SEM image of the surface morphology of the PLNT film annealed at 600 °C for 30 min is shown in Fig. 1(a). It shows that the film was extremely

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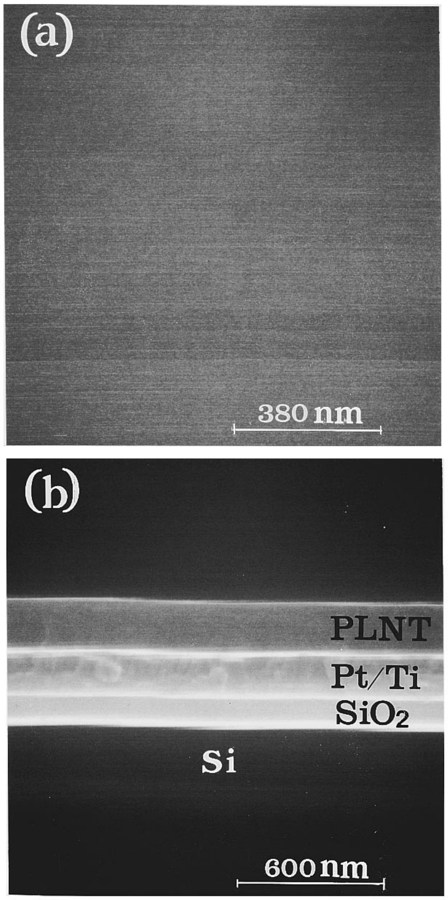

FIG. 1. SEM images of (a) surface morphology and (b) cross section for 200 nm thick PLNT film annealed at 600 °C for 30 min.

smooth and had a very fine grain structure with no cracks. Figure 1(b) shows the cross-sectional SEM image for the same film, in which each layer exhibits a very dense, uniform, and sharp interface. The surface morphology of the film did not change significantly on 300 nm thick film.

Figure 2 shows the frequency dependence of the dielectric constant and conductance of PLNT films with thickness of 200 and 300 nm, measured at a frequency range from 100 Hz to 40 MHz. The measured dielectric constant and conductance at 100 kHz is 611 and 6 μS for 200 nm thick film,

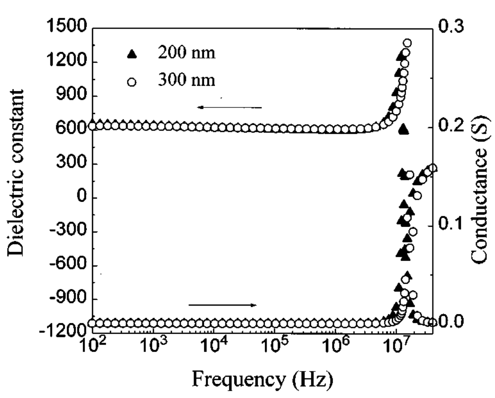

FIG. 2. Frequency dependence of dielectric constant and conductance of PLNT thin films with thickness of 200 and 300 nm.

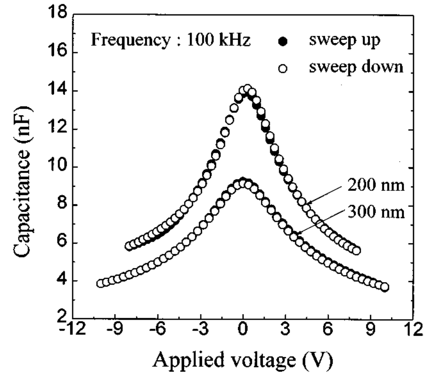

FIG. 3. Capacitance–voltage ($C-V$) characteristics of PLNT thin films with thicknesses of 200 and 300 nm at a frequency of 100 kHz.

and 619 and 4 μS for 300 nm thick film, respectively. The dielectric constant of the PLNT films was large compared to the others reported for paraelectric $(Ba,Sr)TiO_3$ films.[7,8] 300 nm thick film has a larger dielectric constant than 200 nm thick film. The dielectric loss was observed to be 0.018 for the films. Also, the dielectric constant and conductance showed no noticeable dispersions with frequency up to 10 MHz, which indicates good quality of the present films. However a large increase in the resonance conductance was observed at a frequency between 10–15 MHz, which may be due to finite resistance of the electrode at higher frequencies. Similar frequency dispersion behavior due to finite resistance of the electrode was reported for other dielectric thin films.[9]

Figure 3 shows the capacitance–voltage ($C-V$) characteristics of PLNT thin film capacitors with an MIM structure. A ramp bias voltage with an ac signal of small amplitude (100 mV) is applied to the PLNT film capacitors, while an applied bias voltage was swept at a ramp rate of 0.5 V/s in both polarities. The capacitances exhibit a strong dependence on the applied voltage originating from polarization saturation in the higher electric field region. The $C-V$ curves show no hysteresis due to polarization reversal showing at conventional ferroelectric thin films such as $Pb(Zr,Ti)O_3$, which indicates that the films are paraelectric in nature. The $C-V$ curves are symmetrical with respect to the point of 0 V and the maximal values of capacitance $C_{\max}$ in both polarities exist at zero bias voltage, which indicates that an internal electric field exists in no dielectric films. The dielectric constants calculated from $C_{\max}$ are 620 for the 200 nm thick film and 624 for the 300 nm thick film.

Figure 4 shows the electric field dependencies of the charge storage densities of PLNT films with thicknesses of 200 and 300 nm. The charge storage density (Q_c) was calculated from $C-V$ curves using the relation $Q_c = \varepsilon_0 \varepsilon_r E$, where ε_0 is the dielectric constant of vacuum, ε_r is the dielectric constant of the PLNT films, and E is an applied electric field. The charge storage densities of the films are increased with increasing electric field. The charge storage densities of 200 and 300 nm thick films are about 62 and 40 fC/μm^2 at an applied field of 100 kV/cm, respectively. For practical 256 Mbit DRAM, it has been predicted that a charge storage density of the order of 40 fC/μm^2 is required for a 200 nm thick film.[10] From the standpoint of the above

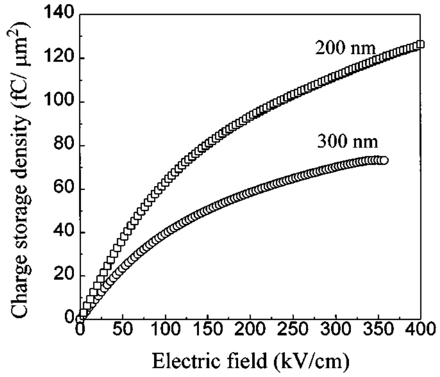

FIG. 4. Electric field dependencies of the charge storage density (Q_c) of PLNT thin films with thicknesses of 200 and 300 nm.

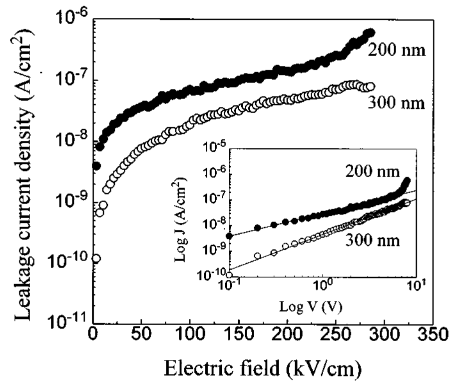

FIG. 6. Leakage current density–electric field ($J-E$) characteristics of PLNT thin films with thickness of 200 and 300 nm.

application, the Q_c of the present PLNT films is sufficiently large, and the 200 nm thick film is preferred to the 300 nm thick film because of its higher dielectric constant and charge storage density.

Polarization–electric field ($P-E$) characteristics were measured using a standard Sawyer–Tower circuit at an input sine wave of 100 kHz in conjunction with a digital storage oscilloscope and a function generator. The load capacitor of 1.41 μF was used. Figure 5 shows the variation of polarization charge hysteresis with applied electric field. The films have no hysteresis, but exhibit a linear behavior at low electric field up to 150 kV/cm and a nonlinear saturation of the polarization in the high electric field region, which establishes the presence of paraelectricity in the present PLNT films, as shown by $C-V$ curves. The polarization or charge storage density for the two films is about 50 fC/μm^2 at an electric field of 100 kV/cm, which is comparable to the value calculated by the $C-V$ curve.

Figure 6 shows the leakage current density–electric field ($J-E$) characteristics for PLNT films with thicknesses of 200 and 300 nm. The $J-E$ characteristics were measured using a computer-controlled high voltage source measurement unit (Keithley 237). With increasing electric field, the leakage current densities of the films increase gradually. The leakage current densities of PLNT films are around 70 nA/cm^2 for 200 nm thick film and 20 nA/cm^2 for 300 nm thick film at an electric field of 100 kV/cm. These values are small enough for the application of 256 Mbit DRAM. 200 nm thick film has a larger leakage current density than 300 nm thick film. The inset in Fig. 6 displays the log J vs log V plot. The leakage current density (J) is nearly linear up to the electric field of 300 kV/cm, which represents the ohmic behavior. The slopes of the linear fitting curves for the log J vs log V plot are 1.02 and 1.39 for 200 and 300 nm thick films, respectively. This linear behavior indicates that only a small amount of space charges and charge traps is formed in the PLNT layers up to the high electric field of 300 kV/cm. These results can be attributed to the growth of a dense PLNT layer with a sharp interface, as shown in Fig. 1(b).

In summary, good quality paraelectric PLNT thin films were deposited by the sol-gel technique on (111)Pt/Ti/SiO_2/Si substrates at a temperature as low as 600 °C, while the films have a fine grain structure and their surface was extremely smooth, dense, and uniform. The PLNT thin films showed paraelectricity and have a dielectric constant around 619, dielectric loss less than 0.018 at 100 kHz, and a leakage current density less than 70 nA/cm^2 at an electric field of 100 kV/cm. Films also exhibited a charge storage density of more than 40 fC/μm^2. These results qualify the paraelectric PLNT thin films for an alternate storage node dielectric in DRAM capacitors.

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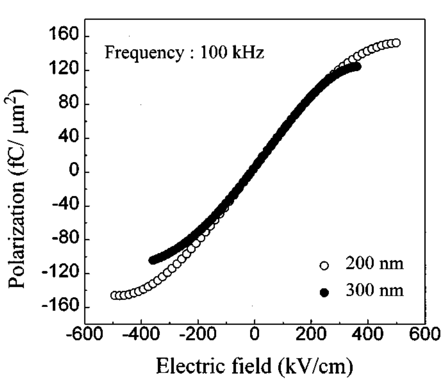

FIG. 5. Polarization–electric field ($P-E$) hysteresis characteristics of PLNT thin films with thicknesses of 200 and 300 nm measured at 100 kHz.

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