

Pulsed excimer laser ablated barium titanate thin films

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Thin films of BaTiO₃ were deposited on platinum coated silicon substrates by excimer laser (248 nm) ablation at 600 °C or *ex situ* crystallized at about the same annealing temperature. Films deposited at 600 °C showed good crystallinity and were characterized for ferroelectricity, dielectric constant, dielectric loss, leakage current, and *C-V* characteristics. The films showed a dielectric constant of 220, a dissipation factor of 0.02, a leakage current of 1.8×10^{-6} A/cm² at a bias of 5 V, and a charge storage density of about 40 fC/μm² at a field of 0.15 MV/cm.

In MOS (metal-oxide-semiconductor) capacitors for DRAMs (dynamic random access memories), the charge storage $C = \epsilon_r \epsilon_0 A/d$, where ϵ_r is the relative permittivity of the dielectric, ϵ_0 is the permittivity of free space, A is the area of the capacitor and is a function of the capacitor structure (e.g., trench or planar design), and d is the thickness of the dielectric layer. The increase in C by increasing A and decreasing d had been a popular approach to increase the storage density in low k gate dielectrics, however, has a limitation in submicron devices as it affects the reliability of the dielectric films. The dielectric constants of ferroelectric materials, in general, are many times larger than the conventional gate dielectrics such as silicon oxide and tantalum oxide. Their use as linear gate dielectrics provides largely increased capacitance and offers the possibility to avoid trenching in submicron devices.¹ Several ferroelectric compositions are available for use in DRAM development and BaTiO₃ with some dopants had been a popular candidate for making multilayer capacitors (MLC) using thick film technology. BaTiO₃ ceramics exhibit a perovskite structure, and are tetragonal from 0 to 130 °C, polarizes along any of the $\langle 100 \rangle$ directions of prototype and possesses ϵ_r of 1900 and 1620 parallel and perpendicular to the poling axis, respectively, under constant stress conditions. Therefore BaTiO₃ thin films have the potential to offer at least an order of magnitude higher capacitance density at relatively larger thicknesses, in a DRAM cell capacitor compared to other gate dielectrics such as SiO₂ and Ta₂O₅. However, the dielectric permittivity of BaTiO₃ thin films has been reported^{2,3} to range between 12 and 1000 depending on the preparative conditions and the crystalline state of the films.

A variety of deposition techniques that have been successfully used to synthesize BaTiO₃ thin films includes radio frequency (rf) diode sputtering,⁴ rf magnetron sputtering,⁴ and evaporation with CO₂ laser.⁵ Most recently, successful deposition of ferroelectrics such as Bi₄Ti₃O₁₂,⁶ PZT,⁷ and Pb₅Ge₃O₁₁,⁸ by excimer laser ablation has been reported. In this letter we report the properties of polycrystalline BaTiO₃ films prepared by excimer laser ablation.

The deposition chamber and procedures of our present pulsed UV excimer laser deposition setup have been previously described in detail.⁸ The sintered target of BaTiO₃

was mounted on a motor driven rotary shaft for a continuous rotation at a constant rpm to ensure uniform ablation rate. Platinum coated silicon (Pt/Ti/SiO₂/Si) and bare silicon substrates were placed parallel to the target at a distance of ≈ 3 cm. The substrates were heated to temperatures of up to 600 °C. The ambient O₂ pressure was maintained at 10 mTorr by a MKS flow meter. Films thus deposited at a fluence of 2 J/cm² were in the range of 0.3–2.0 μm in thickness as measured by a Taylor–Hobson Talysurf profilometer. Some films were also deposited without substrate heating. These films were annealed in the presence of O₂ for 2 h at 650 °C. The crystallographic structure of the films was examined by CuKα x-ray diffraction (XRD). Gold top electrodes were deposited for electrical characterization and the dielectric properties were measured as a function of frequency by using a low frequency (LF) impedance analyzer (Hewlett-Packard 4192A). The ferroelectricity was investigated in terms of polarization hysteresis behavior by employing a computer controlled modified Sawyer–Tower circuit and also by measuring the capacitance, at 100 KHz, as a function of a swept positive to negative voltage bias (*C-V* curves) in a MFM (metal-ferroelectric-metal) configuration. The current-voltage (*I-V*) measurements were done by measuring the current through the sample (which was shielded from external noise) with an electrometer (Keithley, Model 617) as a function of dc voltage.

Figure 1 shows the x-ray diffraction patterns of the films deposited on platinum coated Si substrates with 2 J/cm² fluence and 10 mTorr of partial pressure of oxygen. However, films either annealed at 650 °C [Fig. 1(b)] or deposited at temperatures of 600 °C [Fig. 1(a)], showed perovskite phase with mainly (110) orientation. However, no significant tetragonal split was observed which may be associated with small grain size of the ablated films. The peaks marked with Δ are due to $k\beta$ peaks from platinum.

The dielectric properties were measured on the BaTiO₃ films in a MFM (metal-ferroelectric-metal) configuration. The variation of dielectric constant and dissipation factor of the excimer laser ablated films as a function of frequency are shown in Fig. 2. The dielectric constant was found to be about 220 at 100 KHz for both *ex situ* and *in situ* grown films whereas the dissipation factor remained between 0.015 and 0.02 for both the films minor differences in dielectric permittivity at higher frequencies may be due to probable differences in grain size and surface structure

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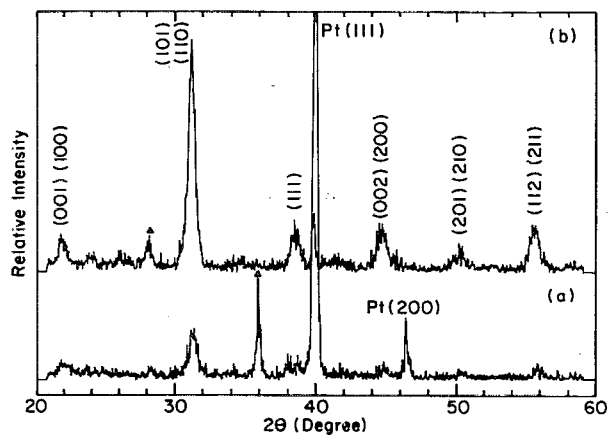


FIG. 1. XRD patterns of the films on platinum coated silicon: (a) deposited at 600 °C, (b) deposited at room temperature and annealed at 600 °C.

which are expected to result from the differences in crystallization procedures. Such difference in surface structure may also allow electrode polarization, causing a small dispersion in dielectric behavior at lower frequencies (100 Hz). However, general observation of BaTiO₃ films of both *ex situ* and *in situ* crystallization, indicated no notable difference in the structural and dielectric behavior in the high frequency regime (100 kHz).

The ferroelectricity was investigated by observing the polarization hysteresis using an automated Sawyer-Tower circuit, at a frequency of 1 KHz. The change in polarization as a function of applied field is presented in Fig. 3 for a film which had a thickness of 1.5 μm. The remanent polarization (P_r) was 0.8 μC/cm² and the coercive field was 40 kV/cm. BaTiO₃ single crystals⁹ exhibit a P_r of 26 μC/cm² at a coercive field of less than 1 kV/cm. However, in the ceramic form, the perovskite BaTiO₃ is known to exhibit a slim polarization loop, which is generally attributed to small grain size. The lower P_r observed in the present excimer laser ablated films may also be ascribed to finer grain size (consistent with SEM observations) and similar values were also found in the reported literature.⁵

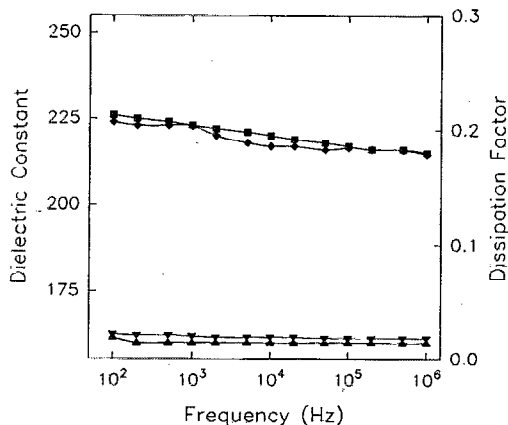


FIG. 2. Dielectric constant and dissipation factor as a function of frequency.

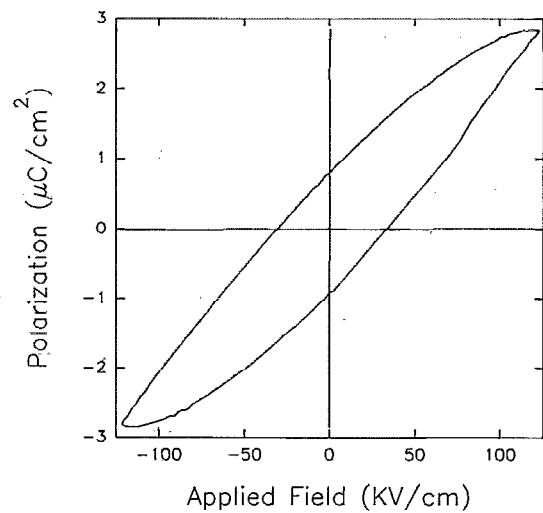


FIG. 3. Polarization hysteresis behavior of *in situ* crystallized films.

Figure 4 shows the capacitance-voltage ($C-V$) characteristics of the *in situ* crystallized films measured at 100 KHz, in a MFM (metal-ferroelectric-metal) capacitor configuration. A symmetric $C-V$ characteristic was observed and initial increase in capacitance with electric field which was mainly due to domain wall switching. However, no significant hysteresis was observed and may be inherent from the slim loop behavior of polarization switching, as also observed under high fields. The charge storage density (Q_c) was calculated using the relation $Q_c = \epsilon_0 \epsilon_r E$, where ϵ_0 is the dielectric constant of vacuum, ϵ_r is the permittivity of the BaTiO₃ film and E is the applied electric field. The films (0.33 μm thick) showed a Q_c of about 40 fC/μm² at an applied field of about 0.15 MV/cm (equivalent to an applied dc voltage of 5 V). The breakdown field of this film was found to be about 0.5 MV/cm. In comparison, consider that to accomplish such storage densities with conventional gate dielectrics such as SiO₂ and Ta₂O₅, the dielectric thicknesses would have to be a few angstroms. In a ferroelectric capacitor Q_c can also be calculated from the

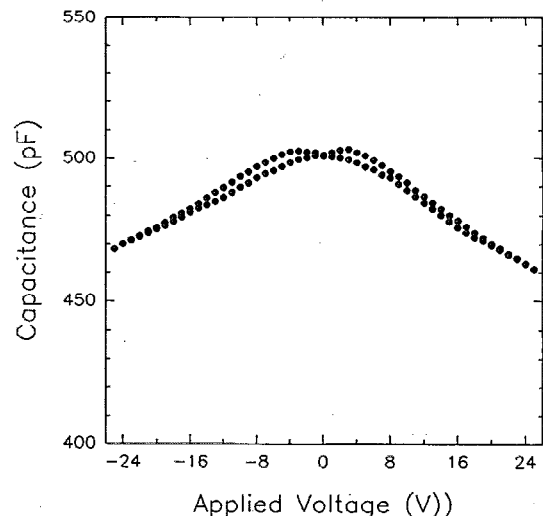


FIG. 4. $C-V$ characteristics of the *in situ* crystallized films.

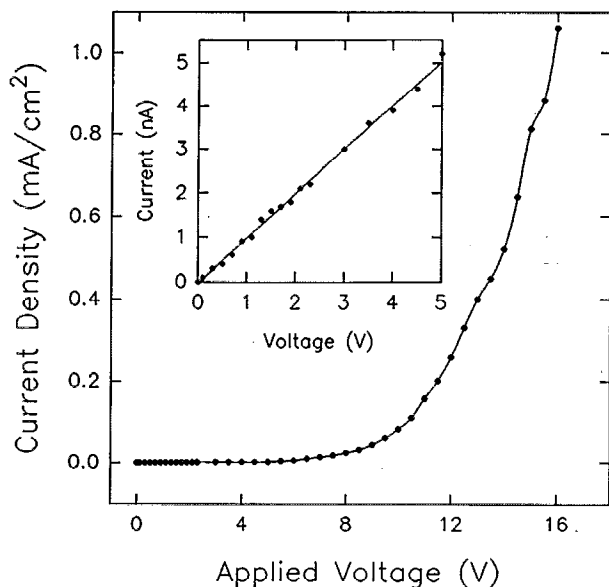
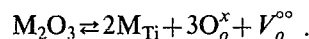


FIG. 5. I - V characteristic of the *in situ* crystallized films.

hysteresis loop and $Q'_c = P_{\max} - P_r$, where P_{\max} is the polarization at the maximum field.¹ The Q'_c calculated from Fig. 3 was found to be $33 \text{ fC}/\mu\text{m}^2$ when interpolated for a field of $0.15 \text{ MV}/\text{cm}$. The discrepancy in Q'_c obtained from two methods could be due to the differences in electric field distribution in the films arising from the inherent nature of the measurements.

The dc characteristics of the films are essential in terms of their leakage current behavior and dielectric breakdown strength and the results on current-voltage behavior are presented in Fig. 5. Resistivity was calculated at 5 V bias and was found to be $2 \times 10^{10} \Omega \text{ cm}$. It was also noted that the reversal of polarity of applied field, caused no asymmetry in the I - V behavior, indicating the absence of formation of any Schottky-type barriers at the interface of the BaTiO_3 film and the metal electrodes. It may be seen from the inset, a slope of 1 suggests that the films showed a near ohmic behavior at lower applied voltages. However, at higher voltages ($V > 5$), the change in slope (> 2) of the I - V characteristic indicates the onset of a space-charge controlled conduction process. Several sources are possible for space-charge related conduction in insulating films, in general, which include defects at grain boundaries, release of trapped charges, and oxygen vacancies causing a localized nonstoichiometry in some regions across the film.¹⁰ The relatively high leakage current ($1.8 \times 10^{-6} \text{ A}/\text{cm}^2$ at a

bias of 5 V) in the ablated BaTiO_3 films could be mainly due to oxygen vacancies. The presence of oxygen vacancies in undoped BaTiO_3 is generally due to unintentional acceptor doping. This leads to the introduction of V_o^{∞} (Kröger-Vink notation¹¹)



The acceptor impurities are charge compensated by oxygen vacancies and the products are doubly ionized oxygen vacancies, V_o^{∞} and charged trivalent cation at the Ti site. These oxygen vacancies will lead to a conduction process controlled by space charge. Similar space-charge controlled conduction was also reported for perovskite PZT thin films and ceramics.¹² Detailed studies are in progress for understanding the space-charge mechanisms in excimer laser ablated BaTiO_3 films.

In conclusion, excimer laser ablated BaTiO_3 films showed stoichiometric films with good surface morphology and showed a dielectric constant of 220, dissipation factor of 0.20, leakage current of $1.8 \times 10^{-6} \text{ A}/\text{cm}^2$, dc resistivity of $2 \times 10^{10} \Omega \text{ cm}$ and charge storage density of $40 \text{ fC}/\mu\text{m}^2$ at a field of $0.15 \text{ MV}/\text{cm}$ (equivalent to an applied dc voltage of 5 V). The excimer laser ablation approach seemed to offer better quality BaTiO_3 films and the measured properties clearly establishes the potential use of BaTiO_3 films for high density DRAM capacitors. Detailed studies are in progress in terms of understanding the time dependent dielectric breakdown and leakage current behavior.

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