$CaBi_2Ta_2O_9$ ferroelectric thin films prepared by pulsed laser deposition

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Thin films of $CaBi_2Ta_2O_9$ (CBT) were deposited on $Pt/TiO_2/SiO_2/Si$ substrates using the pulsed laser deposition technique at temperatures ranging from 500 to 700 °C. The presence of (115) and (00$\underline{10}$) orientations confirm the phase formation at the lower temperature (500 °C). Microstructure evolution of CBT films with oxygen pressure of 100–200 mTorr at a substrate temperature of 650 °C shows that the films deposited at lower pressure have a relatively smaller grain size and less surface roughness. The films grown at 650 °C exhibited a maximum polarization of ($2P_m$) 17 $\mu C/cm^2$, remanent polarization of ($2P_r$) 8 $\mu C/cm^2$ and coercive field of (E_c) 128 kV/cm, with fatigue endurance up to 10^{10} switching cycles. The higher dielectric constant (~115 at 100 kHz) with a relatively lower dissipation factor (0.02) at higher growth temperature (700 °C) was explained by the increased grain size. The higher leakage current density ($\sim 10^{-7}$ A/cm^2) at higher deposition temperature is attributed to the interfacial diffusion of the film and the substrate.

Ferroelectric thin films attracted sizable attention due to their applications such as memory devices, pyrosensors, etc. $Pb(Zr,Ti)O_3$ (PZT) had been the most studied compound belonging to a perovskite family. In spite of a significant number of studies evident in the literature, PZT has been hindered by its failure properties. This prompted a search for new compound ferroelectric thin films that had less propensity for fatigue and could be used for memory devices. The Bi-layered compounds were found to be commensurate with such expectation. The properties of ferroelectricity in Aurivillius layer compounds with general formula $(A_{n-1}B_nO_{3n+1})^{2-}(Bi_2O_2)^{2+}$, where A=Ba, Sr, Ca, Pb, and B=Ti, Ta, Nb was discovered by Smolenskii, Isupov, and Agranovskaya.[1] The lattice structure of this type of compound is composed of n number of $[(A_{n-1}B_nO_{3n+1})^{2-}]$ unit cells sandwiched between $(Bi_2O_2)^{2+}$ slabs.[2] Recently, some of these layered compounds, particularly $SrBi_2Ta_2O_9$ (SBT), are recognized as prime candidates for nonvolatile random access memory device,[3] due to relatively lower leakage current, lower operating voltage, faster switching, smaller coercive field, and negligible fatigue up to 10^{12} electric cycles in thin film form on platinum bottom electrode. It was reported that the substitution of A-site cation in $ABi_2Ta_2O_9$ layer compounds increases structural distortion. This, in turn, leads to significant enhancement of ferroelectric polarizability.[4] Considering this direction, the quest to formulate new compounds continues. Thin films of a large number of ferroelectric materials have been investigated for microelectronic devices.[5–7] These also include compounds of the Aurivillius family such as $BaBi_2Ta_2O_9$, $CaBi_2Ta_2O_9$ (CBT), $SrBi_2Nb_2O_9$, etc., in thin film form. Films of these kinds of layer compounds have good ferroelectric properties on the metal electrode such as platinum.

In most cases, pulsed laser deposition (PLD) can provide higher-quality oxide films at lower crystallization temperature than the other deposition techniques. The processing at lower deposition temperatures has the advantage of reducing the interfacial diffusion between the film and Pt substrate. There are a large number of reports on the processing of SBT thin films.[8–10] Recently Kato[11] *et al.* processed CBT films using the metalorganic method. In this report, we investigated the growth of polycrystalline CBT thin films on $Pt/TiO_2/SiO_2/Si$ substrates by PLD technique at relatively lower processing temperatures and studied the structural and electrical properties with different growth parameters such as substrate temperature and oxygen pressure during ablation.

Thin films of CBT have been deposited on $Pt/TiO_2/SiO_2/Si$ substrates using a 248 nm KrF excimer laser with a pulse repetition rate of 5 Hz and a fluence of 2.5–3.0 J/cm^2. The film growth rate was 0.75 nm/s. The distance between the target and substrate was maintained at 5 cm during deposition. A ceramic target of 3.5 cm diameter with 15% excess bismuth was prepared by conventional powder processing route. During deposition the substrate temperature (T_s) was varied from 500 to 700 °C with oxygen pressures at 100 and 200 mTorr to maintain better stoichiometry of the film. The phase formation and crystallographic strucutre was identified by using an x-ray diffractometer (Siemens D5000) with Cu $K\alpha$ radiation. The surface morphology of the as-deposited films was observed by atomic force microscopy (Nanoscope IIIa, Digital Instruments). Direct current sputtered circular gold dots ($\phi \approx 500$ μm) were used as the top electrode for electrical measurements. The dielectric behavior was characterized by measuring the frequency
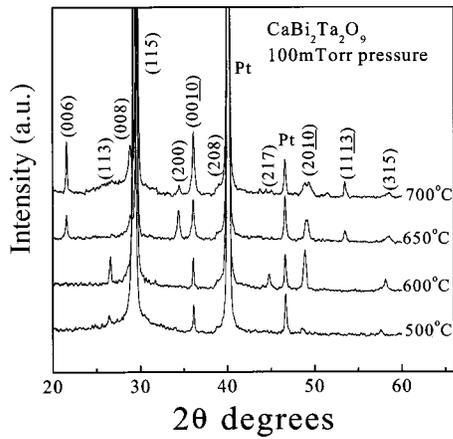
FIG. 1. X-ray diffractograms of as-grown CaBi$_2$Ta$_2$O$_9$ films at various substrate temperatures.

FIG. 3. Polarization-field hysteresis loop of CBT films deposited at different substrate temperatures.

dispersion characteristics of the capacitance and loss factor in a frequency range from 1 kHz to 1 MHz with an oscillating voltage of 100 mV by using an impedance analyzer (HP 4294A). The $P-E$ hysteresis loops and fatigue behavior were measured by using a Radiant tester RT 6000 HVS. Leakage current behavior was studied by a programmable electrometer (Keithley 6517A) interfaced to a computer with a voltage step of 0.2 V and delay time of 60 s.

X-ray diffraction (XRD) patterns of as-grown CBT films at 100 mTorr oxygen pressure and substrate temperature ranging between 500 and 700 °C are illustrated in Fig. 1. The presence of strong (115) and (00$\underline{10}$) peaks in the film deposited at 500 °C establishes the phase formation at lower temperatures. Preferential orientation along the c axis, confirmed by the strong diffraction lines (006), (008), and (00$\underline{10}$), increases with an increase in substrate temperature. With temperature, the systematic shift towards a higher diffraction angle of the most intense (115) reflection could be due to thermal stress during the growth of the films. As the substrate temperature was increased, the peaks in the XRD pattern became sharper and full width at half maximum decreased, which implies better crystallinity and an increase in crystallite size with increasing substrate temperature. The extra Bi in the target helps to reduce crystallization temperature and does not form any secondary phase.

The effect of oxygen partial pressure on the surface morphology of CBT films deposited at 650 °C, is shown in Fig. 2. Films at a pressure of 100 mTorr exhibited relatively lower grain size (43 nm) compared to that at 200 mTorr (81 nm). The surface roughness is also comparatively larger in the films deposited at 200 mTorr (5.61 nm) than those de-
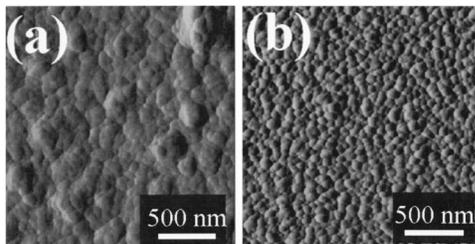
posited at 100 mTorr (2.4 nm). This behavior may be arising from the increased scattering of ablated species with increasing pressure and is found consistent with that reported for other materials. All the deposited films exhibited a relatively smooth surface and uniform grain size.

The $P-E$ hysteresis loops of as-grown CBT thin films were measured at an applied field of 310 kV/cm. Figure 3 shows the measured ferroelectric properties as a function of deposition temperature. Although hysteresis was observed at growth temperature of above 600 °C, the loops were poorly saturated. The values of remanent polarization ($2P_r$) and coercive field (E_c) were: 2.16, 8, 6.76 μC/cm^2 and 32, 128, 49 kV/cm for the films deposited at 600, 650, and 700 °C, respectively. The appearance of hysteresis loop clearly established that CBT in thin film form can retain its ferroelectric properties. The bulky hysteresis loop, with higher coercive field in comparison to SBT, might be due to higher electronegativity of Ca at A site. Such nonsaturation was also reported for sol-gel derived CBT thin films.[12] It is also worth mentioning that nonsaturation observed in the loop may be attributed to possible dc conduction mechanism. The fatigue characteristics of CBT films grown at 650 °C are shown in Fig. 4. The sample was fatigued by applying bipolar pulses (amplitude 7 V, width 1 μs) at 500 kHz. There is a minimal ($\leq$15%) degradation of remanent polarization observed after 10^{10} switching cycles making it competitive with other layer

FIG. 2. Atomic force microscopy micrographs of CBT films deposited at 650 °C with oxygen pressures (a) 100 and (b) 200 mTorr.
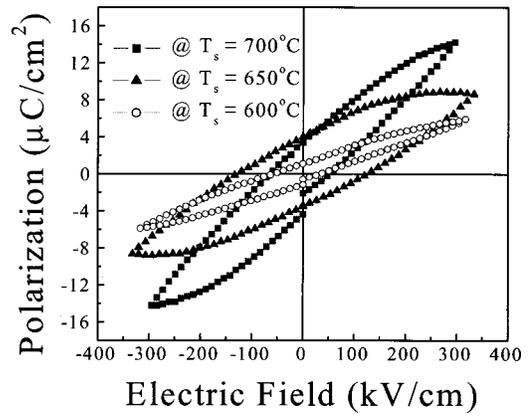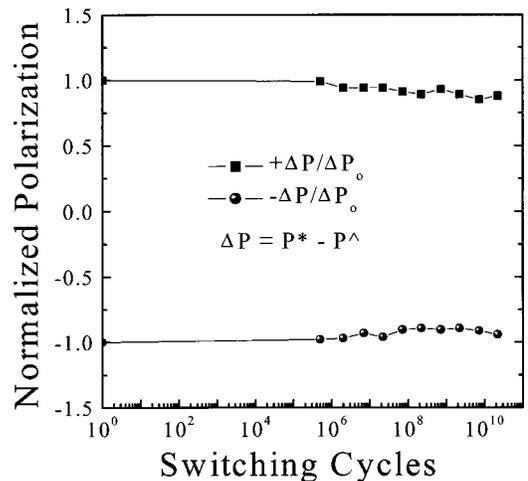

FIG. 4. Polarization fatigue characteristics of CBT films grown at 650 °C.
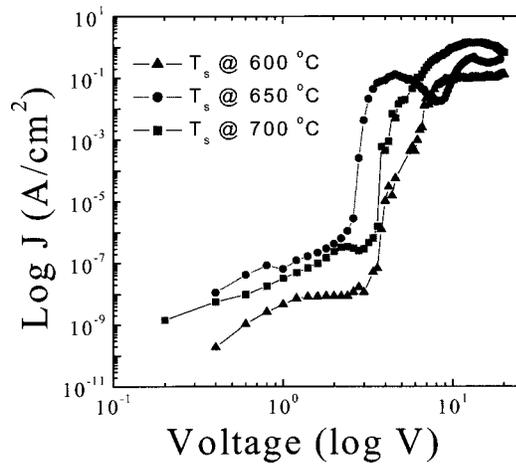
FIG. 5. Leakage current behavior of CBT films at different growth temperatures.

FIG. 6. Frequency dependence of dielectric constant and dissipation factor of CBT films grown at 650 and 700 °C.

compounds, currently being exploited for ferroelectric devices.

The current–voltage characteristics of the as-grown CBT films at various substrate temperatures are shown in Fig. 5. At a lower deposition temperature the leakage current density (J) remains low; in contrast, as the deposition temperature increases leakage current densities increase. Thus, the film deposited at 600 °C had leakage current density $\sim 10^{-9}$ A/cm^2 which is markedly lower than the films deposited at relatively higher growth temperatures at 650 and 700 °C ($\sim 10^{-7}$ A/cm^2). This behavior could be attributed to the interfacial diffusion of bismuth into the Pt electrode at higher growth temperature which leads to higher leakage current density. Irrespective of the deposition temperature, all the films exhibited typical space charge limited conduction characteristics, i.e., at lower applied voltage the current varies almost linearly with voltage whereas beyond the trap filled limited voltage, the current shoots up a couple of orders of magnitude.

Figure 6 shows the room temperature data of frequency dependent dielectric constants and dissipation factors of CBT films deposited at two different substrate temperatures. The data indicated negligible dispersion with frequency. The dielectric constant was estimated to be about 94 and 115 at 100 kHz for samples deposited at 650 and 750 °C, respectively. The higher dielectric constant at higher substrate temperatures might be due to the increased grain size of the material. However, the dissipation factor of CBT films deposited at 650 °C was observed to be relatively lower (~ 0.01) than that of 700 °C deposited film (~ 0.02). These results imply that higher substrate temperatures might lead to diffusion of bismuth into Pt electrode, and might contribute to the relatively higher dielectric loss. It is also worth mentioning that the oxidation state of the films deposited at 650 °C may be different from that of 700 °C. It was found consistent with that reported for the sol-gel derived CBT films.[11]
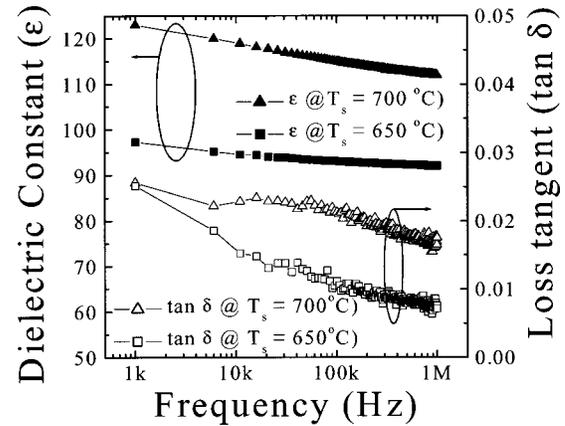
In summary, thin films of CBT were successfully grown on platinized Si substrates by pulsed laser deposition technique using a laser energy density of ~ 2.5 J/cm^2. Polycrystalline, single phase films of CBT were obtained at a relatively lower temperature in the range of 600 °C. The dense uniform grains are obtained at 200 mTorr oxygen pressure. The measured values of remanent polarization ($2P_r$) and coercive field (E_c) were: 2.16, 8, 6.76 μC/cm^2 and 32, 128, 49 kV/cm for the films deposited at 600, 650, and 700 °C, respectively. There is a minimal degradation ($\leqslant 15\%$) of remanent polarization up to 10^{10} switching cycles. Higher leakage current density ($\sim 10^{-7}$ A/cm^2) at higher growth temperature could be the contribution of interfacial diffusion of the film and the substrate. The higher dielectric constant (~ 115) with relatively lower dissipation factor ($\leqslant 2\%$) is attributed to the increased grain size at higher substrate temperature.

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