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Dielectric properties of pulsed-laser-deposited calcium titanate thin films

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We have deposited $CaTiO_3$ thin films on $SrRuO_3$ electrode layers on $SrTiO_3$ and $LaAlO_3$ substrates by pulsed laser deposition. The low-frequency dielectric properties were measured from 4 to 300 K. We found that the dielectric constants of 1-μm-thick $CaTiO_3$ films are very close to that observed in the bulk materials. The dielectric loss depends on the temperature and is on the order of 10^{-4} at low temperature. The dielectric constants of the films can be tuned by electric field by 6% at room temperature and 10% at 200 K. © *2000 American Institute of Physics.* [S0003-6951(00)01321-8]

Several ferroelectric materials, e.g., $(Ba,Sr)TiO_3$ (BST), and the incipient ferroelectric $SrTiO_3$ (STO) have been investigated for various electronics applications such as in dynamic random access memory (DRAM)[1] and in tunable microwave devices.[2,3] The high dielectric constant ϵ, low dielectric loss tan δ, and the dielectric nonlinearity, characterized by $[\epsilon(0)-\epsilon(E)]/\epsilon(0)$ are the materials parameters that enable such applications. However, although the bulk BST and STO show high dielectric constant, large tunability, and low loss, the thin films of these materials have shown inferior properties. While extensive research is being focused on improving the properties of BST and STO thin films,[4,5] it is desirable to investigate other ferroelectric and high-ϵ materials which could be better suited for these applications. Similar to STO, $CaTiO_3$ (CTO) is another incipient ferroelectric.[6] It has the same perovskite ABO_3 structure as STO and BST with the B cation being Ti and the A cation being Ca. In the bulk, the structure of CTO is cubic above 1580 K, tetragonal between 1500 and 1580 K, and orthorhombic below 1500 K.[7] To our knowledge, there are only a few reports on the properties of CTO films.[8,9] In this letter, we report results of high quality epitaxial CTO thin films on $LaAlO_3$ (LAO) and STO substrates. The low-frequency dielectric measurements show that the films exhibit similar dielectric constant and loss tangent values to those in bulk CTO, and their dielectric constant is tunable by electric field. The result suggests that CTO is a potential candidate for high-ϵ and tunable device applications.

The CTO films were grown by pulsed laser deposition. A $SrRuO_3$ (SRO) electrode layer was used between the CTO film and the substrate. The CTO/SRO bilayers were deposited *in situ* with substrate temperature of 750 °C, oxygen pressure of 100 mTorr, laser pulsed energy density of 1.4 J/cm^2, and deposition rate of 0.1 nm/pulse. The SRO electrode layer thickness was 350 nm, and CTO films of two thicknesses, 400 nm and 1 μm, are reported here. After the deposition, the bilayer films were cooled to room temperature in 500 Torr of O_2. A top Au electrode with a thickness of about 400 nm was thermally evaporated to form a parallel-plate capacitor structure for dielectric measurement. The structural properties of the films were characterized by x-ray diffraction (XRD). The dielectric constant and loss tangent were measured at 1 kHz using a Hewlett-Packard 4284A Precision *LCR* meter and/or a Keithley 3330 LCZ meter. Much attention was paid to the accuracy of the dielectric loss measurement, which has been discussed in detail in Ref. 10.

Figure 1 shows the XRD result for a 1 μm CTO/350 nm SRO bilayer film on STO (100) substrate. At room temperature, the lattice constants for the bulk orthorhombic CTO are $a=5.3888$ Å, $b=5.4393$ Å, and $c=7.6482$ Å.[7] In the θ–2θ scan of the CTO film in Fig. 1(a), except for a weak (111) peak from the SRO layer, only the (00*l*) peaks of the CTO are present along with those of the STO substrate and SRO buffer layers. This shows that the CTO film grows with *c*

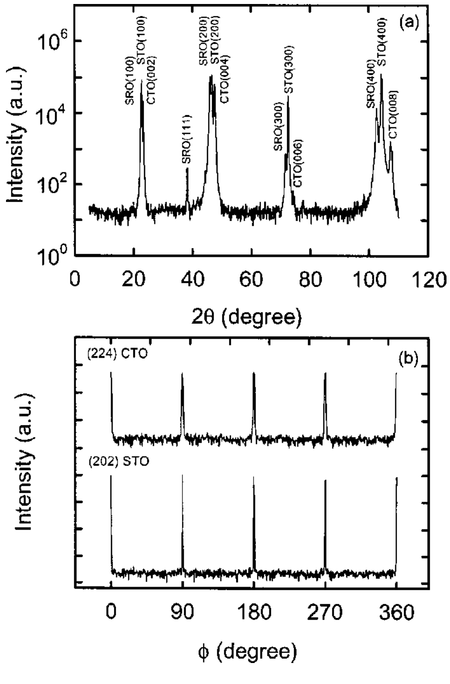

FIG. 1. X-ray diffraction of a 1 μm CTO film grown on SRO electrode layer on STO substrate: (a) the θ–2θ scan and (b) the ϕ scans using the (202) peaks for the STO substrate/SRO buffer layer and the (224) peak for the CTO film.

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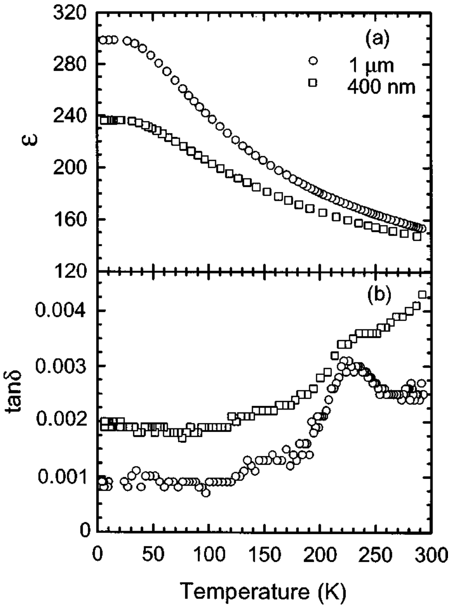

FIG. 2. Temperature dependence of (a) the dielectric constant ϵ and (b) the loss tangent tan δ, of a 1 μm and a 400 nm CTO films grown on SRO electrode layers on LAO substrates. The measurements were carried out in a parallel-plate capacitor geometry at 1 kHz.

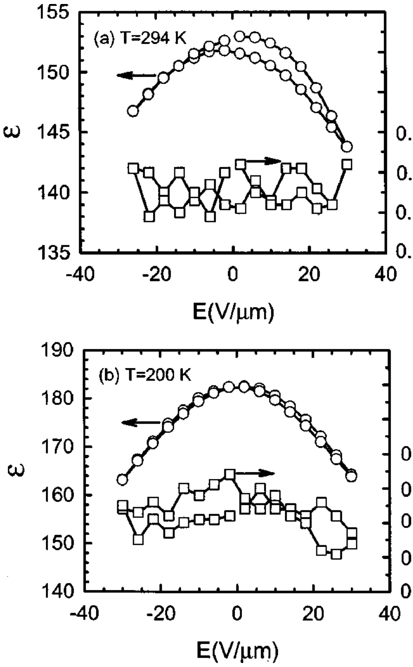

FIG. 3. The electric-field dependence of the dielectric constant and loss tangent for the 1 μm CTO film grown on SRO electrode layer on STO substrate at (a) room temperature and (b) $T = 200$ K.

axis normal to the substrate surface. The *c*-axis lattice constant of the CTO film is 7.649 Å, slightly higher than that of the bulk crystal. In Fig. 1(b), ϕ scans for the STO substrate/SRO buffer layer and the CTO film are shown. The (202) diffraction peaks for the substrate and buffer layer are used, which overlap each other. The (224) diffraction peak is used for the CTO film. Only four peaks, 90° apart, are observed for the CTO films, which are at the same angles with those of the substrate/buffer layer. This indicates that the CTO film is in-plane aligned with the substrate/buffer layer. Similar high quality epitaxial growth is also observed in the films on LAO substrate.

In Fig. 2, low-frequency dielectric constant and loss tangent are plotted as a function of temperature for (a) 1 μm and (b) 400 nm CTO films on LAO substrate. In the 1-μm-thick film ϵ is about 150 at room temperature and increases to 300 at low temperature as the temperature decreases. Unlike STO thin films where the low-temperature dielectric constant ($\sim 10^3$) is much lower than the bulk value (over 10^4) even in 2.5-μm-thick films, the ϵ of the 1 μm CTO film is very similar to those in bulk CTO.[6,11] The dielectric constant reported here is much higher than the previously reported CTO thin film values in the literature.[8] On the other hand, the loss tangent of the film is low. The maximum tan δ is about 3.3×10^{-3} at $T = 230$ K, and it decreases to $< 1 \times 10^{-3}$ below 110 K. These loss tangent values are also very similar to those found in CTO single crystal fibers measured at 100 kHz.[11] The origin of the loss peak around 230 K, which is not observed in bulk samples, is not clear. For the 400 nm CTO film, the dielectric constant is lower and loss tangent higher than in the 1 μm film. The ϵ increases from about 150 at room temperature to 240 at low temperature, and tan δ is about 4.5×10^{-3} at room temperature and decreases to $\sim 2 \times 10^{-3}$ at low temperature. No obvious peak is seen in the tan δ vs T curve. This reduction of ϵ in thinner films can be expected from the ''dead layer'' effect.[12,13] The existence of interfacial dead layers at one or both electrodes with low dielectric constant, treated as a capacitor series connected with the film bulk, can explain the thickness dependence of the dielectric constant and loss in ferroelectric thin films.

In STO thin films, even after the dead layer correction the dielectric constant for the volume of the film material is still well below the bulk value.[13] By measuring the soft-mode phonon frequency, we have found that this decrease is due to the soft-mode hardening in the STO films, consistent with the Lyddane–Sachs–Teller relation between the optical–phonon frequencies and dielectric constant.[14] This effect has very important implications for the potential of ferroelectric thin films in high-storage-density capacitor applications, such as in DRAM.[1] The dielectric constant of CTO is much smaller than in STO, especially at low temperatures, which indicates that the soft mode is harder in CTO than in STO. However, the result in Fig. 2 suggests that the soft mode in CTO will not become significantly harder when it is made in the thin film form. The thickness dependence of ϵ may result only from the dead layer effect without additional soft-mode hardening. This property could be explored for high-ϵ applications using CTO thin films: although the dielectric constant of the bulk CTO is lower than those of BST and STO, the reduction of ϵ as the film thickness decreases is also much weaker in CTO thin films.

The dielectric constants of the CTO thin films are tunable by electric field. Figure 3 shows the electric-field dependence of the dielectric constant and loss tangent for the 1 μm CTO film on STO substrate at two different temperatures. At $T = 294$ K, ϵ is suppressed by 6% when an electric field of 30 V/μm is applied. The loss tangent is around 3×10^{-3} and does not change much with the electric field. When the film is cooled to 200 K, the tuning increases to 10% for the same applied electric field, and the maximum tan δ remains about 3×10^{-3} although the zero field value decreases as the temperature decreases. Using the figure of merit for frequency and phase agile materials,

$$K = \frac{\epsilon(0) - \epsilon(E_{\mathrm{Max}})}{\epsilon(0)} \cdot \frac{1}{(\tan\delta)_{\mathrm{Max}}}, \tag{1}$$

where E_{Max} here is 30 V/μm and $(\tan\delta)_{\mathrm{Max}}$ is the maximum loss under all the applied fields, we obtain $K \approx 20$ at room temperature and 30 at 200 K. Although the K value is not extraordinarily large compared to that in STO and BST, the low ϵ value of CTO is attractive for microwave-frequency applications. This provides an additional possibility in balancing K and ϵ through materials engineering for optimum device performances.

In summary, high quality epitaxial CTO thin films have been grown by pulsed laser deposition. The low-frequency dielectric properties in the 1μm film are found to be close to those in CTO bulk materials. This could be important for using CTO thin films in high-ϵ applications. The dielectric constant of the films is tunable by electric field and the loss is low, making CTO a potential candidate for tunable device applications.

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