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Electric and dielectric behavior of $CaCu_3Ti_4O_{12}$-based thin films obtained by soft chemical method

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ABSTRACT

$CaCu_3Ti_4O_{12}$ (stoichiometric) and $Ca_{1.1}Cu_{2.9}Ti_4O_{12}$ (non-stoichiometric) thin films have been prepared by the soft chemical method on $Pt/Ti/SiO_2/Si$ substrates, and their electrical and dielectric properties have been compared as a function of the annealing temperature. The crystalline structure and the surface morphology of the films were markedly affected by the annealing temperature and excess calcium. The films show frequency-independent dielectric properties at room temperature which is similar to those properties obtained in single-crystal or epitaxial thin films. The room temperature dielectric constant of the 570-nm-thick CCTO thin films annealed at 600 °C at 10 kHz was found to be 124. The best non-ohmic behavior ($\alpha = 12.6$) presented by the film with excess calcium annealed at 500 °C. Resistive hysteresis on the *I–V* curves was observed which indicates these films can be used in resistance random access memory (ReRAM).

1. Introduction

Strong demands for miniaturization of electronic devices and the elimination of lead-based compounds have focused much attention on the so-called high-*k* materials due to their applications as capacitor and memory devices. Among several materials nonferroelectric lead-free compounds such as $Cu_2Ta_4O_{12}$, $AFe_{1/2}B_{1/2}O_3$ (A = Ba, Sr, Ca; B = Nb, Ta, Sb), $CaCu_3Ti_4O_{12}$ (CCTO) have attracted considerable attention due to their electric and dielectric properties [1]. The high dielectric permittivity (10^4–10^5) is constant in the temperature range of 100–600 K and for frequencies up to 10^6 Hz. Furthermore, structural studies show that the CCTO maintains a cubic structure for all temperatures without phase transitions. Neutron powder diffraction and high-resolution X-ray diffraction (XRD) [2] have shown that there is no evidence of any lattice distortion in CCTO from 100 K to 600 K which is very desirable for practical electronic application.

To apply CCTO in microelectronic devices and to give a more fundamental understanding of its physical properties, some groups have grown high-quality epitaxial CCTO films [3,4]. Several studies have shown that CCTO has optical [2], photoluminescence [5] and sensor [6] properties and two resistance states (high and low), which enable their potential use in resistance random access memory (ReRAM) [7]. Films have an advantage over bulk materials for future application in microelectronics and several attempts have been made to grow CCTO thin films on various substrates [3,4]. Most research has been reported on the preparation of CCTO thin films based on physical deposition techniques such as pulsed-laser deposition (PLD) [8,9]. Several researchers have reported the use of chemical solution deposition methods (CSD) for thin film preparation [10]. Among various methods used to prepare thin films the soft chemical "polymeric precursor method" has advantages over other production techniques such as its low cost, good compositional homogeneity, relatively low processing temperatures and the ability to coat large substrate areas [11]. This method has been used to prepare different types of materials, such as $BaTiO_3$ and PZT, among others [12].

In this paper, we report the growth and electrical and dielectric characterization of CCTO thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrates by a polymeric precursor method. The effects of annealing temperature and excess calcium on the morphology and electrical and dielectric properties of CCTO thin films have been studied.

2. Experimental procedure

Thin films were synthesized by the polymeric precursor method (PPM). Calcium carbonate ($CaCO_3$, Aldrich, 99.999%), titanium(IV) isopropoxide ($C_{12}H_{28}O_4Ti$, Aldrich, 99.999%), copper(II) carbonate basic ($CuCO_3{\cdot}Cu{\cdot}(OH)_2$, Aldrich, 99.99%), ethylene glycol (99% purity, J.T. Baker) and anhydrous citric acid (99.5% purity, J.T. Baker) were used as starting materials. Titanium(IV) isopropoxide citrate was diluted in aqueous solutions of citric acid under constant stirring at 50 °C. Then the calcium and copper precursors were added to the solution, respectively, and the

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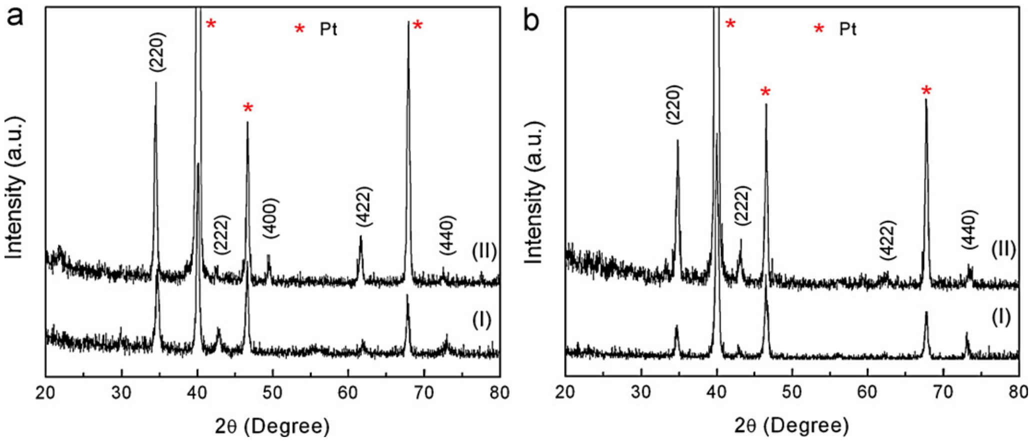

Fig. 1. X-ray diffraction data for CCTO (a) stoichiometric and (b) non-stoichiometric CCTO thin films deposited by the soft chemical method at (I) 500 °C and (II) 600 °C for 2 h in ambient atmosphere.

citrate solution was stirred at 95 °C to obtain a clear and homogenous solution. After homogenization, ethylene glycol was added to promote the citrate polymerization. The metal/citric acid/ethylene glycol ratio was fixed at 1:4:16. The viscosity of the resulting solution was adjusted to 20 cp by controlling the water content using a Brookfield viscosimeter. More details of the precursor method have been described in detail elsewhere [13]. The solution layer was deposited on $Pt(1\,1\,1)/Ti/SiO_2/Si$ substrates by spinning the deposition solution at 5000 rpm for 30 s. The films were heat-treated at 350 °C for 4 h in a conventional oven to remove organic material and then annealed at 500 °C and 600 °C for 2 h in an ambient atmosphere. This procedure was performed layer by layer ten times. To study the influence of excess calcium in the CCTO thin films, two compositions were prepared: $CaCu_3Ti_4O_{12}$ (stoichiometric) and $Ca_{1.1}Cu_{2.9}Ti_4O_{12}$ (non-stoichiometric).

CCTO films were characterized by X-ray diffraction (XRD, Rigaku, Model Rint 2000) at 40 kV and 150 mA from $2\theta^\circ$ (20–80) following the phase evolution. The

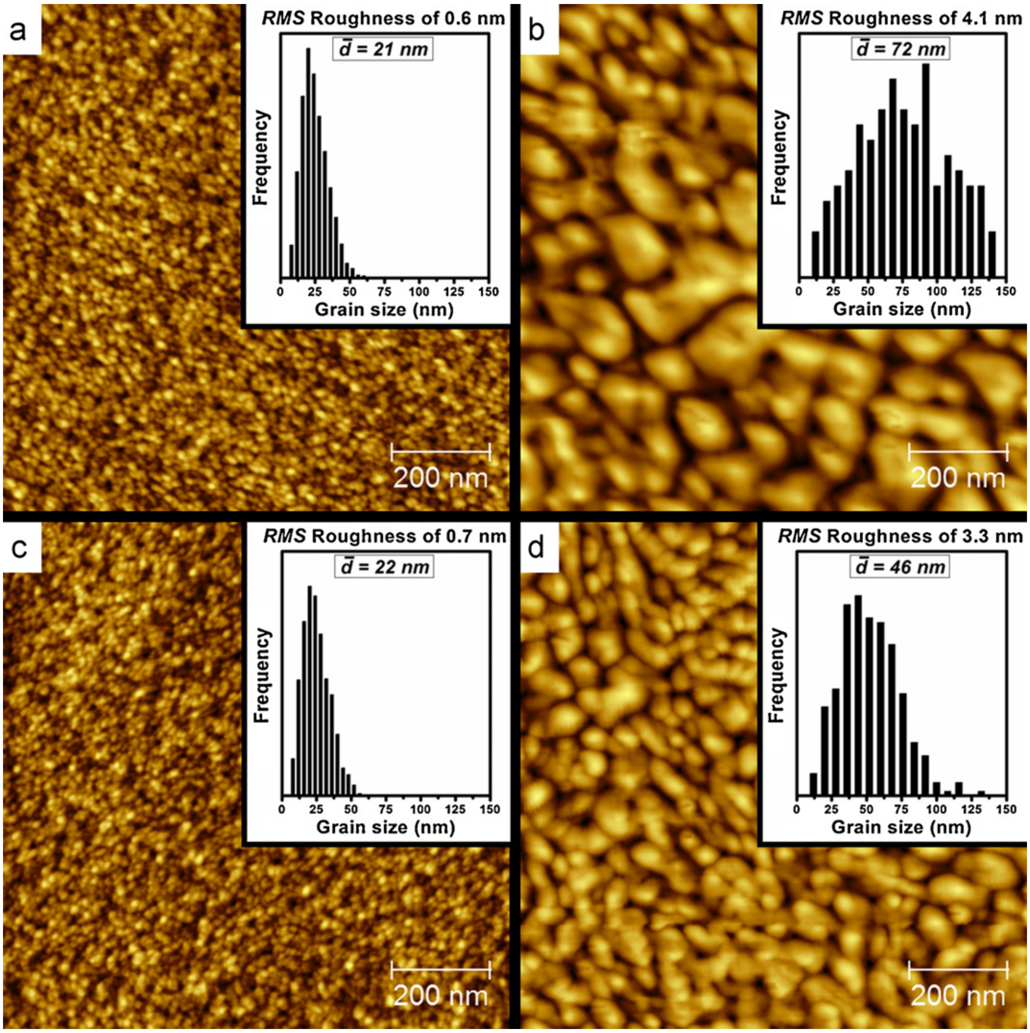

Fig. 2. Atomic Force Microscopy for (a and b) stoichiometric and (c and d) non-stoichiometric CCTO thin films.

Table 1
Morphological and electrical properties of CCTO thin films annealed at different temperatures.

	Stoichiometric		Non-stoichiometric	
	500 °C	600 °C	500 °C	600 °C
Average grain size (nm)	21	72	22	46
Average roughness (nm)	0.6	4.1	0.7	3.3
Average thickness (nm)	500	570	490	570
Non-linear coefficient	6.3	2.5	12.6	3.0
Dielectric permittivity (10 kHz)	65	124	35	92
Dielectric Loss (10 kHz)	0.2	0.18	0.15	0.1

thickness of the annealed films was analyzed using a field emission gun scanning electron microscope (FEG-SEM, JEOL, Model 7500F) (images not shown here). Atomic Force Microscopy technique was used to analyze the surface of the films (AFM, Digital Instruments, Model NanoScope IIIa). Top Au electrodes (300 μm) were prepared by sputtering through a shadow mask at room temperature and acquiring a metal–semiconductor–metal (MSM) capacitor configuration for electrical and dielectric measurements. The current–voltage characteristic was determined with a pick amperimeter (*Keithley 6430*) with a 10 μA as the current compliance (it is used here to prevent permanent damage to the films). Dielectric permittivity (ε_r) and the dissipation factor ($\tan\delta$) were obtained by impedance spectroscopy measurements in the frequency range from 100 Hz to 2 MHz by employing a frequency response analyzer (HP, Model 4192A). All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of stoichiometric and non-stoichiometric CCTO thin films deposited on Pt/Ti/SiO$_2$/Si substrates and annealed at 500 °C and 600 °C for 2 h. The formation of CaCu$_3$Ti$_4$O$_{12}$ cubic phase belonging to the *Im*-3 space group (JCPDS 70-367) is apparent. The characteristic peaks of the Pt substrate can also be observed in these patterns. In stoichiometric CCTO films annealed at 600 °C, the presence of the (4 0 0) peak is noticeable. However, this peak is absent in stoichiometric CCTO films annealed at 500 °C which can be related to the crystallinity improvement of the film due to the increased annealing temperature. On the other hand, the (4 0 0) peak is not observable in the non-stoichiometric CCTO thin film at both annealing temperatures which indicates that in non-stoichiometric CCTO films, the slight variation in the Ca/Cu ratio can influence the crystallinity of this phase due to increased strain in the film caused by excess calcium [14–16].

The surface morphology of stoichiometric and non-stoichiometric CCTO thin films performed by AFM measurements is shown in Fig. 2. The average grain size and surface roughness of thin films were estimated using Gwyddion Free Software. The surface morphology was obtained using an area of 1 μm × 1 μm. Stoichiometric and non-stoichiometric CCTO thin films show a dependence of average grain size and roughness with the annealing temperature. In both systems the grain size and roughness increase when the temperature increases. Furthermore, the variation in the average grain size and roughness for non-stoichiometric films annealed at 600 °C is lower than for stoichiometric films annealed at the same temperature. The significant reduction of grain growth in non-stoichiometric CCTO thin films can be related to excess calcium due to increased strain in the film. Table 1 presents the average grain size, roughness and thickness for stoichiometric and non-stoichiometric CCTO thin film.

Fig. 3 depicts the *I*–*V* curves of stoichiometric and non-stoichiometric films. The non-linear coefficient increase in non-stoichiometric samples is an important consideration for varistors and memory device applications. It can be seen that there are two clearly different regions: an insulating region essentially controlled by potential barriers located at grain boundaries and a region within grains. It is also proposed that the transport of charge inside grains has a linear *I*–*V* relationship. As shown in Fig. 2, CCTO-based films annealed at 600 °C exhibit a larger grain size which suggests a larger contribution from intra-grain transport. Another region which is essentially conductive and driving can be explained by means of conductive paths. When established within the grain boundaries, conduction paths, charge the *I*–*V* relationship from linearity to non-linearity. When the conduction paths are ruptured, the barriers formed by grain boundaries are recovered, and the *I*–*V* relationship return to non-linearity. At higher field strengths the current density increases exponentially which implies that at least one part of the conductivity results from the Schottky emission mechanism. The larger non-coefficient values in both films annealed at 500 °C can be attributed to the small grain size (see AFM in Fig. 3). The non-linear coefficients of films are shown in the Table 1. Chung et al. [17] have demonstrated that the presences of potential barriers at CCTO in the region of grain boundaries are Schottky-type barriers. Non-stoichiometric films have a non-linear coefficient larger than found in the CCTO stoichiometric film annealed at the same temperature which may be related to lower grain size in non-stoichiometric films due to excess calcium.

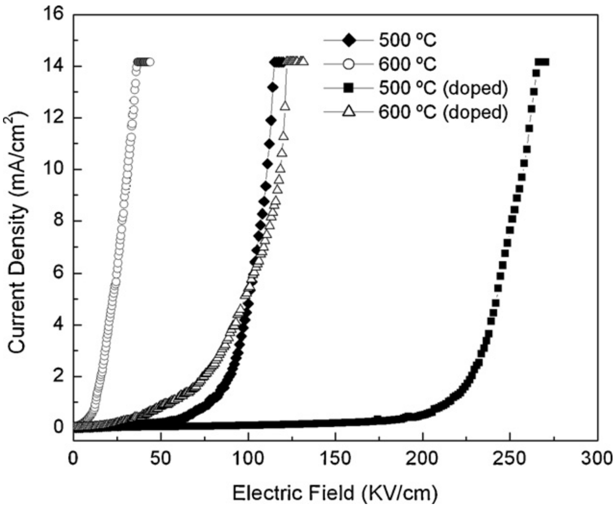

Fig. 3. Current density versus electric field for stoichiometric and non-stoichiometric CCTO thin films.

Current–voltage characteristics of the stoichiometric and non-stoichiometric samples were performed at room temperature with the voltage sweep from $-V_{\text{máx}}$ to 0 to $+V_{\text{máx}}$ to 0 to $-V_{\text{máx}}$ and a current compliance limited to 10 μA in the measurement unit (see Fig. 4). Hysteresis curves observed in these plots are usually related to resistive switching effects commonly observed in heterostructured ferroelectric thin films [18]. This switching mechanism as a function of polarity is a CCTO intrinsic effect and may be related to intrinsic dipole formation in the CCTO due to intra-granular defects [19] and/or to trapped state relaxation [20]. It is observed that stoichiometric films have a larger decrease in this effect with an increase in the annealing temperature while the non-stoichiometric films maintain this effect which can be occurring due to excess calcium inhibiting grain growth.

Fig. 5 shows the variation of dielectric permittivity and dielectric loss as a function of frequency for the CCTO-based film. The dielectric permittivity for a stoichiometric CCTO film annealed at 600 °C was 124 at 10 kHz. The large dielectric permittivity of CCTO has been interpreted as an extrinsic mechanism which was assumed to come from the sample microstructure such as grain boundary (IBLC model) or interface effects [21]. In recent studies we have reported that the giant dielectric constant in the CCTO is a consequence of the formation of a nanoscale barrier layer capacitor [19]. Based on this model, we conclude that thin films have lower dielectric permittivity due to a lower concentration of defects when compared with crystals or ceramics. The reduced dimensions and

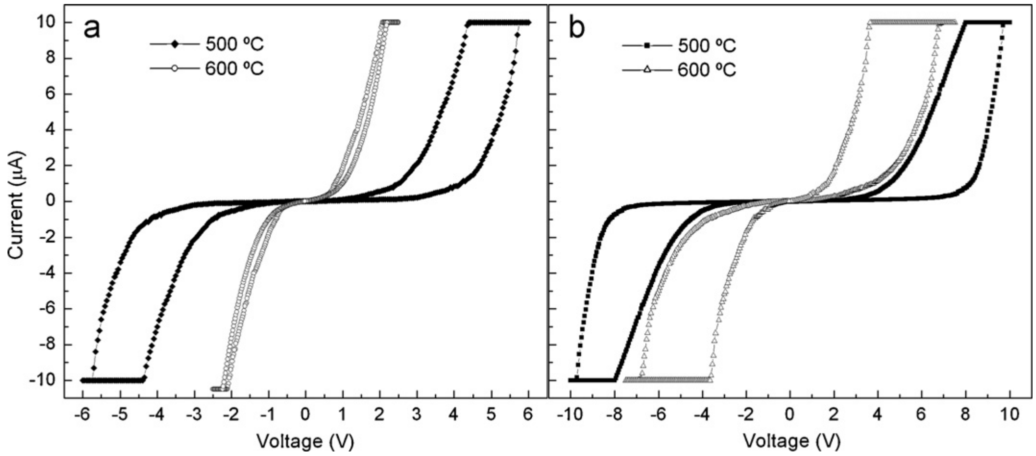

Fig. 4. *I–V* hysteresis curve for (a) stoichiometric and (b) non-stoichiometric CCTO thin films.

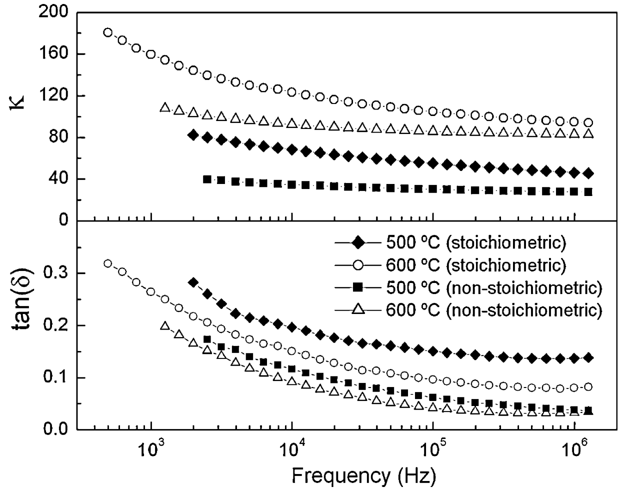

Fig. 5. Dielectric permittivity and dielectric loss for (a) stoichiometric and (b) non-stoichiometric CCTO thin films.

low annealing temperature of CCTO thin films may not have favored the formation of planar defects which suppress the dielectric properties. Finally, the dielectric loss in the thin film is actually lower than in the ceramics which may be as indication that ceramics have more defects than the thin films because the dielectric permittivity in thin film (∼124) is much lower than in crystals ($\geq 10^5$) (see Table 1). As can be seen from Fig. 5, the dispersion of dielectric permittivity by frequency is low which indicates that films possess low defect concentrations at the interface film-substrate. The low dispersion of the dielectric permittivity and the absence of any relaxation peak in tan δ indicate that Maxwell–Wagner relaxations and interfacial polarizations in the film/electrode may be negligible in the film. Non-stoichiometric CCTO thin films have a lower dielectric permittivity than stoichiometric films which are according with observed to non-stoichiometric CCTO ceramics [16].

4. Conclusions

Polycrystalline stoichiometric and non-stoichiometric CCTO thin films were prepared by the soft chemical method. XRD studies revealed the polycrystalline nature of the film belonging to the *Im*-3 space group. The film exhibited homogeneous morphology with grain size in the range of 20–70 nm. The stoichiometric CCTO film annealed at 600 °C has a dielectric constant of 124 at 10 kHz. The best non-ohmic behavior was a non-stoichiometric sample annealed at 500 °C ($\alpha = 12.6$). Resistive switching also was observed in this films which is an intrinsic effect of the material. These interesting results suggest the possibility of the manufacture of ReRAM based on CCTO thin films.

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