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Preparation of $CaCu_3Ti_4O_{12}$ thin films by chemical solution deposition

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Recently, considerable attention has been given to the perovskite-like compound $CaCu_3Ti_4O_{12}$ (CCTO) exhibiting a high dielectric constant value of ~10 000 over a wide temperature range from 100 to 400 K [1–3]. The dielectric properties make CCTO a desirable material for microelectric applications such as static and dynamic random access memories, high dielectric capacitors, and thin film devices. Ordinarily, dielectric constants higher than 1000 are related to ferroelectric or relaxor properties. However, this material exhibits no crystallographic structural phase transition, associated with spontaneous polarization, by high-resolution X-ray [2] and neutron powder diffraction [1]. The origin of giant static dielectric constant is not fully understood, though explanations in terms of atomic structure [1], microstructure [1, 3–5], and extrinsic interface structure [6] have been proposed. To investigate the nature of the novel properties and to realize the application of CCTO, it is necessary to further conduct various experiments, for example doping in different lattice sites, fabrication of thin films, and so on.

CCTO thin films have been prepared by pulsed laser deposition and the investigations showed that the films had the same unusual properties as bulk and single crystals [7–9]. In this paper, we report the preparation of the films by a chemical solution deposition (CSD) method. The CSD method has proven to be a promising technique for fabricating oxide thin films. In general, the CSD technique has the advantages of good homogeneity, precise composition control, simple operation, and low cost without using high vacuum.

The CCTO thin films were fabricated by the CSD method in the following way. The starting materials were the toluene solution of calcium and copper naphthenates, and tetrabutyl titanate with A.R. purity. They were first weighed and mixed stoichiometrically based on the chemical formula $CaCu_3Ti_4O_{12}$ and then diluted with toluene in a ratio of 1:1, obtaining the so-called CCTO precursor solution. The thermal decomposition behavior of the precursor solution was investigated by thermal analysis to determine the appropriate temperature of pyrolysis. The mixed solution was spin-coated at a speed of 2000 rpm for 10 s onto the $LaAlO_3$ (001) substrates. Then the coated films were directly put into a tubular furnace pre-heated to 500 °C holding for 15 min. This procedure of coating and pyrolysis was repeated two or three times so as to obtain the desired films of approximately 100-nm thickness. Finally, the sample was fired at 790 °C for 2 hr and then furnace-cooled to room temperature. All the preparations were preformed in air.

The thermogravimetric and differential thermal analysis (TG–DTA) were carried out from room temperature to 1000 °C at a heating rate of 15 °C/min on a WCT-2 Thermal Analyzer made by Beijing Optical Equipment Company. X-ray diffraction (XRD) was performed on a Philips X'Pert X-ray diffractometer using Cu K_α radiations. Samples' surface morphology was examined by an atomic force microscope (AFM-II) made by Zhejiang University.

The TG–DTA curves of the CCTO precursor solution are shown in Fig. 1. Three steps of weight loss were observed in the TG curve. The weight loss around 80 °C corresponds to the evaporation of the organic solvent toluene. The others were due to the decomposition of copper naphthenate, calcium naphthenate, and tetrabutyl titanate. A large exothermic peak observed at about 480 °C in the DTA curve was caused by the combustion of the organic compounds. Therefore, it is necessary to increase the temperature very rapidly to about 500 °C in the pyrolysis process, in order to obtain homogenous noncrystalline or microcrystalline thin films. As for the sintering condition, we found that 790 °C was an optimal temperature at which smooth CCTO thin films can be obtained.

Fig. 2 shows the patterns of XRD θ–2θ scan for the CCTO thin films grown on the $LaAlO_3$ (001) substrate. Accompanied with the very strong (00*l*) peaks of $LaAlO_3$ substrate, strong sharp reflections can be identified as (002), (004), and (006) diffractions for the

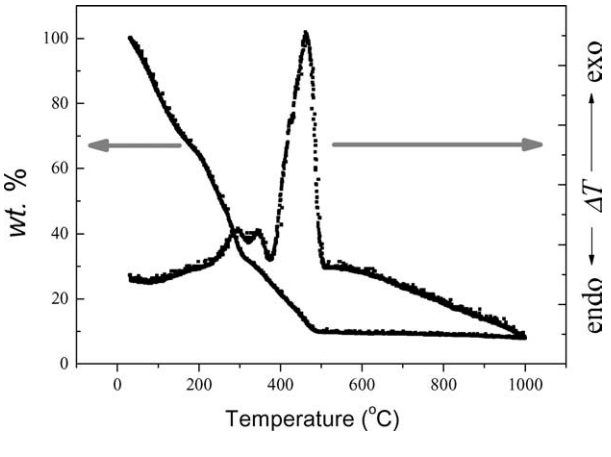

Figure 1 TG–DTA curves of CCTO precursor solution, a stoichiometric mixture of copper and calcium naphthenates, and tetrabutyl titanate with toluene as solvent.

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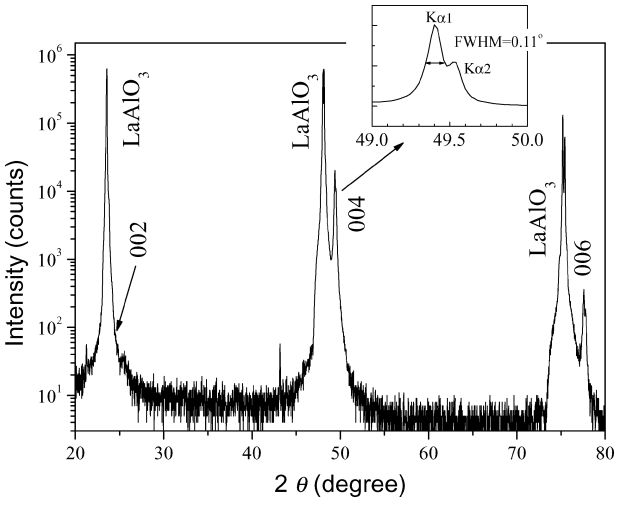

Figure 2 XRD patterns of as-prepared $CaCu_3Ti_4O_{12}$ thin films on the (001) $LaAlO_3$ substrates by chemical solution deposition. Note that logarithm scale is applied for the intensity axis. The inset gives an expanded plot for the (004) reflection.

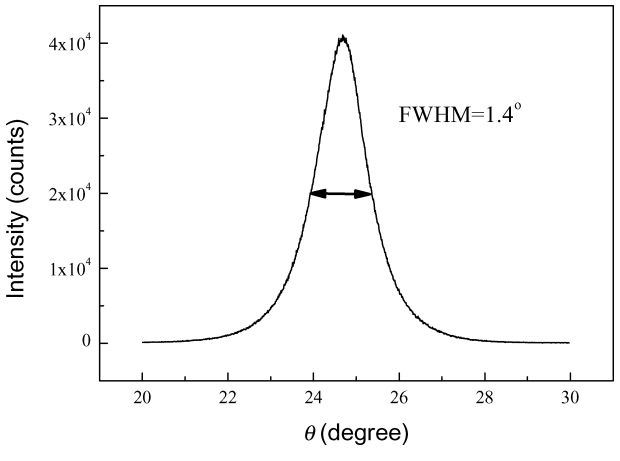

Figure 3 XRD rocking curve (θ-scan) of the (004) reflection of the $CaCu_3Ti_4O_{12}$ thin films.

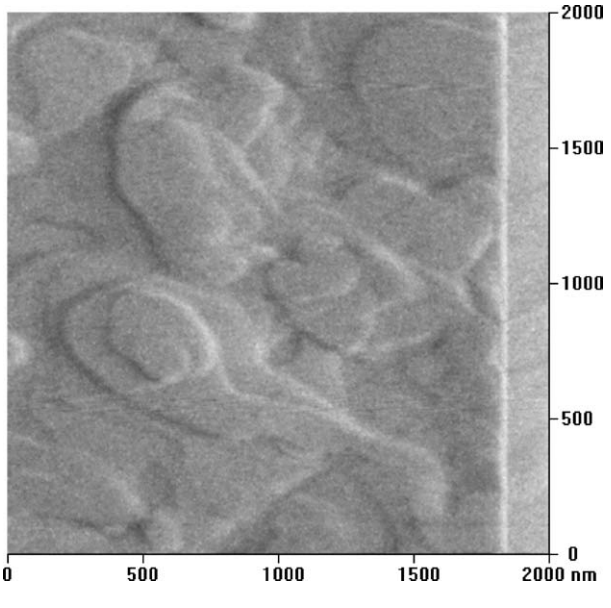

Figure 4 Typical AFM image of the surface of $CaCu_3Ti_4O_{12}$ thin films. The average roughness was measured as $R_a = 1$ nm.

cubic CCTO phase at $2\theta = 24.15°$, 49.40°, and 77.58°, respectively. The lattice parameter is then calculated as $c = 0.738$ nm, consistent with the previous reports [1, 2]. The full width at half maximum (FWHM) for the peaks is only 0.11°, comparable to that of the single crystal substrate. These observations indicate that the films grow epitaxially on the $LaAlO_3$ (001) substrate. The rocking curve (θ-scan) of the (004) reflection of the CCTO thin films is shown in Fig. 3. The peak is symmetrical and the FWHM value is about 1.4°, suggesting well crystallizations for the epitaxial thin films.

The surface morphology of the films was investigated by AFM over an area of 2 μm × 2 μm. Fig. 4 shows the typical image. It is seen that the film is in single-crystal form, confirming the above XRD result. In addition, helical growth steps can be clearly seen, suggesting that the growth belongs to the two-dimensional mechanism. The average roughness is 1 nm, suggesting that the Burgers vector for the helical dislocation is ∼10 Å, nearly identical to the cell parameter of CCTO. Nevertheless, more experiments are needed to clarify the mechanism of the solid-state epitaxy.

In conclusion, $CaCu_3Ti_4O_{12}$ thin films have been successfully prepared on $LaAlO_3$ (001) substrates by chemical solution deposition, using calcium and copper naphthenates and tetrabutyl titanate as starting materials. X-ray diffraction and atomic force microscopy measurements show that the films grow epitaxially along the *c*-axis of $LaAlO_3$ single crystal substrates. Our preliminary dielectric measurements confirmed high dielectric constant for this material. Details of the dielectric properties will appear elsewhere.

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