Preparation of high dielectric constant thin films of CaCu$_3$Ti$_4$O$_{12}$ by sol–gel

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Abstract. Preparation of sol–gel derived CaCu$_3$Ti$_4$O$_{12}$ (CCTO) thin films using two different sols and their characterization including their dielectric response are reported. The properties of CCTO films depend heavily on solvents used to prepare the sols. Dielectric constant as high as ~900 at 100 kHz could be obtained when acetic acid was used to prepare the sol; in contrast, use of hexanoic acid in the sol yielded films with a much lower dielectric constant. The variation in grain and grain boundary conductivities with temperature has been measured. Activation energies of 0.08 eV and 0.68 eV have been found for grain and grain boundary conduction, respectively.

Keywords. Sol–gel preparation; thin film; electrical properties.

1. Introduction

High dielectric constant ceramics are of interest for use in electronic circuits, microwave devices and other applications. The ceramic, CaCu$_3$Ti$_4$O$_{12}$ (CCTO), is at present of considerable research interest because of its high dielectric constant (~$10^5$) which is independent of temperature and frequency over a wide range near room temperature. CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has a perovskite-related structure (general formula, ABO$_3$) in which Ca$^{2+}$ and Cu$^{2+}$ share the A-site (Deschanvres et al 1967; Bochu et al 1979; Subramanian et al 2000). The size difference between Ca$^{2+}$ and Cu$^{2+}$ causes the TiO$_6$ octahedra to undergo substantial tilting, leading to a body centred cubic supercell of space group Im3 in which the Ti$^{4+}$ ions occupy centrosymmetric position in the octahedral sites. The angle of tilt is sufficiently large that the Cu$^{2+}$ ions occupy an essentially square-planer environment (Adams et al 2006). High dielectric constant, as shown by CCTO, is usually found in ferroelectric materials; however, no evidence of a phase transition (paraelectric to ferroelectric) in CCTO has so far been found.

The most widely accepted mechanism for the high dielectric constant in CCTO is a grain boundary layer capacitor model invoking semiconducting grains and insulating grain boundaries. Several models have been proposed to explain the difference in the conductivity between the grains and the grain boundaries (Li et al 2004, 2006; Zhang and Tang 2004; Fang et al 2006; Fang and Mei 2007). Zhang and Tang (2004) found evidence for the existence of Ti$^{3+}$ as well as Ti$^{4+}$ ions in CCTO and attributed the high grain conductivity to polaron transport along Ti$^{3+}$–O–Ti$^{4+}$ linked path. The observed segregation of Cu ions to grain boundaries led Fang et al (2006) and Fang and Mei (2007) to suggest that Cu ions act as acceptors and increase the grain boundary resistivity while the electron hopping between Cu$^{3+}$ and Cu$^{2+}$ is thought to be the origin of the high conductivity of grains.

Considerable amount of work has been done on bulk CCTO ceramics (Subramanian et al 2000; Adams et al 2006; Fang et al 2006; Fang and Mei 2007; Prakash and Varma 2007). However, the reported studies on thin films of CCTO, especially those prepared by chemical solution methods, are scarce (Lu et al 2004; Feng et al 2006; Jimenez et al 2007). Lu et al (2004) deposited CCTO films on LaAlO$_3$ substrates using a sol prepared from titania butoxide and naphthenates of Ca and Cu in toluene solution. A single crystal film was obtained. The same group (Feng et al 2006) also reported the deposition of CCTO films on SrTiO$_3$ substrates. They did not report any dielectric measurements on their films. Recently, Jimenez et al (2007) used a titanium diol based sol to deposit CCTO films on platinum coated Si substrates. They reported a dielectric constant of 280 at 100 kHz, which is nearly constant between 150 K and 300 K. This is much lower than that reported for CCTO ceramics (Subramanian et al 2000). The dielectric properties of sol–gel prepared thin films are known to be very sensitive to the constitution of the sol. In the present work, we report the preparation of CCTO thin films by a sol–gel method using two different sols. It is seen that quite high dielectric constant can be obtained by using acetic acid as the solvent for the precursors.
2. Experimental

Two different sols were prepared for the deposition of CCTO films. To prepare sol-1, titanium butoxide \( [\text{Ti(OCH}_3\text{H}_9\text{)}_4] \), 97\% was mixed with acetic acid and stirred for 30 min inside a glove box with controlled humidity. Calculated amounts of precursors (calcium acetate, \( \text{Ca(OOCCH}_3\text{)}_2\cdot\text{H}_2\text{O}, 99\% \) and monohydrated copper acetate, \( \text{Cu(OOCCH}_3\text{)}_2\cdot\text{H}_2\text{O}, 99\% \)) were mixed with 15 ml of acetic acid and 15 ml of ethanol and stirred for 30 min. Both the above solutions were then mixed and to this about 10 ml of 2-methoxy ethanol was added. This solution was stirred at 100°C on a hot plate for 30 min and then cooled to room temperature. To this 10 ml of diethanolamine (DEA) was added and the solution was again stirred for 30 min. A light blue transparent sol was obtained.

Sol-2 was prepared by dissolving titanium butoxide in 2-ethyl hexanoic acid. The calculated stoichiometric amounts of monohydrated calcium acetate and monohydrated copper acetate were then mixed into the solution at room temperature. The solution was refluxed at 120°C for 30 min.

The sols as prepared above were filtered through a 0.2 \( \mu \text{m} \) syringe filter and were used for film preparation by spin coating at 5000 rpm for 30 s on (111) oriented Pt/Ti/SiO\(_2\)/Si substrates. After each coating, the films were fired at 500°C for 5 min followed by annealing at 750°C for 10 min. The final annealing was performed at 750°C for 2 h. The thickness of the films was measured by a profilometer (Tencor Instruments Alfa-step 500).

To measure the electrical properties, circular Pt electrodes of 0.2 mm diameter were deposited on these films through a shadow mask by d.c. magnetron sputtering. All the dielectric properties were studied in metal–insulator–metal configuration using an impedance analyser (HP 4192 A).

3. Results and discussion

Figure 1 shows X-ray diffractograms of the CCTO films prepared using the two sols. In both cases, the perovskite phase formation occurred as revealed by comparing with standard X-ray data [JCPDF File No. 21-0140]. The films have no preferred orientation, though the (220) line is the strongest of all.

Figure 2 shows the dielectric constant and loss for the two types of films. The films prepared using sol-1 show a high dielectric constant (~900 at 100 kHz). This is much higher than the dielectric constant of chemical solution deposited thin film reported earlier (Jimenez et al 2007). The dielectric constant of the films prepared using sol-2 was much lower (350 at 100 kHz) although they had a lower dielectric loss (figure 2). As the thickness of the films in the two cases was nearly the same (~500 nm), these differences can be attributed to the microstructures of the films (Ni et al 2006). The porosity and fine details of the microstructure in the sol–gel films depend in a complex way upon the relative rates of drying and gelation and the ease of removal of the organics (Brinker and Scherrer 1990). The microstructures of the two films are shown in figures 3(a) and (b), respectively. From the SEM micrographs, the grain size distributions of the two films were determined. This is shown in figure 4. The distribution in case of sol-2 is much wider, with there being significant number of grains, > 500 nm. Moreover, this film (sol-2) has a considerable number of large pores with size extending up to ~ 260 nm whereas the film from sol-1 has much less porosity and the pores are also smaller. The difference in the electrical properties of the two films can be attributed to these differences in grain size distribution and porosity (Adams et al 2006). The films prepared us-