

Chemical solution deposition of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin film

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MS received 24 November 2008; revised 25 January 2010

Abstract. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) thin film was successfully deposited on boron doped silica substrate by chemical solution deposition and rapid thermal processing. The phase and microstructure of the deposited films were studied as a function of sintering temperature, employing X-ray diffractometry and scanning electron microscopy. Dielectric properties of the films were measured at room temperature using impedance spectroscopy. Polycrystalline pure phase CCTO thin films with (220) preferential orientation was obtained at a sintering temperature of 750°C. There was a bimodal size distribution of grains. The dielectric constant and loss factor at 1 kHz obtained for a film sintered at 750°C was $k \sim 2000$ and $\tan \delta \sim 0.05$.

Keywords. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$; thin film; chemical solution deposition; dielectric properties.

1. Introduction

The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) compound has recently attracted considerable research interest due to its unusually high and weakly temperature dependent dielectric permittivity ($k \sim 10^4$ – 10^5). No structural phase transition is reported in CCTO in the temperature range 100–600 K and the material has been projected as a potential alternative for the currently used ferroelectrics for miniaturization of microelectronics (Ramirez *et al* 2000; Subramanian *et al* 2000; Homes *et al* 2001; Adams *et al* 2002; Cohen *et al* 2003; Lukenheimer *et al* 2004). CCTO has a distorted, complex cubic perovskite like structure with unit cell parameter, $a \sim 7.393$ Å (Bochu *et al* 1979). The unusual dielectric property of CCTO was first explained by Subramanian *et al* (2000) in terms of local dipole moments associated with off-centre displacement of Ti ions. An extrinsic explanation based on insulating twin boundaries through single crystal studies has been reported here. Impedance spectroscopic studies showed that CCTO is electrically heterogeneous with semiconducting grains and insulating grain boundaries and the high dielectric constant was attributed to internal barrier layer capacitance (IBLC) (Adams *et al* 2002). Lukenheimer *et al* (2004) explained the behaviour through interfacial electrode polarization due to the development of schottky barriers between the sample and electrode interface. Presence of schottky type grain boundaries within CCTO was confirmed using microcontact current–voltage measurements and Kelvin probe force microscopy (Chung *et al* 2004). Intrinsic explanations such as existence of highly polarizable relaxation modes (Ramirez *et al* 2000) and relaxor

like slowing down of dipolar fluctuations in nano-size domains (Homes *et al* 2001) were reported to be the reason for the colossal dielectric constant (CDC). However, most of the recently reported studies supported that CDC is microstructural dependent and is due to the development of schottky barriers between grain/domain boundaries and the semiconducting grains (Adams *et al* 2006; Briže *et al* 2006; Liu *et al* 2007; Martin *et al* 2008; Sun *et al* 2008).

The thin film state of CCTO possesses more importance for realizing commercial application in integrated circuits. Besides pulsed-laser deposition (PLD) and metal organic chemical vapour deposition (MOCVD), chemical solution deposition (CSD) is an attractive and economic method for making oxide thin films with good homogeneity and composition control (Schwartz 1997). However, only few studies were reported on CCTO thin films produced by CSD (Lu *et al* 2004; Feng *et al* 2006; Jiménez *et al* 2007). Also reports on dielectric properties of CCTO thin films produced by CSD are limited (Jiménez *et al* 2007).

In the present work, we report the deposition of CCTO thin film using chemical solution deposition, spin coating and rapid thermal processing. A new precursor solution was used for the purpose. The phase and microstructure of the prepared films were studied as a function of sintering temperature. Dielectric properties of the film were measured at room temperature as a function of measuring frequency from 1 kHz–1 MHz.

2. Experimental

2.1 Thin film processing

The starting chemicals for the precursor solution were high purity calcium acetylacetonate ($\text{Ca}(\text{C}_5\text{H}_7\text{O}_2)_2$,

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99.95%; Aldrich, USA), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%; Junsei, Japan) and titanium butoxide ($\text{Ti}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$; 97%, Sigma-Aldrich, USA). The precursor chemicals were weighed and mixed in the molar ratio of $\text{Ca}:\text{Cu}:\text{Ti} = 1:3:4$. The solvent used was 2-methoxy ethanol ($\text{C}_3\text{H}_8\text{O}_2$, 99.9%, Sigma-Aldrich, USA). The selection of the precursor chemicals was done with a view to favour maximum chelating effect. The total volume of the reagents to the solvent was kept in a ratio of 1:2. The mixed solution was subjected to stirring using a magnetic stirrer for 10 h. Spin coating was carried out at 3000 rpm for 20 s. The substrate used was commercially available heavily boron-doped silicon. The coated film was subjected to pyrolysis at a temperature of 500°C for 2 min in air. The heating rate used from room temperature to the pyrolysis temperature was $\sim 50^\circ\text{C}/\text{s}$ (time of heating, 10 s). The procedure of coating and pyrolysis was repeated two to three times in order to obtain a desired film thickness of ~ 500 nm. Lastly the film was subjected to sintering at different temperatures ranging from 700 – 800°C for 8 min in air. A heating rate of $\sim 75^\circ\text{C}/\text{min}$ was used from the pyrolysis temperature to the sintering temperature (time of heating from 500 – 800°C , 4 min). The final pyrolysis and sintering were performed in a single step. Rapid thermal annealing (RTA, ULVAC-RIKO, MILA-3000) was employed. The cooling rate was $\sim 25^\circ\text{C}/\text{min}$. Selection of the pyrolysis and sintering temperature was in accordance with the TG/DTA studies of the dried precursor solution (not shown here). Selection of optimized temperature, time and heating rate for both pyrolysis and sintering was essential for getting pure phase CCTO. Figure 1 shows a flow chart of the film processing.

2.2 Phase and microstructure

The crystalline structure of sintered films was examined using X-ray diffraction (XRD, X'pert Pro, Philips) using $\text{CuK}\alpha$ radiation. Scanning electron microscope was used to study the film surface morphology as well as for film thickness measurements (FE-SEM, Hitachi 4800). Before SEM observation, thin gold film was deposited on the sample surface.

2.3 Dielectric properties

An impedance analyzer (HP 4194A, Hewlett-Packard) was used to measure the capacitance and dielectric loss of the film in the frequency range 1 kHz–1 MHz at room temperature, $25 \pm 1^\circ\text{C}$. Dielectric constant was calculated from the obtained capacitance values and the film thickness. Top platinum electrodes with an area of $5 \times 10^{-8} \text{ m}^2$ were deposited by d.c. magnetron sputtering on the film surface using a shadow mask for the dielectric measurements. The time of platinum sputtering was 20 min.

3. Results and discussion

3.1 Phase and microstructure

Figure 2 represents the XRD patterns recorded for the CCTO films as a function of sintering temperature. At the temperature range of 600 – 700°C , CuO was the main constituent of the crystallized phase. Along with the CuO phase, anatase and rutile forms of TiO_2 were detected. The unidentified peaks may correspond to titanium or

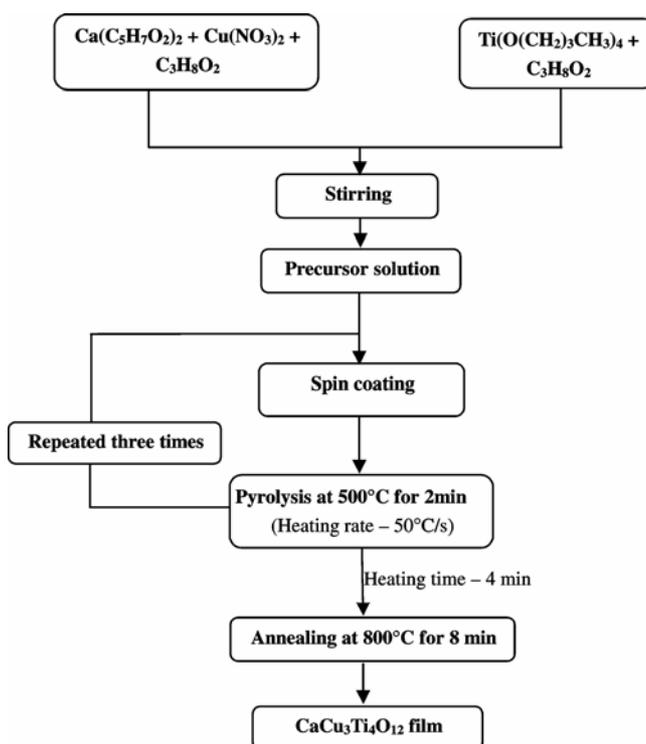


Figure 1. Flow chart for CCTO thin film processing.

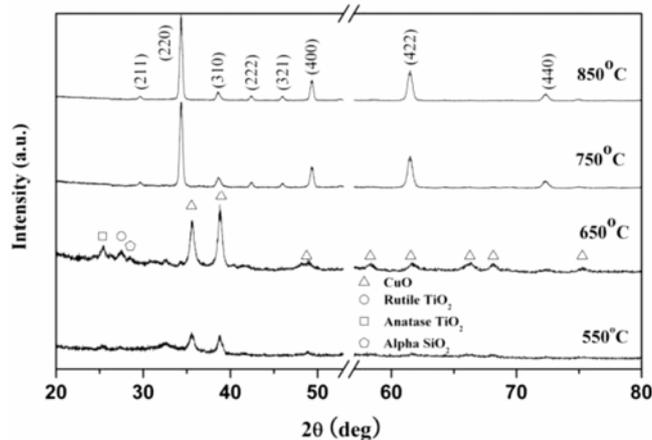


Figure 2. XRD pattern recorded as a function of sintering temperature. The substrate peak was removed for clarity.

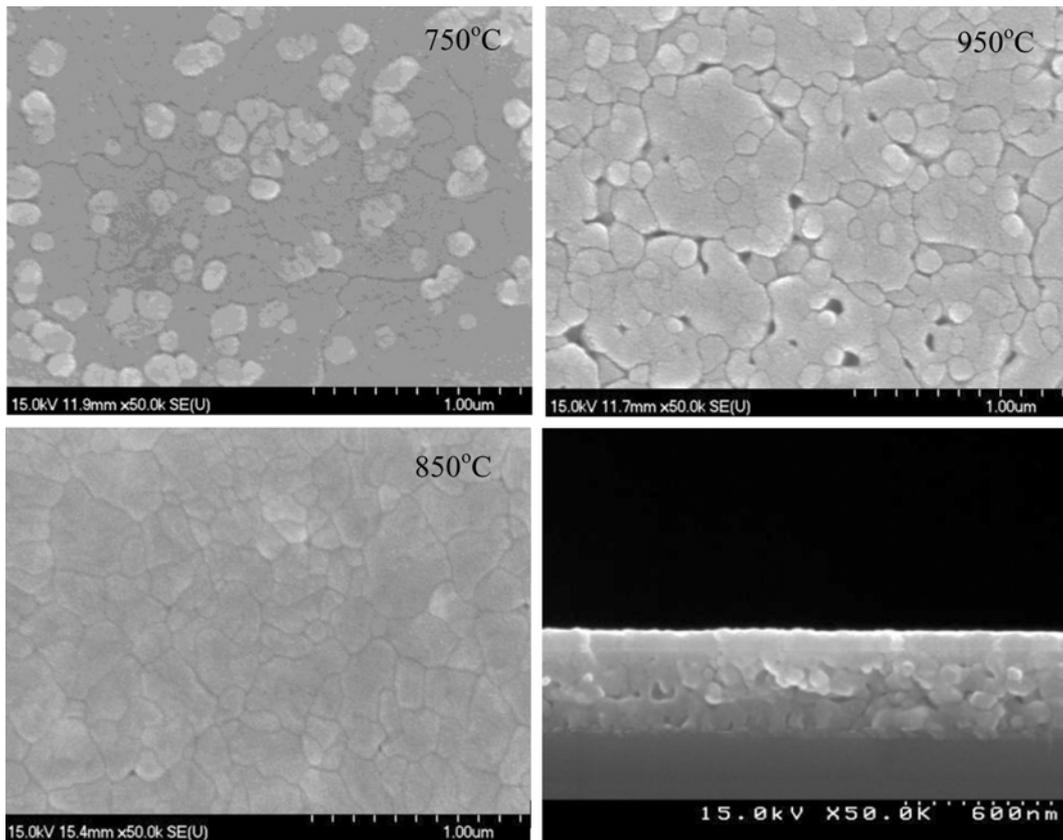


Figure 3. SEM images of CCTO thin films as a function of sintering temperature.

silicon based compounds. However, when the sintering temperature was increased to 750°C, the second phases disappeared and pure phase CCTO thin film was obtained. The film exhibited (220) preferential orientation. The diffraction patterns showed distinct (220), (400), (422) and (440) peaks along with low intensity peaks. The peaks match with the corresponding peaks in bulk CCTO, revealing polycrystalline nature of the film with cubic perovskite structure (space group, $Im\bar{3}$) (Bochu *et al* 1979). With further increase in sintering temperature and sintering time, no major structural changes were observed.

Representative SEM surface and lateral images obtained for the CCTO films as a function of sintering temperature is shown in figure 3. The SEM images support the XRD results revealing polycrystalline nature. The film exhibited exaggerated grain growth and duplex microstructure consisting of large grains in excess of 400 nm in length and small grains of <200 nm. The exaggerated grain growth may be attributed to the CuO based liquid phase sintering (Leret *et al* 2007). Trapped pores were observed in large grains and in grain boundaries when the sintering temperature was above 900°C. The pores may have developed from the abnormal grain growth and the grain boundaries moving quickly during the sintering process (Liu *et al* 2007). Due to the ex-

aggerated grain growth, any significant variation in grain growth with sintering temperature was not observed. Lateral view image in the figure corresponds to a three-time spin coated film sintered at 800°C. The image indicates a well densified structure with some columnar grains. The average thickness of a three-time spin coated film was ~400 nm. The interface between the CCTO film and bottom electrode was sharp implying negligible inter-diffusion across the interface.

3.2 Dielectric properties

The variation of k and the dielectric loss recorded for the films as a function of frequency of measurement is shown in figure 4. The dielectric measurements were carried out in four selected frequencies, viz. 1 kHz, 100 kHz, 500 kHz and 1 MHz. The CCTO film sintered at 750°C showed a k value of ~2100 and a loss tangent of ~0.06 at 1 kHz. The decrease in k when sintering temperature was above 900°C is associated with the trapped porosity as observed by SEM. At higher measuring frequencies, k decreased gradually, accompanied by a corresponding increase in loss factor.

The large k at lower frequencies is suggested to be associated with the Maxwell-Wagner contributions of

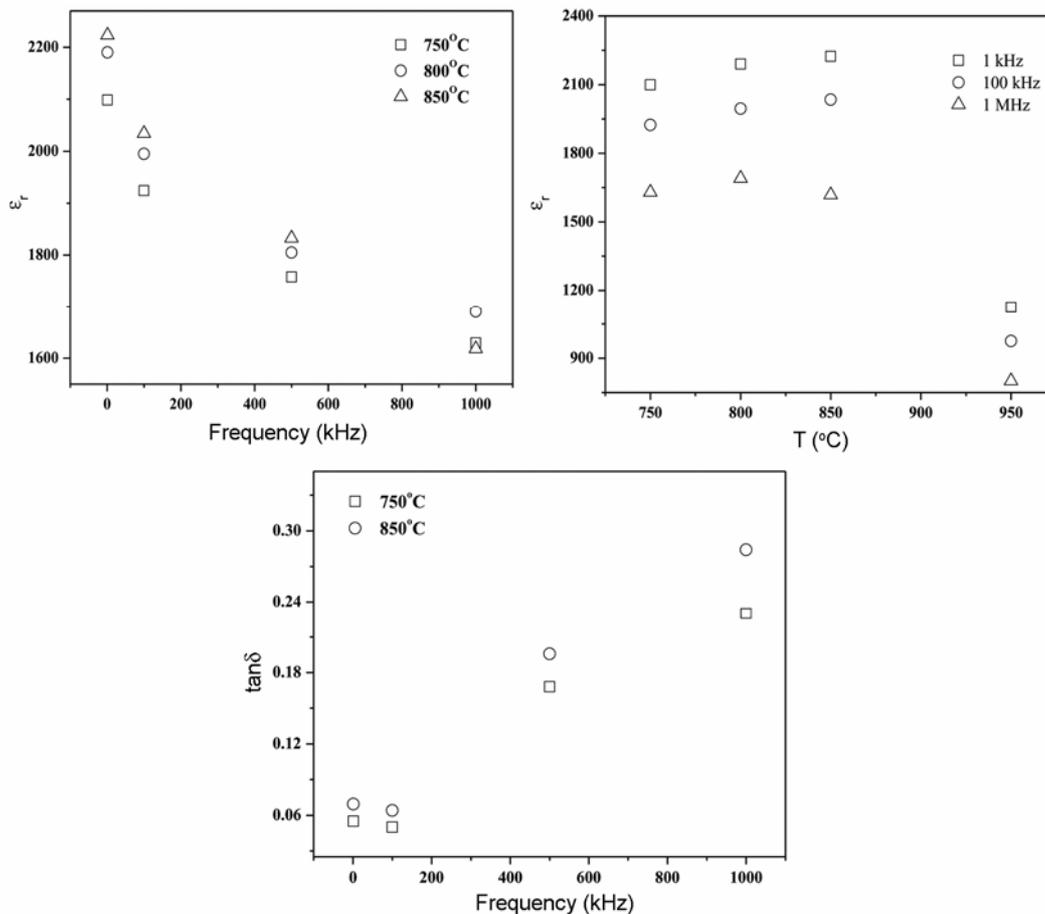


Figure 4. Dielectric constant and dielectric loss of CCTO thin film at different sintering temperatures as a function of measuring frequency.

depletion layers at grain boundaries or interfaces between the sample and contacts (Adams *et al* 2002; Lukenheimer *et al* 2004). So far, the internal barrier layer capacitor (IBLC) model has been widely accepted as the most likely mechanism to elucidate the CDC in CCTO. The difference of conductivity between grain boundary and grain volume causes the charge accumulation on the grain boundary on a mesoscopic scale, which results in large quantity boundary barrier layer capacitors. On a macroscopic scale, the electrode contact effect may play a significant role in CDC. Liu *et al* (2008) showed that electrode and grain boundary act as two depletion layers with distinct relaxation. On increasing the frequency, the space charge polarization relaxes leading to decrease in k . It has been shown that the frequency of dielectric relaxation was much lower in the case of CCTO film when compared to that of the bulk ceramic (Shri Prakash *et al* 2008). The dielectric properties of the film obtained in the present work is comparable with that reported for polycrystalline CCTO thin films (Si *et al* 2002; Fang and Shen 2003; Fang *et al* 2004; Shri Prakash *et al* 2008). The high dielectric constant obtained for the CCTO film

in the present study indicates its possible application in microelectronic devices.

4. Conclusions

Highly oriented CCTO thin films were successfully deposited on boron doped silica substrate at a sintering temperature of 750°C. Effect of sintering temperature on the phase and microstructure of the film was investigated. The film formed was polycrystalline in nature with (220) preferential orientation. SEM microstructures of the films revealed a bimodal size distribution of grains. Dielectric constant and loss tangent at 1 kHz obtained for the film sintered at 750°C was $k \sim 2000$ and $\tan \delta \sim 0.05$, respectively.

Acknowledgement

The authors express their sincere gratitude to Professor Yong Soo Cho, Department of Materials Science and Engineering, Yonsei University, Korea.

References

- Adams T B, Sinclair D C and West A R 2002 *Adv. Mater.* **14** 1321
- Adams T B, Sinclair D C and West A R 2006 *Phys. Rev.* **B73** 094124
- Bochu B, Deschizeaux M N and Joubert J C 1979 *J. Solid State Chem.* **29** 291
- Brize V, Gruener G, Wolfman J, Fstyeyeva K, Tabellout M and Gervais F 2006 *Mater. Sci. Eng.* **B129** 135
- Chung S Y, Kim I L and Kang S J L 2004 *Nat. Mater.* **3** 774
- Cohen M H, Neaton J B, He L and Vanderbilt D 2003 *J. Appl. Phys.* **94** 3299
- Fang L and Shen M 2003 *Thin Solid Films* **440** 60
- Fang L, Shen M and Cao W 2004 *J. Appl. Phys.* **95** 6483
- Feng L, Wang Y, Yan Y, Cao G and Jiao Z 2006 *Appl. Surf. Sci.* **253** 2268
- Homes C C, Vogt T, Shapiro S M, Wakimoto S and Ramirez A P 2001 *Science* **293** 673
- Jiménez R, Calzada M L, Bretos I, Goes J C and Sombra A S B 2007 *J. Eur. Ceram. Soc.* **27** 3829
- Leret P, Fernandez J F, de Frutos J and Fernandez-Hevia D 2007 *J. Eur. Ceram. Soc.* **27** 3901
- Liu L, Fan H, Fang P and Jin L 2007 *Solid State Commun.* **142** 573
- Liu L, Fan H, Wang L, Chen X and Fang P 2008 *Philos. Mag.* **88** 537
- Lu W, Feng L, Cao G and Jiao Z 2004 *J. Mater. Sci.* **39** 3523
- Lukenheimer P, Fichtl R, Ebbinghaus S G and Loidl A 2004 *Phys. Rev.* **B70** 172102
- Martin L, Guillemet-Fritsch S, Durand B, Levchenko A A, Navrotsky A and Lebey T 2008 *J. Am. Ceram. Soc.* **91** 485
- Ramirez A P, Subramanian M A, Gardel M G, Blumberg G, Li D, Vogt T and Shapiro S M 2000 *Solid State Commun.* **115** 217
- Schwartz R W 1997 *Chem. Mater.* **9** 2325
- Shri Prakash B, Varma K B R, Michau D and Maglione M 2008 *Thin Solid Films* **516** 2874
- Si W, Cruz E M, Johnson P D, Barnes P W, Woodward P and Ramirez A P 2002 *Appl. Phys. Lett.* **81** 2056
- Subramanian M A, Li D, Duan N, Reisner B A and Sleight A W 2000 *J. Solid State Chem.* **151** 323
- Sun D L, Wu A Y and Yin S T 2008 *J. Am. Ceram. Soc.* **91** 169