

Stabilization of Nanostructured-oriented CaCuO₂ Thinfilms

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Abstract. Nanostructured *c*-axis oriented thin films of CaCuO₂ have been grown on the single crystalline (110) NdGaO₃ and (100) LaAlO₃ substrates using pulsed laser deposition technique. The structural characterization confirms that the grown CaCuO₂ films are in single phase with (00*l*) oriented on both the substrates. An energy dispersive X-ray spectroscopic study ensures the stoichiometric growth of the film. Nanostructured morphology of CCO film is confirmed by the scanning electron microscopy.

INTRODUCTION

The ACuO₂ (A =Ca, Sr, Ba) layer compound has attracted huge interest because they play an important role in the high temperature superconducting properties in the cuprate based systems. All these ACuO₂ compounds have the tetragonal structure (*P4/mmm*). In these compounds, the CuO₂ layers are separated from each other by alkaline earth metals in the *c*-direction. The two dimensional CuO₂ sheets are known to play a pivotal role in realizing high temperature superconducting behavior in systems similar to cuprates [1]. The bulk form of the CaCuO₂ is stable in the high pressure conditions, but can be stabilized in the form of a thin film via optimizing the growth conditions. Recently D. D. Castro *et al.*, reported the high transition temperature in the superlattices of the CaCuO₂/SrTiO₃, which is around 40K, mainly because of the extra oxygen in the Ca plane which gives the Pyramidal Co-ordination to Cu²⁺ ion and causes the hole doping in the CuO₂ infinite layer [2]. CaCuO₂(CCO) reveals antiferromagnetic ground state with charge transfer gap between the two dimensional CuO₂ sheets being ~1.5eV [3] which is modified by any distortion causing non-planer co-ordination of Cu ion. CaCuO₂ is also very interesting for the thermopower investigation. The Figure of Merit (*ZT*) is defined by $ZT = S^2 \sigma T / \kappa$ where *S*, σ , *T*, κ are Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity respectively. For the better performance of the thermoelectric material, it should be highly electrical conducting and having low thermal conductivity. It is suggested that the properties of CCO can be maneuvered by applying external pressure, and that can be because of chemical substitution and/or substrate induced epitaxial strain in thin film form. However, not much information is available about the growth nature of CCO on different substrates. The lattice parameters of CCO in the tetragonal structure (*P4/mmm*) are $a = 3.855 \text{ \AA}$ and $c = 3.179 \text{ \AA}$. NdGaO₃ (NGO) substrates have the orthorhombic (*Pbn2₁*) structure with lattice parameters of $a = 5.433 \text{ \AA}$, $b = 5.503 \text{ \AA}$, and $c = 7.715 \text{ \AA}$. The calculated lattice parameters of the pseudocubic cell structure of NdGaO₃ are $a = 3.866 \text{ \AA}$ and $c = 3.857 \text{ \AA}$, whereas the lattice parameter of LaAlO₃ substrate is 3.789 \AA . The lattice mismatch between CCO and NGO substrate is around 0.25%, while in the case of LAO it is around 1.8%. Therefore, NGO substrate is very good for the synthesis of CCO thin films in the view of lattice structure and thermal expansion matching. Therefore, in the present study on the growth nature of CCO films on these two substrates, which offer different strain due to lattice mismatch between the substrate and film.

EXPERIMENTAL DETAILS

Oriented thin films of CCO were grown on the single crystalline (110) NGO and (100) LAO substrates using pulsed laser deposition (PLD) technique. PLD set up consists of a KrF excimer laser source of wavelength $\lambda = 248 \text{ nm}$. Mixed phase CaCuO₂ target was used to deposit the single phase CCO films. The target was prepared by the conventional solid state reaction method. The substrate temperature, oxygen partial pressure, laser energy

density, and cooling conditions were varied to stabilize the single phase of CCO thin films. Finally, the laser energy of 300 mJ, repetition rate of 2 Hz, 200 mTorr of oxygen partial pressure, and 780°C substrate temperature was fixed to deposit the CCO thin films. The growth rate for each film was calculated around 0.17Å/pulse. After the deposition, films were cooled to room temperature at an ambient oxygen pressure. CCO films of different thickness from 4 nm to 120 nm were grown at the same growth conditions, only varying the no. of laser shots.

For structural characterization, Bruker X-ray diffractometer equipped with Cu K α (1.5406Å) radiation was used. The grown films were also characterized by Raman spectroscopy using Micro-Raman system (Jobin-Yvon Horiba LabRAM) with the excitation laser source of Argon-473nm. A field emission scanning electron microscope (FESEM) (FEI NOVA Nano Sem 450) was used to study the surface morphology of the film. The composition of the films was determined by using an attached energy dispersive analysis of X-ray (EDAX) unit.

RESULTS AND DISCUSSIONS

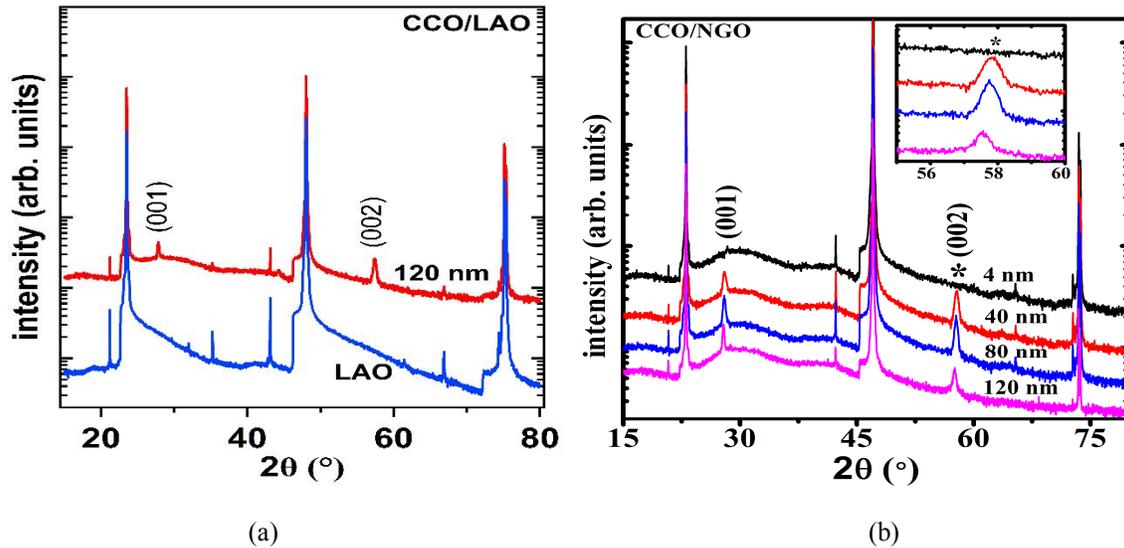


FIGURE 1. (a) XRD patterns of CaCuO $_2$ films grown on (110) NGO substrates and (b) (100) LAO substrates.

The crystal structure of CCO films grown on (100) LAO and (110) NGO substrates of different thickness were characterized by the XRD studies as shown in the fig. 1(a) and fig. 1(b) respectively. The peak at 2θ value 27.86° and 57.44° is mentioned as (001) and (002) orientation of CCO thin films, while the other peaks are from the substrate. Absence of any impurity peaks confirms the single phase of CCO films on (110) NGO and (100) LAO substrates.

To confirm the phase information, Raman measurement was performed with an excitation source of 473nm on the grown films. The Raman modes of the NGO substrate coincides with that of the CCO films, and that makes these modes undistinguishable. Therefore, in Fig. 2, we show Raman modes of the film grown on LAO substrate. The Raman modes of deposited CCO film are clearly seen at 236 cm $^{-1}$, 430 cm $^{-1}$, 466 cm $^{-1}$, 553 cm $^{-1}$, and a characteristic hump near 700 cm $^{-1}$. The Raman modes at 430 cm $^{-1}$ and 550 cm $^{-1}$ correspond to the bending in the CuO $_2$ plane and the CuO stretching mode respectively. The broad spectral band around the 700 cm $^{-1}$ is corresponding to the damped harmonic oscillator contribution. The substrate modes are clearly visible at 486 cm $^{-1}$ and 777 cm $^{-1}$. The Raman spectrum of CCO film further confirms the single phase nature of the grown tetragonal CCO film [5].

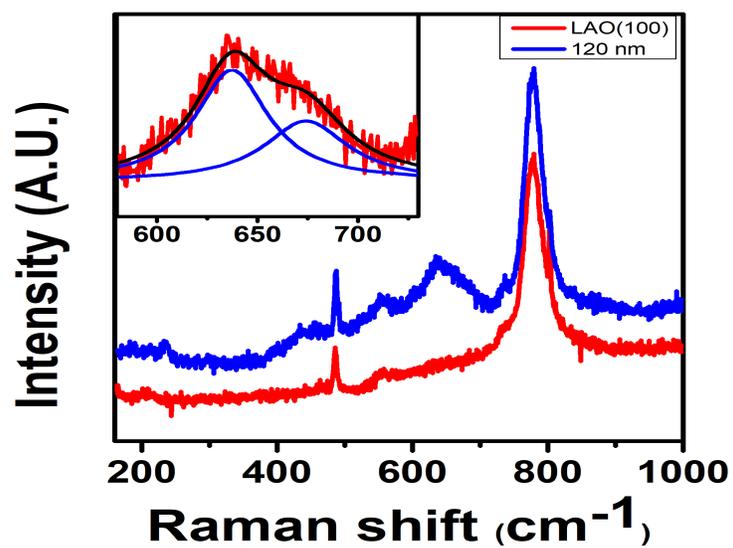


Figure 2. Raman spectra of CaCuO₂ film grown on (100) LAO substrate.

MORPHOLOGICAL PROPERTIES

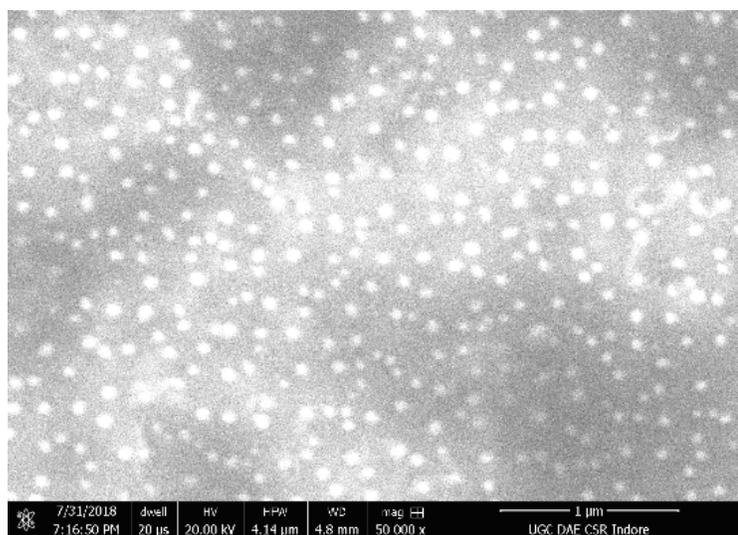


Figure 3. SEM image of CCO film grown on (110) NGO substrate

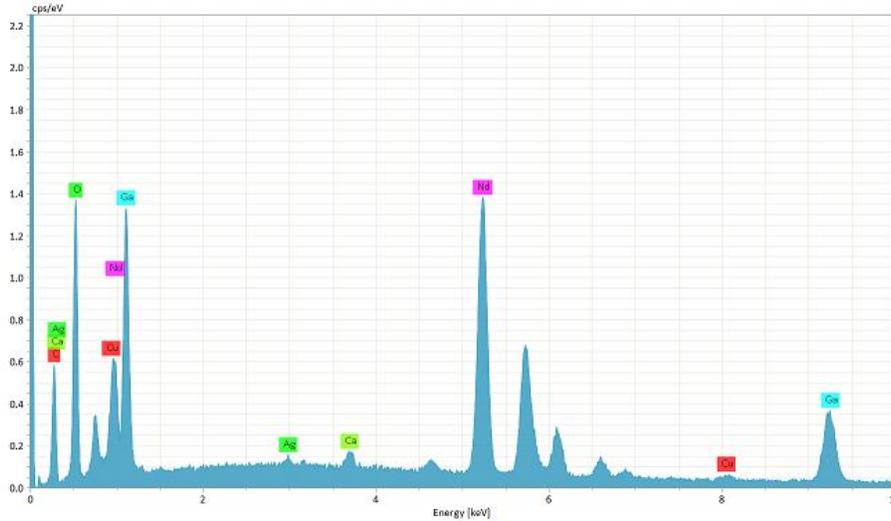


Fig.4 EDAX spectra of CCO film grown on (110) NGO substrate

Scanning electron micrograph (SEM) of 80 nm thick *c*-oriented CCO film grown on NGO substrate is shown in fig.3. In the SEM picture, nano-size particles of grown CCO film are clearly seen which confirms the island growth of the oriented CCO films. The size of the nanoparticles is around 65 nm, while the grain size for the same film is around 19.8 nm for the same thickness film which was calculated by Debye-Scherrer formula from XRD pattern. The bright spots are showing the *c*-oriented CCO film and the darker area is showing the substrate. Fig.4 is representing the EDAX results of the same film confirms the stoichiometric amount of Ca and Cu present in the studied CCO thin film. The contribution of Nd, Ga comes in the spectra because of the NdGaO₃ substrate.

CONCLUSION

In summary, we studied the growth mechanism, structural properties and surface micrograph of CaCuO₂ thin film deposited on single crystal (110) NdGaO₃ and (100) LaAlO₃ substrates. The growth of the film highly depends on the growth conditions. The island growth is responsible for the nanostructured *c*-oriented thin film as observed in the SEM images. These nanostructured CCO film can be a good candidate for the thermoelectric materials.

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REFERENCES

1. D.Fuchs, P.Muller, A.Sleem, Journal of Applied Physics **112** 103529-103537 (2012).
2. D. Di Castro, M. Salvato, A. Tebano, D. Innocenti, C. Aruta, Phys. Rev. B **8** 134524-134530 (2012).
3. Y.Tokura, S.Koshihara, T.Arima, H.Tagaki, S.Ishibashi, T.Ido, and S.Ushida, Phys. Rev. B **41** 11657-11660 (1990).
4. X.M.Quin, Q.Q. Liu, Y. Yu, Z.X.BaO, Science and technology of advanced materials **6** 828-832 (2005).
5. D.Di Castro, S. Caramazza, D. Innocenti, G. Balestrino, Journal of Applied Physics, **103** 191903-191907 (2013).