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Pulsed laser deposition of homo- and hetero-epitaxial thin films of the exotic $La_5Ca_9Cu_{24}O_{41}$ compound on oxide and Si substrates

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Pristine and transition metal-doped $La_5Ca_9Cu_{24}O_{41}$ thin films were fabricated by pulsed laser deposition in oxygen atmosphere. The effect of magnetic doping, type of substrate and growth temperature on the crystallographic orientation and surface topography of the films was investigated. X-ray diffraction data reveals that pristine $La_5Ca_9Cu_{24}O_{41}$ films are grown homo- and hetero-epitaxially on $La_5Ca_9Cu_{24}O_{41}$ (0 0 1) and $La_4Ca_{10}Cu_{24}O_{41}$ (0 0 1) single crystals, respectively, whereas those deposited on Si (0 0 1) single crystals are highly b-axis oriented. In addition, (1%) Ni-, Co- and Fe- doped $La_5Ca_9Cu_{24}O_{41}$ films fabricated on $SrTiO_3$ (0 0 1), MgO (0 0 1) and Si (0 0 1) substrates are highly b-axis oriented.

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1. Introduction

Novel cuprate oxides - known are spin-ladder materials - are exploited as a new generation thermal management materials. The complex insulating compound $La_5Ca_9Cu_{24}O_{41}$ (LCCO-5/9) with high-and-anisotropic thermal conductivity [1] is of great interest for possible application in micro- and nano-electronic devices in need of tunable heat conduction. The large magnetic thermal conductivity of LCCO-5/9 with quasi one-dimensional spin arrangement in chains or ladders could be used for the guidance of the heat dissipation onto a heat sink.

The peculiar thermal properties of the title compound have been studied extensively in high-purity single crystals grown by the travelling-solvent-floating-zone (TSZF) method [1, 2]. However, the integration of this promising material in devices requires the availability of thin films with preferred orientation along the c-axis in order to exploit the anisotropic thermal conductivity. In addition, the magnetic origin of the compound's thermal conductivity opens the way to control it by external means (e.g., magnetic field or light) by introducing in the lattice sites of Cu^{2+} ions other magnetic ions with switchable spin states. The task of fabricating stoichiometric epitaxial or even highly textured films for this compound is formidable because the unit cell contains 316 atoms and the crystal structure is rather complex, i.e., the incommensurate composite structure consists of two orthorhombic symmetry sublattices – CuO_2 (chains) and $Sr_2Cu_2O_3$ (ladders) [3, 4]. The planes of the Cu_2O_3 ladders are stacked along the b-axis alternating with 1D CuO_2 chain sheets.

In this paper, we report on our successful attempt to fabricate thin films of the title compound - pristine and doped with magnetic impurities (Ni, Co, Fe) - by pulsed laser deposition (PLD) using various substrates and growth temperatures.

2. Experimental

Thin films of LCCO-5/9 (pristine and doped) were fabricated by PLD using a KrF laser (248 nm; COMPexPro 201) at an oxygen partial pressure (PO_2) of 20 Pa with a fluence of 2 J/cm^2 and a repetition rate of 10 Hz. The target was located at a distance of 4 cm from the substrate and was continuously rotated to ensure fresh ablation site for each incoming laser pulse of 25 ns duration. The targets used for the deposition of the films were prepared by the solid state reaction method using high purity powders of the cations, pelletized and sintered at 900°C for 72 h [5].

Single crystals of LCCO-5/9 (0 0 1), $La_4Ca_{10}Cu_{24}O_{41}$ (LCCO-4/10) (0 0 1), $SrTiO_3$ (0 0 1), MgO (0 0 1) and Si (0 0 1) were used as deposition substrates. The lattice parameters of the substrates are shown in Table I. Single crystals of LCCO-5/9 (0 0 1) and LCCO-4/10 (0 0 1) were used as substrates to show that is possible to obtain c-axis epitaxial films. $SrTiO_3$ (0 0 1) and MgO (0 0 1) substrates were used because of the good and bad lattice matching with the title compound, respectively; whereas Si substrates were used because the ultimate goal is to integrate the title compound in Si-based micro- and nano-devices. The (0 0 1) oriented single crystals of LCCO-5/9

and LCCO-4/10 were synthesized using the TSZF method (for more experimental details see Ref. [2]). The rest of the substrates were acquired from commercial vendors. The rock salt MgO and the perovskite $SrTiO_3$ (STO) substrates were used as received. On the other hand, Si substrates were cleaned in acetone, methanol, isopropanol and distilled water ultrasonically and blown dried using high purity N_2 gas. The native oxide layer was not removed prior to deposition. The LCCO-5/9 and LCCO-4/10 substrates were attached on the heater using Ag paint while the rest of the substrates were attached mechanically using pins. The films were grown at temperatures in the range of 500 - 850°C and the post deposition cooling took place under 20 Pa of oxygen ambient and a rate of 8.3°C per min. The crystallographic structure and surface topography of the films was examined using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively. Energy Dispersive X-Ray Spectroscopy (EDX) was used to confirm that the chemical stoichiometry of the fabricated films is similar to that of the used targets.

Table 1. Lattice parameters of the substrates used for the deposition of pristine and doped LCCO-5/9 thin films.

Lattice parameters / Substrates	a (nm)	b (nm)	c (nm)
LCCO-5/9	1.1301	1.2612	2.7602
LCCO-4/10	1.1292	1.2573	2.7589
$SrTiO_3$	0.3905	0.3905	0.3905
MgO	0.4213	0.4213	0.4213
Si	0.5431	0.5431	0.5431

3. Results and discussion

In Ref. [5] we reported that using a fluence of 2 J/cm^2 and PO_2 of 20 Pa during the PLD process results in the successful ablation of LCCO-5/9 pellets, target-to-film stoichiometric transfer and partial elimination of particle generation. Here we report on a new set of experiments in which we kept the above deposition parameters fixed. Initially, a ~ 1.5 μm- thick LCCO-5/9 film was grown on an LCCO-5/9 (0 0 1) single crystal heated to 685°C. In Fig. 1 the XRD patterns of the LCCO-5/9 (0 0 1) substrate prior to deposition and of the grown LCCO-5/9 film are shown. The high intensity peaks corresponding to *(0 0 l)* reflections and the lower intensity peak of (0 2 14) / (6 0 0) reflection are only visible, indicating that the film of the exotic LCCO-5/9 compound is c-axis oriented. Note that the film covered the entire surface area of the LCCO-5/9 single crystal (i.e., there was no thickness step) so the contribution from the single crystal to the XRD pattern of the film is minimal. Since the composition of the substrate and the film is the same this constitutes a case of homo-epitaxial growth.

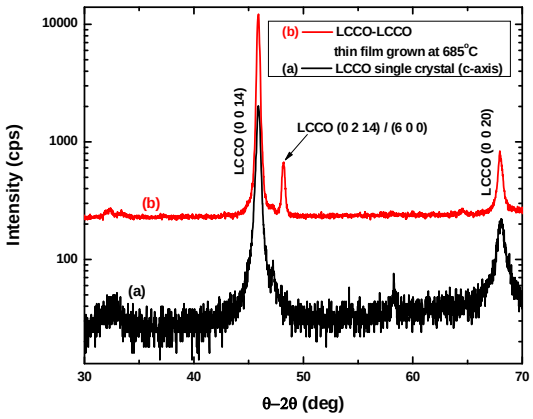


Fig. 1. XRD patterns of (a) a LCCO-5/9 (0 0 1) single crystal and (b) a homo-epitaxial LCCO-5/9 thin film deposited on LCCO-5/9 (0 0 1) substrate at 685 °C.

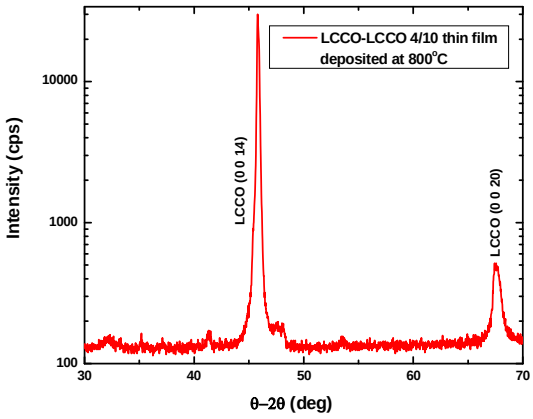


Fig. 2. XRD pattern for the LCCO-5/9 film grown on an LCCO-4/10 (0 0 1) substrate at 800°C.

Fig. 2 shows the XRD spectrum obtained for an LCCO-5/9 film deposited on an LCCO-4/10 (0 0 1) single crystal at 800°C. The only visible peaks correspond to *(0 0 l)* reflections and thus the film is clearly c-axis oriented. Since the composition of the substrate and the film is different this constitutes a case of hetero-epitaxial growth. The surface topography of the LCCO-5/9 films deposited on LCCO-5/9 (0 0 1) and LCCO-4/10 (0 0 1) substrates is illustrated in the SEM images of Fig. 3 (a) and (b), respectively. In Fig. 3 (a) the granularity of the film is apparent with grain size ~ 100 x 200 nm^2. The long and short side of the platelet grains are aligned along the a- and b-axis of the single crystal substrate indicating that a polycrystalline homo-epitaxial film is obtained. In Fig. 3 (b) the grain boundaries are not well-defined; the grains have begun to coalesce, and development of a single

crystalline film has commenced. Ex-situ post annealing of the film at 900°C for 10 h led to partial melting of the film and formation of grains with two distinctly different sizes, slight colour change and random polycrystalline orientation.

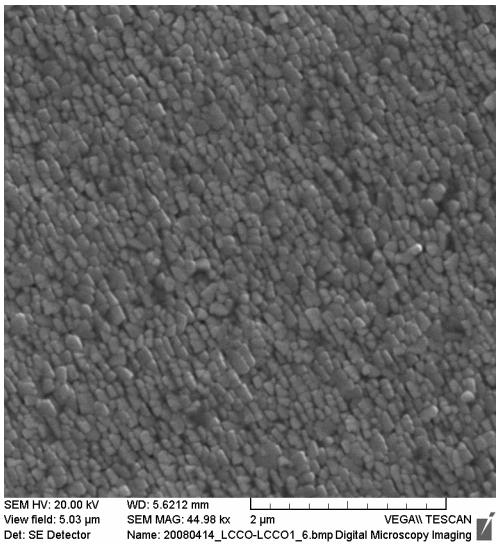


Fig. 3. a) Granular textured c-axis oriented LCCO-5/9 thin film on LCCO-5/9 (0 0 1) substrate with grain size 100 x 200 nm^2. b) LCCO-5/9 thin film on LCCO-4/10 (0 0 1) substrate with diffused grain boundaries.

Thin films using (1%) Ni, Co and Fe doped LCCO-5/9 targets were fabricated on STO (0 0 1) substrates at 750°C. In Fig. 4 the XRD patterns of the grown films are illustrated where only peaks corresponding to *(0 k 0)* reflections of the LCCO-5/9 compound and to *(h 0 0)* reflections of the STO substrate are evident. The (0 4 0) LCCO-5/9 peak exhibits the highest intensity for all three films indicating that the films are preferentially oriented with the b-axis normal to the substrate surface. High intensity peaks of the substrate are also present in all XRD patterns owing to the step formed on one side of the films for film thickness measurement. The b-axis lattice parameter was calculated for each doped film, resulting to $b_{Fe\text{-}doped}$ = 1.262 nm, $b_{Co\text{-}doped}$ = 1.263 nm, and $b_{Ni\text{-}doped}$ = 1.259 nm. These values compare well with that of the pristine LCCO-5/9 ($b_{pristine}$ = 1.261 nm). The fact that $b_{Fe\text{-}doped} \approx b_{pristine}$ maybe an indication that Fe is not incorporated substitutionally in the LCCO-5/9 lattice under this growth condition; on the other hand, the greater difference between $b_{Co\text{-}doped}$ and $b_{Ni\text{-}doped}$ with $b_{pristine}$ may be an indication that Co- and Ni-ions substitute for Cu-ions resulting to lattice tension and compression, respectively, due to slightly different ionic radii. These indications are in agreement with thermal conductivity results on this type of films.

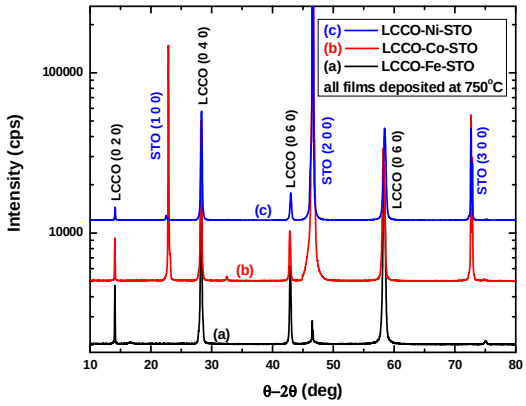


Fig. 4. XRD spectra of (1%) Fe (a), Co (b) and Ni (c) doped LCCO-5/9 thin films deposited on STO (1 0 0) single crystal substrates at 750°C. Only the LCCO-5/9 (0 k 0) and STO (h 0 0) reflections are present.

LCCO-5/9 Ni (1 %) doped films were grown on Si, MgO and STO single crystals in order to examine the effect of substrate (due to different lattice parameters and interface interactions) on the crystallographic orientation of the films. The XRD patterns of such films deposited at 750°C are shown in Fig. 5. Both Ni:LCCO-5/9-Si and Ni:LCCO-5/9-MgO are highly b-axis oriented with the presence in the XRD spectra of the low intensity peak corresponding to (0 2 16) / (6 0 0) reflections. On the other hand, the XRD spectrum of the Ni:LCCO-5/9-STO doped film exhibits only peaks corresponding to *(0 k 0)* reflections (epitaxial-like growth) due to better lattice matching.

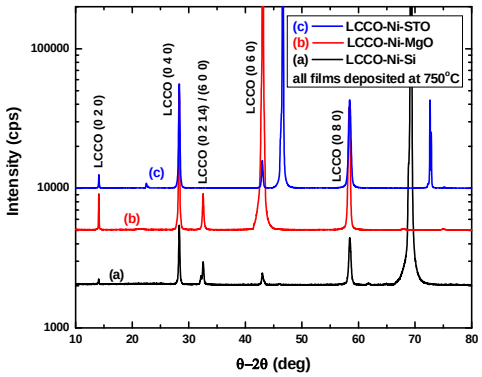


Fig. 5. XRD patterns of (1%) Ni doped LCCO-5/9 films deposited on Si (0 0 1) (a), MgO (0 0 1) (b), and STO (0 0 1) (c) substrates at 750°C.

Micro- and nano-scale devices and technologies are mostly Si-based; therefore, special attention was paid to the PLD fabrication of LCCO-5/9 thin films on Si substrates. Thin films of the pristine LCCO-5/9 compound were grown on Si (0 0 1) substrates at temperatures of 500, 600, 700, 800 and 850°C. The XRD patterns of these films are shown in Fig. 6. The film deposited at 500°C exhibits weak crystallinity while further increase of growth temperature to 600°C seemed to promote b-axis oriented growth of the film. The films deposited at 700 and 800°C exhibited several new low-intensity peaks in addition to those corresponding to *(0 k 0)* reflections indicating a reduction in b-axis texturing. Finally, the films deposited at 850°C exhibit random polycrystalline orientation and granular topography. A comparison of the XRD spectra shown in Figures 4, 5 and 6 reveals that for substrates with bad lattice matching b-axis oriented films were obtained at lower substrate temperatures (Si substrate deposition at 600°C) than for substrates with good lattice matching (STO substrate deposition at 750°C). A similar observation has been reported for Y-Ba-Cu-O thin films by Jeschke *et al.* [6].

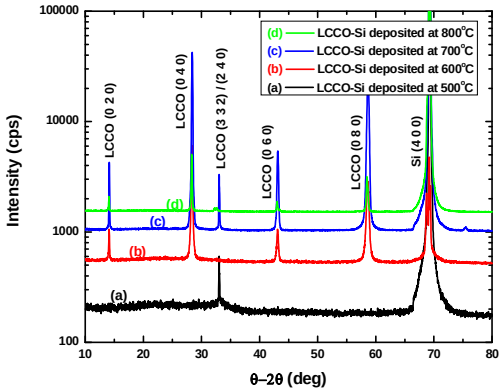
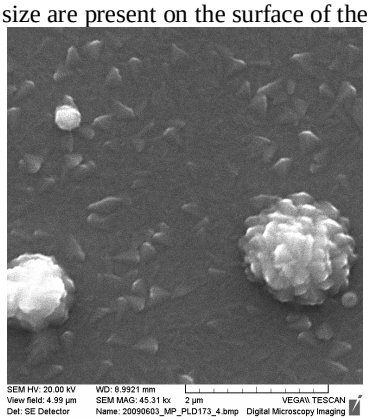
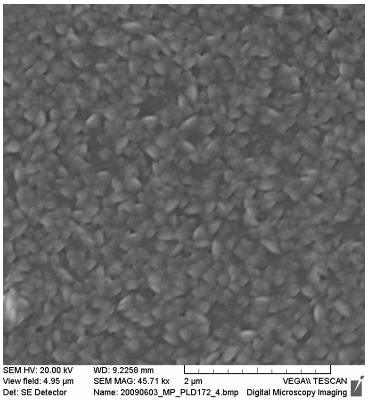


Fig. 6. XRD patterns of pristine LCCO-5/9 thin films grown on Si (1 0 0) at (a) 500°C, (b) 600°C, (c) 700°C and (d) 800°C, respectively.

The three representative SEM images shown in Fig. 7 demonstrate the effect of substrate type and growth temperature on the topography of the films. A comparison of images (a) and (b) indicates that growth at the same temperature but on a better lattice matched substrate leads to films with less surface roughness and less grain coarsening. The orientation of the grains parallel to the substrate surface seems to be random. On the other hand, image (c) reveals that in the case of Si (0 0 1) substrate and low growth temperature - contrary to expectations - the film appears to be smoother in comparison to films shown in (a) and (b). In all cases spherical-like particulates of variable size are present on the surface of the films.



a



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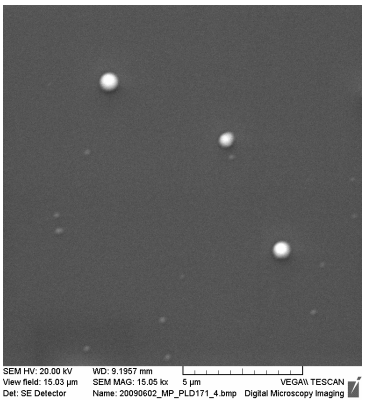

c

Fig. 7. SEM images of (a) Ni:LCCO-5/9-STO film deposited at 750°C, (b) Ni:LCCO-5/9-MgO film deposited at 750°C and (c) LCCO-5/9-Si film deposited at 500°C.

SEM images (not shown here) revealed the appearance of cracks in both pristine and doped LCCO-5/9 films deposited on Si substrates at temperatures between 600 and 800°C. The films grown under these conditions exhibited preferred b-axis orientation. For quasi-amorphous films with small degree of polycrystallinity and granular polycrystalline films deposited at 500 and 850°C, respectively, no cracks were observed. It appears that the crack formation depends on the type of substrate (i.e., thermal expansion coefficient mismatch), deposition temperature and crystallographic orientation of the deposited films.

The formation of cracks is a more common occurrence in oxide films deposited on Si substrates rather than on other commonly used oxide substrates [7]. This is mainly attributed to the thermal expansion coefficient and/or lattice parameter mismatch between oxide compounds and Si substrates. In addition Si is a covalent material whereas most of the oxides are ionic compounds; thus the probability of the oxide ions sticking to the Si surface is low.

4. Conclusions

Homo- and hetero-epitaxial LCCO-5/9 films were grown by PLD on LCCO-5/9 (001) and LCCO-4/10 (001) single crystal substrates, respectively, for the first time. In addition strongly b-axis oriented pristine and doped LCCO-5/9 films were grown on STO (0 0 1), MgO (0 0 1) and Si (0 0 1) single crystals at temperatures between 500 and 850°C. All the films are single phase, stoichiometric and stable in air. Pristine LCCO-5/9 thin films on Si exhibited high b-axis texturing at lower growth temperatures than those in the case of better lattice-matched substrates. Crack formation was observed only in the case of LCCO-5/9 films on Si substrates and for growth temperatures in the range 600-800°C.

Acknowledgements

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