Growth of $La_{2-x}Sr_xCuO_4$ Thin Films with *c*-Axis Orientation on SiO_2 Layer by *in situ* Post-annealing in Pulsed Laser Deposition

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The first high-T_C cuprate, $La_{2-x}Sr_xCuO_4$ (LSCO) is known to be correlated with Mott insulators that become metallic and superconducting upon doping with charge carriers.[1] A large number of studies have been performed on bulk samples of LSCO due to its simple chemical composition and crystal structures as well as its rich physical properties.[2] The high-speed switching devices applying the metal-insulator transition (MIT) were predicted as an important application.[3] However, the preparation of the thin film of LSCO is critical in developing devices such as thermal switches, thermochromatic coatings and non-volatile memory.[4] The electrical and transport properties of LSCO-based thin films are highly sensitive to the degree of *c*-axis orientation because the charge carriers move through *c*-axis channels. A large number of iso-structural substrates, such as $NdGaO_3$, $LaAlO_3$, and $SrTiO_3$, which have small lattice mismatches with LSCO, have been used to obtain highly oriented LSCO thin films.[5] However, these cannot be used as common substrates in developing MIT devices because it is too difficult and too expensive to prepare their single crystalline structures.

In this letter, we report the first results of experiments investigating pulsed laser deposition (PLD) and high-pressure post-annealing in oxygen on a SiO_2 layer which is largely lattice-mismatched with LSCO, which leads to *c*-axis oriented LSCO thin films. Thermal SiO_2 is the common oxide most frequently used on Si wafers and is known as the highest quality oxide of low defect density and low impurity content, thereby acting as a gate oxide in the manufacture of MIT devices.

The polycrystalline LSCO target was prepared by a conventional solid-state reaction. Stoichiometric amounts of La_2O_3 (99.9%, preheated at 900 °C for 12 h), SrO (99.99%) and CuO (99.9%) were thoroughly mixed and heated at 1050 °C for 24 hrs in air. The powder was ground and pressed into pellets under a pressure of about 50 MPa and sintered at 1000 °C for 24 h. An amorphous 100-nm-thick SiO_2 film was grown on a (100) Si wafer using thermal oxidation at 925 °C. The oxidation ambient was composed of O_2 and H_2. LSCO thin films were deposited on SiO_2 films at various temperatures using a frequency tripled Nd:YAG Laser (Quantel, Brilliant II) with 5-ns of pulse width. Laser pulses of 5 Hz were focused onto the rotating target using a quartz lens with a 35 cm focal length at a 45° oblique incidence, and the energy density of approximately 2 J/cm^2. A substrate was set at a distance of 50 mm parallel to the target surface. The grown films were subsequently post-annealed in ambient oxygen at various temperatures. The structural and phase identifications were carried out using an X-ray diffractometer (MacScience Co. MXP-3V) with Cu-K_α radiation. Cross-sectional views of the deposited films were obtained using a scanning electron microscope (SEM) (Hitachi Co. S-4200).

Figure 1 shows the XRD spectra of thin films of the parent material, $La_{2-x}Sr_xCuO_4$ ($x = 0$). The as-deposited thin film at 800 °C has the predominant preferential orientation of (113) direction. This is consistent with the result of Wang *et al.* that the (00*l*) orientation is always accompanied by (113) orientations, even on a substrate with small lattice mismatch such as $LaAlO_3$.[6] However, the thin film post-annealed at 700 °C for 1 hr under oxygen atmosphere of 1000 mTorr after deposition at 500 °C has the diffraction peaks of (00*l*) with $l = 2n$, which suggests that the films consist of entirely *c*-axis-oriented grains. The post-annealing step is usually carried out to improve the properties of as-deposited thin films, such as crystallinity, grain size and stoichiometry of the light component in the thin film processes.

The parent compound can be doped by substituting some of the La^{3+} with Sr^{2+}. As a result, the x holes are added to the Cu-O plane in LSCO and the electrical properties of the LSCO thin film are changed. Figure 2 shows the XRD diffraction patterns of LSCO thin films post-annealed at 800

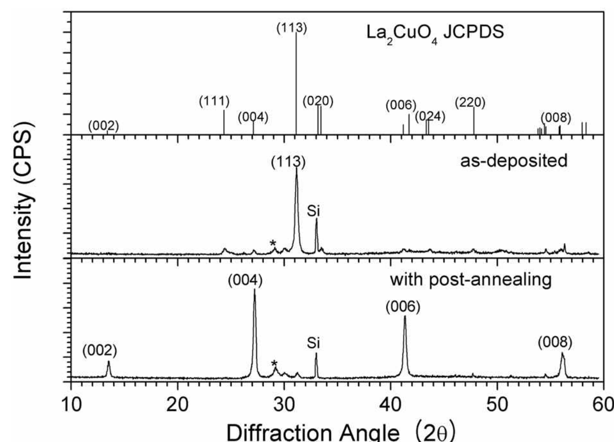

Figure 1. XRD patterns of $La_{2-x}Sr_xCuO_4$ ($x = 0$) deposited on SiO_2 layer: (a) as-deposited at 800 °C. (b) post-annealed at 700 °C after deposition at 500 °C.

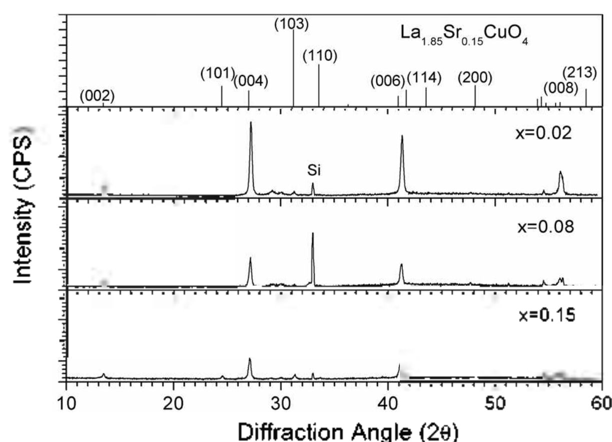

Figure 2. X-ray patterns of LSCO thin films post-annealed at 800 °C for 1 hr under oxygen atmosphere of 1000 mTorr after grown at 500 °C against Sr contents.

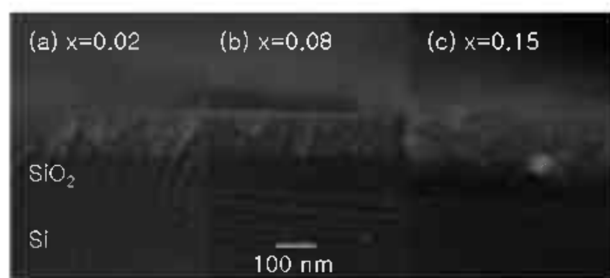

Figure 3. Cross-sectional view of SEM images of LSCO thin films against Sr contents.

after deposition at 500 °C on the SiO_2 layer according to a variation in the Sr content. The X-ray diffraction patterns indicate that all of the films are nearly single phases and are *c*-axis oriented. As shown in the SEM images in Figure 3, the LSCO thin films have a thickness of 100 nm with textured structures on the SiO_2 layer. The *c*-axis length (c_0) of thin films slightly increases from 13.12 Å to 13.20 Å as the Sr content increases, which is consistent with Sato's result.[7]

Figure 4 shows the Hall coefficient and carrier concentration of $La_{2-x}Sr_xCuO_4$ thin films against the Sr content at 300 K. The Hall coefficient is predicted to decrease almost in proportion to the reciprocal Sr content in the low-composition range. This behavior has been explained on the basis of the Mott-Hubbard picture in which Sr doping provides one mobile hole in the lower-filled band. The measured Hall coefficient in this study decreases more rapidly than expected from the model. The deviation from the reciprocal Sr content might be ascribed to the oxygen vacancies, according to Tagaki's suggestion.[8] The rapid decreases in the Hall coefficients are more similar to those of poly-crystalline LSCO films, where the *c*-axis is partially normal to the film surface, rather than to that of single crystalline film.[9] This indicates that LSCO thin films deposited in this study are not epitaxial but *c*-axis oriented polycrystalline films, which agrees with the SEM images of thin films.

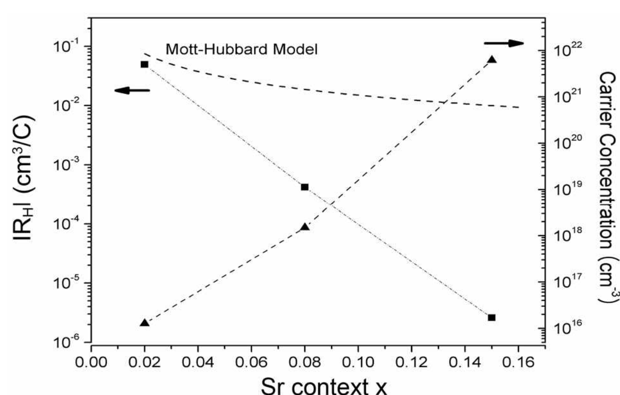

Figure 4. Hall coefficient and carrier concentraion of LSCO thin films against Sr contents.

In this study, the post-annealing process is certain to play a decisive role in the structural self-reorientation of a LSCO thin film after growth. Though no thermochemical data is available for crystal arrangement of a LSCO thin film, it might be interpreted that a (00*l*) orientation is thermochemically stable. As a result, the poorly crystallized thin film deposited at 500 °C is suggested to lead the *c*-axis orientation by self-organization during post-annealing at higher temperature.[10] Thermodynamic control in the formation of a LSCO thin film is not thought to be overly affected by substrate type. This suggests that it is possible to prepare *c*-axis oriented LSCO thin films on the common oxide substrates in order to fabricate the MIT devices, which should be addressed by further studies.

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