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Atomic Layer-by-Layer Deposition of La-Sr-Cu-O Films

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La-Sr-Cu-O films have been prepared as-deposited condition by an atomic layer-by-layer deposition technique in a high vacuum evaporation system with multi-electron-beam-gun sources. The film quality is crucially dependent on the substrate temperature, oxidation gas, and source material. It is found that the layer-by-layer successive deposition of the three elements is superior to the simultaneous deposition.

A lot of attempts for the preparation of cuprous oxide superconductor films have appeared primarily to accomplish an application accessibility, and also to control the material structure more or less artificially. Important achievements in the latter sense have been reported by Terashima et al.$^{1)}$ with a molecular-beam-epitaxy technique, and by Kawai et al.$^{2)}$ with a laser-ablation technique. They have succeeded in the "layer-by-layer deposition" of two-dimensional materials, such as Y-Ba-Cu-O or Bi-Sr-Ca-Cu-O systems. A less two-dimensional material, La-Sr-Cu-O system, however, has not yet been prepared by a complete layer-by-layer deposition (LBL) technique.$^{3)}$ In this paper, we report the construction of a relevant high vacuum evaporation system for an LBL deposition of La-Sr-Cu-O systems, and some preliminary but significant results on the characterization of the obtained films.

Our evaporation system is consisted of three independent electron-beam (EB) guns which can be operated by the feed-back signals from each corresponding thickness monitor (quartz oscillator, INFICON XTC). A schematic drawing of the vessel is shown in Fig. 1. $SrTiO_3$ crystal was mainly used for substrate in this experiment because of the similarity in the lattice parameters and thermal expansion coefficients between film and substrate. A substrate crystal was set under a silicon carbide heater which could raise the substrate temperature

(Ts) up to 800 °C. The oxidation process is especially important to obtain crystalline film in the preparation of oxide superconducting thin films. As the oxidizing reagent active species of oxygen, such as ozone, NO_2 or N_2O have been usually used.$^{4-6)}$ In our case oxidizing gas, O_2 or NO_2, was introduced through the feed-through-tube to the substrate surface during the deposition, and the gas pressure around the sample was maintained at $2\text{-}3*10^{-5}$ Torr. In order to keep the proper oxidizing gas pressure and the high enough vacuum around the EB-guns($\approx 1*10^{-5}$ Torr), a differential pumping system is set-in with the use of two turbo-molecular pumps (550 l/s for upper part and 280 l/s for lower part, respectively).

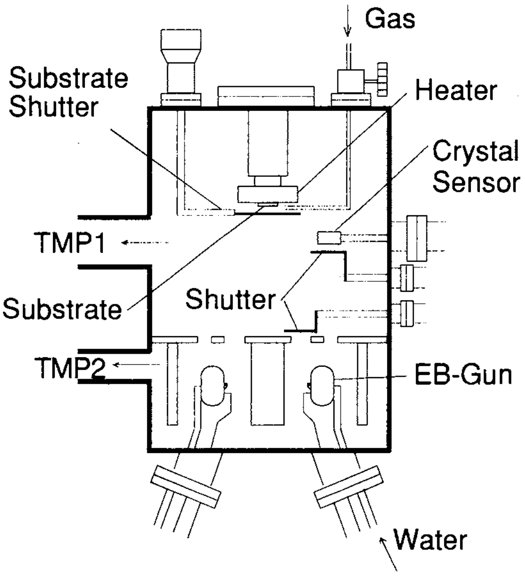

Fig. 1. A schematic drawing of the Layer-by-Layer Deposition vessel with a gas inlet and EB-Guns.

The evaporation-rate of each material was kept constant with regulating the EB-currents by the signals from each thickness monitor. The thickness of each layer was monitored by each quartz-oscillator and regulated by each air-pressure shutter between the EB-gun and substrate which is driven by the monitor signal. All system is fully automatically controlled by an NEC PC-9801 computer and each step of deposition is programmable in advance.

The structure of a film was analyzed at room temperature by an X-ray diffractometry (MAC Science MXP^3). The chemical composition was detected with an ICP analysis (Seiko Instruments Inc. SPS7000) and/or an X-ray micro-analysis (XMA, Hitachi S-450).

In order to know how high temperature is required enough for crystallization in this series of films, we applied the post-sintering for the La-Cu-O film which was prepared on the room temperature substrate ($SrTiO_3$(100)). The post-sintering was carried out for about 15 minutes at the temperature of 600-800 °C under the proper oxygen-gas flow. The composition of post-sintered La-Cu-O film was not totally 2-1-4 stoichiometry, but the 2-1-4 phase was clearly grown in the 700 °C -sintered sample. Therefore, the substrate temperature for as-grown crystalline film should be 700 °C or higher.

La-Sr-Cu-O thin films were fabricated as follows. Metallic copper was always used as the source of copper element, and as for lanthanum and strontium pure metals or their oxides. Each cycle of [Cu;0.1 nm, La;0.6 nm, and Sr;0.1 nm] was accumulated by 20-50 times on a $SrTiO_3$(100) substrate at the temperature of

600-800 °C with the average rate of 0.01 nm/s. Total thickness of a fabricated film was typically 10-30 nm.

O_2 or NO_2 was used as an oxidizing gas during a deposition with a flow rate of 0.5 cm^3/min. N_2O was less effective for the oxidizing and crystallizing process.

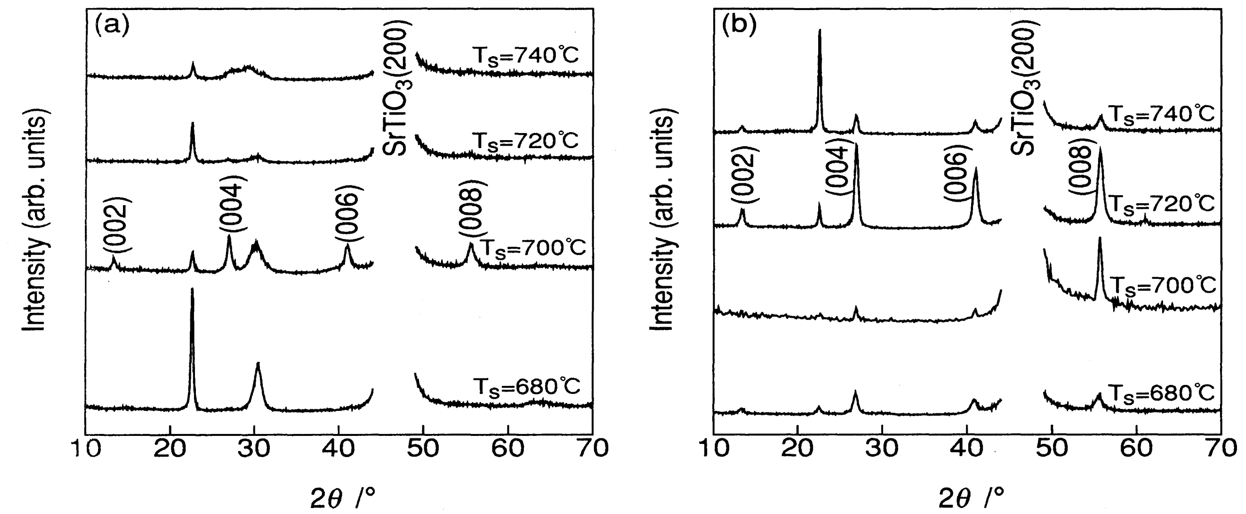

Fig. 2. Substrate-temperature dependence for the structure of La-Sr-Cu-O thin films grown by metal oxide evaporation for lanthanum and strontium. (a) Depostited with NO $_2$ and (b) with O_2. The intensity of each line can not always be compared with each other.

La-Sr-Cu-O film which was grown by pure metal evaporation showed no $La_{2-x}Sr_xCuO_4$ phase even when the substrate temperature was higher than 720 °C with NO_2 oxidation. This fact means that the pure metal evaporation for lanthanum and strontium is no longer favorable in our system.

Thus, we have tried metal oxide evaporation for lanthanum and strontium, and compared the oxidation and crystallization effect by O_2 and NO_2.

In the case of NO_2 oxidation, the optimum temperature was around 700 °C and the film was not only crystalline but also well oriented in c-

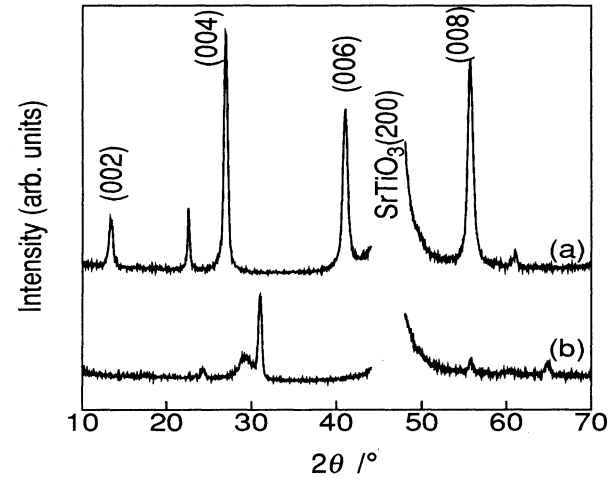

Fig. 3. X-Ray diffraction patterns of La-Sr-Cu-O films(as-grown). (a) Successive deposition and (b) simultaneous deposition. The pattern(a) is the same as the one at Ts=720 °C in Fig.2(b).

axis direction which is normal to the substrate plane, as shown in Fig. 2(a). These features were more evident for the O_2 oxidation case at a little higher substrate temperature, 720 °C, as shown in Fig. 2(b). Moreover, the chemical composition (stoichiometry) of this film (720 °C -grown) was almost single phase as $La_{2-x}Sr_xCuO_4$. The sample of higher temperature substrate (740 °C) showed rather less crystalline nature as shown in Fig.2. The diffraction line around 23° in Fig. 2 is assigned to substrate, $SrTiO_3$(100).

Thus, we can conclude that the optimum condition for $La_{2-x}Sr_xCuO_4$ film by atomic layer-by-layer deposition in our system is the following: The sequential unit of Cu;0.1 nm , La;0.6 nm, and Sr;0.1 nm should be evaporated from the sources of La_2O_3, SrO, and Cu-metal on to the $SrTiO_3$(100) substrate kept at 720 °C with O_2 gas oxidation.

The advantageous of the layer-by-layer successive deposition is quite evident if we compare the result with that of simultaneous deposition of each element. In Fig. 3 the comparison of X-ray diffraction patterns is shown for the films deposited under similar conditions except for a point that one was deposited successively and the other was simultaneously. In our evaporation system better result for simultaneous deposition could not be realized.

In summary we have found the optimum condition for the deposition of La-Sr-Cu-O films at atomic-level regulation. Next step is to develop this technique for further versatile, in structure and in composition, film fabrication so as to accomplish highly metallic and superconducting films.

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