

In-situ Optical Monitoring of Oxide Superconductor Growth for Layer-by-Layer Chemical Vapor Deposition

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We have investigated a novel method of in-situ optical diagnostics for layer-by-layer chemical vapor deposition (CVD) of oxide superconductor films. The variations of the optical reflection from the growing surface during the growth of films of CuO and YBaCuO are presented. This method can be used as a diagnostics tool to monitor (i) the atomic arrangement on the growing surface like RHEED oscillation and (ii) the surface chemistry; e.g., the decomposition of precursors, the surface adsorption/desorption of precursors, and the oxidization of metals.

1. INTRODUCTION

Atomic layer epitaxy (ALE) with built-in self-limiting growth mechanism[1] is the most promising method of crystal growth of device-quality oxide superconductor films with atomic-scale smooth surface for wafer-scale large uniformity. One of the advantages of chemical vapor deposition (CVD) is a variety of selections of precursors among which self-limiting adsorption can be found. Some basic results of experiments for atomic layer CVD of YBaCuO films[2, 3] have already been obtained. However, we have many problems yet to be solved. If we acquire in-situ monitoring method like RHEED oscillation in MBE, the progress towards implementation of ALE will be accelerated. In order to monitor the atomic layer growth in the low-pressure CVD environment, where electron beam methods, e.g., RHEED cannot be applied, optical diagnostics, e.g., surface photo absorption (SPA) [4] and reflectance difference spectroscopy (RDS) [5] originally developed for GaAs metalorganic CVD are suitable methods.

In this report, we propose a novel in-situ optical diagnostic method[6] for crystal growth monitoring of oxide superconductor films, and present results applied in layer-by-layer CVD of CuO and YBaCuO films. This optical diagnostics have two merits of monitoring; (i) the atomic arrangement on the growing surface like RHEED oscillation and (ii) the surface chemistry; e.g., the decomposition of precursors, the surface adsorption/desorption of precursors, and the

oxidization of metals.

2. EXPERIMENTAL

An experimental set-up for optical reflectance measurement equipped with a layer-by-layer CVD apparatus is shown in Fig. 1.

The light source is a laser diode with an emission wavelength of 780nm, the cw light power of approximately 5mW, and the spot size of approximately 2mm. A silicon photodiode is employed to detect the reflected light. The incident angle of the laser beam is 60°.

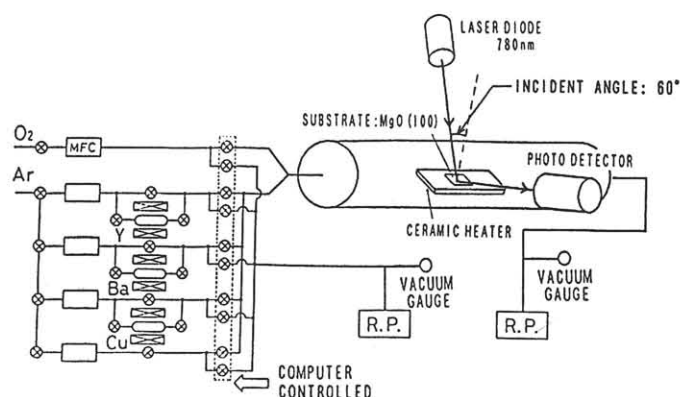


Figure 1. The layer-by-layer CVD apparatus equipped with the experimental set-up for the optical reflectance measurement.

Reactor chamber is a horizontal pyrex tube. Reactive pressure is about 1Torr. CVD precursors are β -diketonate complex, such as Y(DPM)_3 , $\text{Ba(DPM)}_2(\text{phen})_2$ and Cu(DPM)_2 , whose vaporizer temperature are 125–140°C, 180–185°C and 105–115°C, respectively. Temperatures of each vaporizer, gas transfer tubes, and a substrate holder are controlled independently. The supplies of argon carrier gases of each precursor, oxygen as an oxidizing agent, and argon as a purging gas are controlled by a computer program, where each flow rate is 200scm. Substrate temperature (T_{sub}) is varied from 350°C to 475°C. (100)MgO substrates are used in this study.

3. RESULTS AND DISCUSSION

Figure 2 shows the sequential chart of the pulsed gas supply of Cu(DPM)_2 and oxygen, the simplest sequential system, and the variation of the optical reflectance on the growing surface held at $T_{\text{sub}}=450^\circ\text{C}$. Purging argon gas was inserted between every supply of Cu(DPM)_2 and oxygen. Significant change of the reflectance signal were observed when Cu(DPM)_2 or oxygen were introduced, while no appreciable change was observed when purging argon was introduced. When Cu(DPM)_2 was supplied, the reflectance signal once decreased and then increased until a saturated value. The transition rate of the reflectance corresponds to the adsorption rate of Cu(DPM)_2 or the decomposition rate to Cu. When oxygen was supplied, the reflectance signal decreased abruptly and then returned to the almost initial value. The X-ray diffraction analysis for films with various oxidization time clarified that oxidization of Cu film proceed with increasing oxidization time and perfect oxidization, CuO(111) phase, was obtained when the reflectance signal reached to the steady-state value. The maximum amplitude of the reflectance

ratio $(\Delta R/R_{\text{MgO}})_{\text{max}}$ was about 60%, where R_{MgO} denotes the reflectance of MgO substrate. The variation of the reflected light signal mimics RHEED oscillation. Cu-stabilized surface has higher reflectivity than oxide surface. The average deposition rate for each cycle of Cu(DPM)_2 and oxygen was 2.7nm, equivalent to about 10 molecular-layers of CuO .

We note the transition time of the reflectance variation between the start of the metal precursors or oxygen supply and the arrival at the saturated value. The reaction rate, which is the reciprocal of the transition time, when Cu(DPM)_2 introduced increases with temperature at low T_{sub} ($<380^\circ\text{C}$), and decreases at high T_{sub} ($>380^\circ\text{C}$). The former process, which has a positive activation energy, may be determined by the thermal decomposition or the adsorption of Cu precursors. The latter process, which has a negative activation energy, may be determined by the desorption of Cu precursors. The reaction rate when oxygen introduced increases with temperature.

Figure 3 shows the sequential chart of the pulsed gas supply of Y(DPM)_3 , $\text{Ba(DPM)}_2(\text{phen})_2$, Cu(DPM)_2 and oxygen, along with the order of metal composition of c-axis $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystal structure, and the variation of the optical reflectance on the growing surface held at $T_{\text{sub}}=450^\circ\text{C}$. Purging argon was supplied between every supply of Y(DPM)_3 , $\text{Ba(DPM)}_2(\text{phen})_2$, Cu(DPM)_2 and oxygen. The phenomena, when Y(DPM)_3 , $\text{Ba(DPM)}_2(\text{phen})_2$, Cu(DPM)_2 or oxygen were introduced, were also similar to those of Cu(DPM)_2 and oxygen. $(\Delta R/R_{\text{MgO}})_{\text{max}}$ of this system was about 130%. Y-, Ba- and Cu-stabilized surface have higher reflectivity than oxide surface. Ba-stabilized surface has higher reflectivity than Y- and Cu-stabilized surface. Moreover, Cu-stabi-

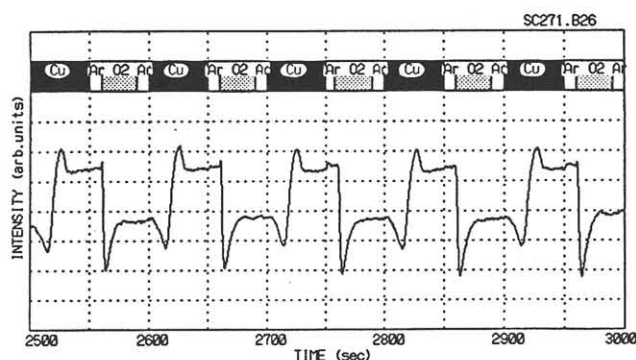


Figure 2. The oscillation of the reflected light signal with the sequential supply of Cu(DPM)_2 and oxygen.

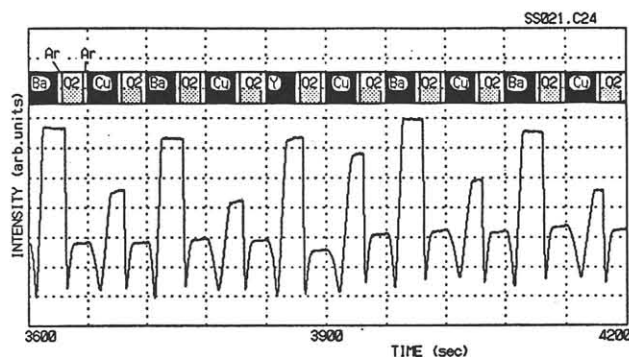


Figure 3. The oscillation of the reflected light signal with the sequential supply of Y(DPM)_3 , $\text{Ba(DPM)}_2(\text{phen})_2$, Cu(DPM)_2 and oxygen.

lized surface on Y-stabilized surface has higher reflectivity than on Ba-stabilized surface. The transition time to reach a saturated value is the shortest for $\text{Ba}(\text{DPM})_2(\text{phen})_2$ cycle. These results suggest that the difference of the adsorbed precursors on the growing surface, not the bulk, is detected by the change of reflectance signals. Each value of the saturated reflectance is determined by refractive coefficient with adsorbed precursors on the growing surface.

4. CONCLUSIONS

We have observed the variation of the optical reflection from the growing surface during the layer-by-layer CVD of oxide superconductors. It is very important to note that these measurements mentioned above provide information about dynamic processes of surface reactions. It is very interesting to note that these phenomena have very big signals that can be observed even with the naked eyes.

This novel method can be used as a diagnostic tool of monitoring the atomic arrangement on the growing surface like RHEED oscillation. Dynamic behaviors of the surface chemical reactions; e.g., the decomposition of precursors, the surface adsorbed/desorbed structure of precursors, and the oxidization of metals can be characterized from the transient behaviors of the reflectance signal.

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