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Fabrication of $YBa_2Cu_3O_{7-x}$ Superconducting Thin Films by Organometallic Chemical Vapor Deposition

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Thin Y–Ba–Cu–O films were fabricated by OMCVD using the tetramethylheptanedione complexes as source materials, and the effects of substrate temperature on crystallographic, electrical, and magnetic properties were examined. Thin films fabricated above 650°C mainly have the orthorhombic $YBa_2Cu_3O_{7-x}$ structure. But, the film fabricated at 650°C reveals the semiconducting property. Thin films fabricated at 700, 750, and 800°C show the superconducting transition. The respective T_c (onset) and T_c ($R = 0$) for these films were 84 and 60 K, 85 and 78 K, and 84 and 82 K. The Meissner effect was confirmed for the film grown at 800°C.

1. Introduction

In 1987, M. K. Wu *et al.* (*1*) reported that $YBa_2Cu_3O_{7-x}$ was an oxide superconducting material whose critical temperature was about 90 K. Since then, much research has been conducted on the family of this material due to the fact that it can be used at the boiling point of liquid nitrogen, making it highly promising for practical use. Studies in thin film technology for this material has been especially concentrated in an attempt to establish applications to the electronics field. The physical vapor deposition such as MBE (*2*), vacuum evaporation (*3*), and sputtering (*4*) have been employed to prepare superconducting thin films from the initial stage. In addition, chemical vapor deposition , in which metal halides are used as source materials, has also been studied (*5*). However, organometallic chemical vapor deposition (OMCVD) has not been employed at the initial stage, since there was no suitable source materials.

Recently, research has shown that β-diketone complexes of Y, Ba, and Cu are suitable source materials for OMCVD of $YBa_2Cu_3O_{7-x}$ thin films (*6–11*). In these studies, thin films with the same excellent superconducting properties as those of ceramic materials could be prepared. However, high temperatures over 780°C were required for preparation. At this temperature, good electric junction between this material and a semiconductor is not possible since reaction proceeds between these materials. Therefore, a concerted effort is required to lower substrate temperature in OMCVD. On the basis of this necessity, the authors have been conducting research on low temperature fabrication technology. This paper reports on the influence of sub-

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strate temperature on crystallographic, electrical, and magnetic properties of Y–Ba–Cu–O film.

2. Experimental

The configuration of the OMCVD apparatus is shown in Fig. 1. The reactor was a quartz tube (16 mm ϕ × 250 mml) and was heated by a conventional electric furnace. $SrTiO_3$ single crystal plates, whose surface plane was (100), were used as the substrates. Source materials of the 2,2,6,6,-tetramethyl-3,5,-heptanedione (THD) complexes of Y, Ba, and Cu ($Y(THD)_3$, $Ba(THD)_2$, and $Cu(THD)_2$) were purchased from Tori Chemical Laboratory, Inc., and used without any pretreatment. These source materials were sublimated in Ar carrier gas and introduced to a reactor. The sublimation temperature and the Ar flow rate for the source materials were the following: $Y(THD)_3$: 110°C, 50 ml/min; $Ba(THD)_2$: 240°C, 50 ml/min; and $Cu(THD)_2$: 115°C, 50 ml/min. Oxygen was mixed with the source gas just before the reactor. The flow rate of O_2 was kept at 100 ml/min, and the pressure during deposition was kept at 10 mmHg. After deposition, thin films were cooled in an O_2 atmosphere at a pressure of 760 mmHg. The average cooling rate was 20°C/min. Substrate temperature was determined by measuring the temperature of substrate surface using a thermocouple.

The thickness of the films were measured by a stylus surface profilometer (Tencor Instruments, Alpha-step 100). The crystallographic characterization of thin films was carried out by scanning electron microscope and X-ray diffraction analyses. The composition was defined by a wet chemical analysis: thin films were dissolved in hydrochloric acid and concentrations of Y, Ba, and Cu were measured by the inductively coupled plasma spectroscopy. The electrical property was examined by the conventional four-probe method and the magnetic property was studied by means of a SQUID-type magnetometer (Quantum Design Corp).

3. Results and Discussion

Thin films were deposited at 800, 750, 700, and 650°C for 1 hr under the above-

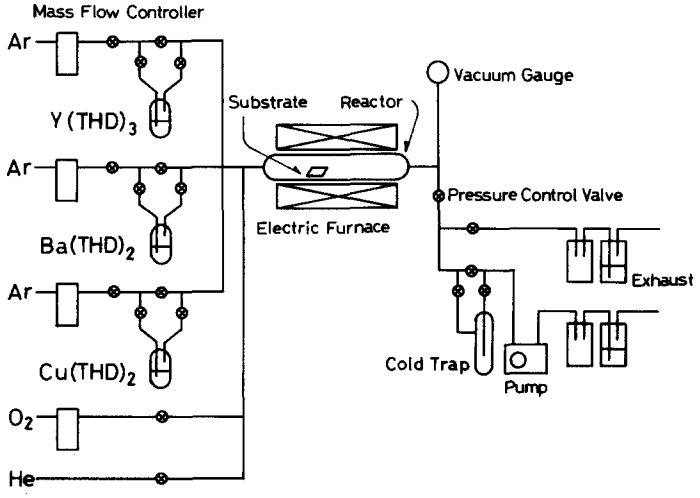

FIG. 1. Schematic diagram of OMCVD apparatus.

mentioned conditions. The thicknesses of these films were 1.3, 0.92, 0.83, and 0.55 μm, respectively. This result indicates that the deposition rate is strongly influenced by substrate temperature.

The scanning electron micrographs of these films are shown in Fig. 2. Thin film fabricated at 800°C consisted of rectangular plate-like crystallites that had merged with each other. In addition, large crystallites, which projected from the surface, were also observed. Furthermore, crystallite size reduced upon lowering the substrate temperature.

The X-ray diffraction patterns of these films are shown in Fig. 3. All the detected diffraction peaks could be indexed to those of orthorhombic $YBa_2Cu_3O_{7-x}$ and substrate. This indicates that fabricated films mainly consisted of orthorhombic $YBa_2Cu_3O_{7-x}$. The lattice constants of these films were defined as a = 3.82 Å, b = 3.90 Å, and c = 11.7 Å from an evaluation, in which the X-ray diffraction analyses of thin films grown on $SrTiO_3$(110) and MgO(100) at the same condition were considered.

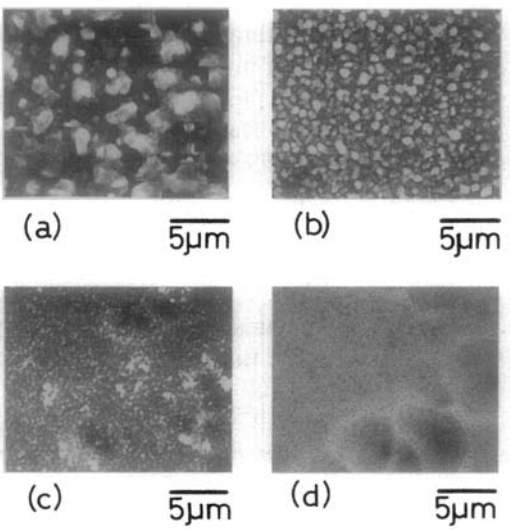

FIG. 2. Scanning electron micrographs of films fabricated at (a) 800, (b) 750, (c) 700, and (d) 650°C.

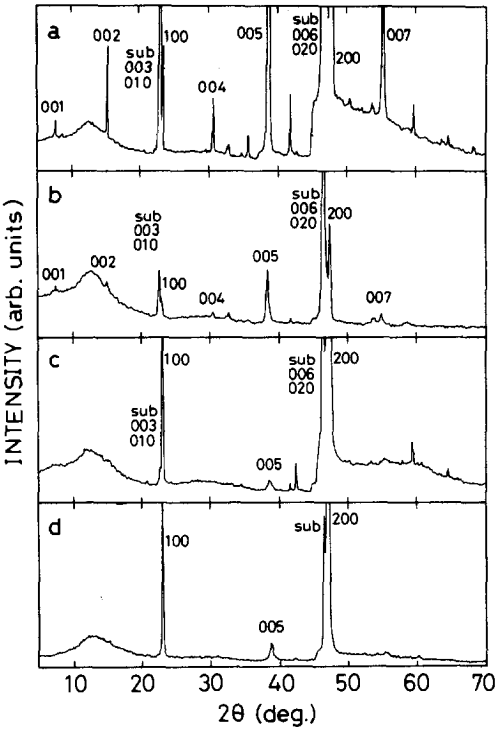

FIG. 3. X-ray diffraction patterns of films fabricated at (a) 800, (b) 750, (c) 700, and (d) 650°C.

Since strong diffraction peaks of (00l) were detected, it was determined that thin films deposited at 800°C had a preferred orientation in which the crystallographic c-axis was perpendicular to the substrate surface plane. In addition, since strong peaks of (h00) were detected, it was determined that preferred growth, in which <100> was perpendicular to the substrate surface plane, was achieved when the substrate temperature was lowered. Furthermore, studies of the full width at half-maximum (FWHM) clarified that crystallographic quality was improved by raising the substrate temperature.

The compositions of films deposited at 800, 750, 700, and 650°C were found to be $Y_{1.0}Ba_{2.1}Cu_{4.2}O_{7-x}$, $Y_{1.0}Ba_{1.9}Cu_{3.1}O_{7-x}$, $Y_{1.0}Ba_{2.1}Cu_{3.3}O_{7-x}$, and $Y_{1.0}Ba_{1.6}Cu_{2.6}O_{7-x}$, respectively. The deviation from the nor-

mal composition should indicate the existence of an extra phase even though an extra peak was not found in the diffraction patterns.

The dependence of resistivity on temperature for these thin films is shown in Fig. 4. The resistivity of a film fabricated at 800°C decreased linearly with decreasing temperature, which is the same as that of metal materials. The onset temperature and zero-resistivity temperature, T_c(onset) and $T_c(R = 0)$, were 84 and 82 K, respectively. Thin film fabricated at 750°C also showed metallic behavior at a higher temperature range and also showed the superconducting transition. The T_c(onset) of this film was 85 K and the $T_c(R = 0)$ was 78 K. Resistivity of film fabricated at 700°C increased with decreasing temperature at a higher temperature range, as with semiconductors. However, this film displayed the superconducting transition. The T_c(onset) was 84 K and $T_c(R = 0)$ was 60 K. On the other hand, thin film fabricated at 650°C clearly displayed the semiconducting property in the temperature range from 4.2 to 300 K.

The degrees of sintering, phase separation, and grain orientation were suggested as the reasons for the differences in the electrical properties (*12,13*). In the case of this study, the electrical properties were thought to be under the influence of the degree of crystallization, especially the degree of ordering along the *c*-axis. This is because thin films, which indicated clear (00*l*) diffraction peaks and small FWHM for (005) diffraction peaks, showed excellent electrical properties. It is very interesting that T_c(onset) was not influenced by the substrate temperature even though $T_c(R = 0)$ and the temperature dependence of resistivity above T_c(onset) were strongly influenced by the substrate temperature. However, the reason is unknown at this stage.

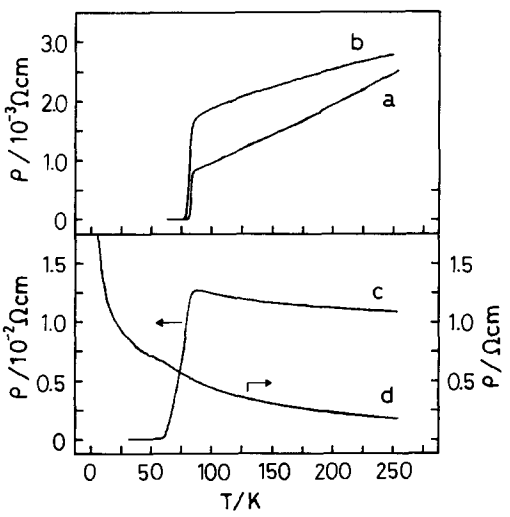

FIG. 4. Effect of substrate temperature on electrical properties: (a) 800, (b) 750, (c) 700, and (d) 650°C.

The magnetic susceptibility of the thin film fabricated at 800°C is shown in Fig. 5. The magnetic susceptibility was measured with decreasing sample temperature from 250 to 4.2 K under 10 G of magnetic field. It was found that magnetic susceptibility obtained a negative value below 84 K. This result coincided with the electrical study in which the T_c(onset) was found to be 84 K. This results also indicates that the Meissner effect was confirmed for this thin film.

In the OMCVD literature (*5–11*) the lowest substrate temperature for preparing superconducting thin films was reported by H. Abe *et al.* (*11*). They reported that superconducting thin films could be grown on MgO(100) substrates and $SrTiO_3$(110) substrates at 780°C. For the MgO substrates, the T_c(onset) was 85 K and the $T_c(R = 0)$ was 65 K. The $T_c(R = 0)$ for the $SrTiO_3$(110) substrates was 20 K. In this study, superconducting thin films were grown on $SrTiO_3$(100) at 700°C. In addition to this result, it was also found that superconducting thin films could be grown on $SrTiO_3$(110) and MgO(100) at 700°C. T_c(onset) for these films were about 84 K, and $T_c(R = 0)$ were 60, and 66 K. From these results, it could be found that the thin films grown in this study had excellent elec-

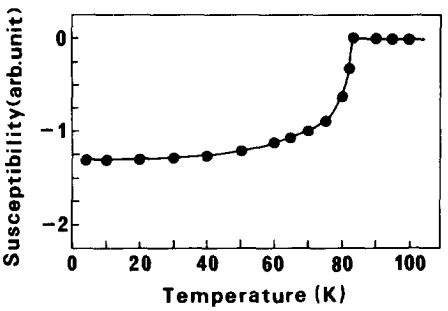

FIG. 5. Magnetic susceptibility of thin film fabricated at 800°C.

trical properties and that electrical properties were influenced with substrate. The precise results on the substrate effect will be reported elsewhere.

It was thought that the improvement in T_c was due to the configuration of the OMCVD apparatus used in this study. In this apparatus, the substrate was located in the middle of the reactor. As a result, the source materials were heated sufficiently before reaching the substrates.

Recently, new methods for growing superconducting thin films at low substrate temperature were reported. Superconducting thin films were prepared at 560°C by rf-magnetron sputtering (*13*), at 400°C by plasma assisted laser deposition (*14*), at about 650°C by reactive plasma evaporation (*15*), and at 650°C by pulsed laser deposition (*16*). Compared to these substrate temperatures, the lowest substrate temperature in this study, 700°C, is high. However, this study may be characterized by the fact that a high energy state such as the plasma state or irradiation of the excimer laser was not employed. Furthermore, these reports seem to suggest that low temperature growth of superconducting thin films by OMCVD can be achieved by employing a high energy state.

4. Conclusion

Thin Y–Ba–Cu–O films were fabricated by OMCVD using the THD complexes of each metal element as source materials in the temperature range from 650 to 800°C. The influence of fabrication temperature on crystallographic, electrical, and magnetic properties was clarified. All the thin films fabricated in this temperature range had the orthorhombic $YBa_2Cu_3O_{7-x}$ structure. In addition, thin films fabricated at 800°C had a preferred orientation in which the crystallographic *c*-axis was perpendicular to the substrate surface plane, and thin film fabricated at 650°C had a preferred orientation in which <100> was perpendicular to the substrate surface plane. Thin film fabricated at 650°C showed semiconducting behavior, even though it had the orthorhombic $YBa_2Cu_3O_{7-x}$ structure. On the other hand, thin films fabricated at a temperature higher than 700°C displayed the superconducting transition. The respective T_c(onset) and $T_c(R = 0)$ were 84 and 82 K for the film fabricated at 800°C, 85 and 78 K for the film fabricated at 750°C, and 84 and 60 K for the film fabricated at 700°C. The T_c(onset) did not depend on the fabrication temperature, but the $T_c(R = 0)$ depended strongly on the fabrication temperature. Furthermore, the Meissner effect was confirmed for the film fabricated at 800°C.

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