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Unit-by-Unit Process of $Bi_2Sr_2CuO_y$ Film Growth with Molecular Beam Epitaxy by Separated Evaporation/Oxidation/Crystallization Technique

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Thin films of $Bi_2Sr_2CuO_y$ were grown with MBE (Molecular Beam Epitaxy) by the separated evaporation/oxidation/crystallization technique on a MgO (100) substrate. The proposed technique is the unit-by-unit process consisting of three steps: multilayer deposition of (Bi-Sr-Cu-Sr-Bi) × 2, low-temperature oxidation (300°C) in low concentration O_3 (O_2/O_3(0.3%)) atmosphere (5×10^{-5} Torr) and crystallization (750°C, 1×10^{-8} Torr). After growth of ten units, clear streaks on the RHEED pattern showing the twin structure and a fairly fine X-ray diffraction pattern were observed.

KEYWORDS: superconductor, Bi-Sr-Cu-O system, MBE, RHEED

The superconducting compounds of the Bi system have been intensively studied by means of various fabrication techniques.[1-4] One of the most interesting fabrication techniques is molecular beam epitaxy (MBE),[5-8] for its potential in high-quality epitaxial film growth under nonequilibrium conditions. Furthermore, in MBE, the unit-by-unit process[7] is attractive for control of Cu–O multilayer growth which affects the film conductivity. In general, a high-temperature superconductor is a short-coherence-length material, so a mono-unit surface and interface flatness are necessary for the heterojunction tunneling devices. Therefore, we focused on the unit-by-unit process. We referred to the process reported by Watanabe *et al.*,[7] the unit-by-unit process of $Bi_2Sr_2CuO_y$ grown by MBE using NO_2 as the oxidizing agent at 300°C, 2×10^{-7} Torr on a $SrTiO_3$(100) substrate. First, layers of Sr/Cu/Sr are evaporated and oxidized with NO_2, 2×10^{-7} Torr. Next, repetition of Bi/Bi/Sr/Cu/Sr evaporation and oxidation are carried out. In our process, the layer evaporation sequence is different. First, layers of Bi/Sr/Cu/Sr/Bi are evaporated onto the MgO(100) substrate. Then oxidation is carried out using the O_2/O_3(0.3%) gas, 5×10^{-5} Torr.

In this letter, we propose a separated evaporation/oxidation/crystallization technique. We also examine the oxidation and crystallization process conditions. The technique proposed is a unit-by-unit process consisting of three steps: (1) deposition ((Bi-Sr-Cu-Sr-Bi) × 2, 200°C), (2) oxidation (300°C) in low-concentration O_3 atmosphere (O_2/O_3(0.3%)), 5×10^{-5} Torr and (3) crystallization at 750°C in 1×10^{-8} Torr.

The RHEED patterns of the films with various process conditions and X-ray diffraction patterns after growth of ten units are studied.

Figure 1 shows the timing chart of the process under study. The MgO (100)-oriented substrate was cleaned for

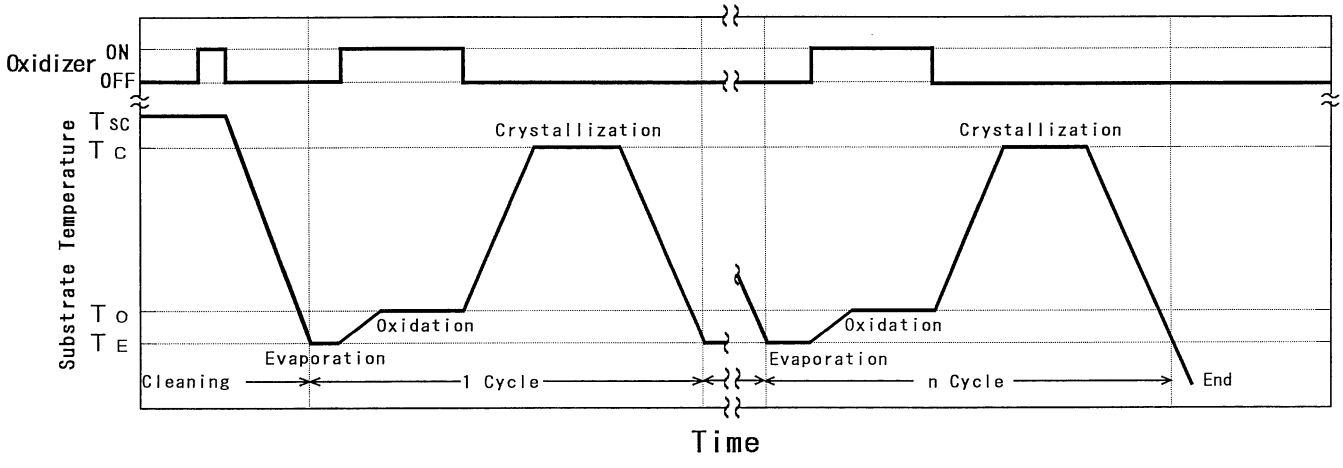

Fig. 1. Timing chart of proposed separated evaporation/oxidation/crystallization technique, where T_A is the cleaning temperature (800°C), T_O the oxidation temperature (300°C), T_E the evaporation temperature (200°C) and T_C the crystallization temperature (750°C).

one hour at 800°C and pressures below 1×10^{-8} Torr, and for five minutes at 800°C, 5×10^{-5} Torr in O_2 atmosphere. The metal layers of (Bi-Sr-Cu-Sr-Bi) × 2 were evaporated onto the cleaned substrate. Substrate temperature was kept at 200°C, 1×10^{-8} Torr during metal evaporation. The thickness of each metal layer was controlled to the accuracy of monolayer thickness using a thickness monitor. In particular, we empirically determined the suitable amount of Bi from the preliminary experiments under various conditions of evaporation and film formation using XPS measurement. In the oxidation process, low concentration O_3 gas of O_2/O_3(0.3%) was used. The typical oxidation conditions were 300°C for one hour, 5×10^{-5} Torr. For crystallization, the sample was kept at 750°C for one hour, 1×10^{-8} Torr. No oxidizer was introduced during the crystallization. The next units are grown by the repetition of the evaporation/oxidation/crystallization process.

This process was carried out with MBE equipment. The MBE equipment used was the ANELVA MBE-620 system. The growth chamber was equipped with Knudsen cells (PBN) of Bi, Sr, Cu and Ca an O_2-introducing port, cryopump (1600 *l*/s), Ti sublimation pump and RHEED system. Deposition rate was monitored by the crystal thickness monitor. The exhaust backpressure was about 10^{-10} Torr. The analysis chamber was connected to the growth chamber through the loading chamber, so the samples were analyzed without breaking the vacuum. The analysis chamber was equipped with the XPS (Shimadzu ASIX-1000) apparatus.

Experimental results are as follows. Before crystallization, the layer was evaluated using X-ray photoelectron spectroscopy (XPS).[9-11] The layer was estimated from the intensity of Cu-2p satellite peaks, to have oxidized adequately. Even for low-temperature oxidation (200~300°C) in low-concentration O_3 atmosphere, sufficiently large Cu-2p satellite peaks were observed. High temperature and strong oxidizing gas were not necessary to oxidlze Cu in the unit layer in this technique.

Figure 2 shows the RHEED pattern change of the MgO[100] azimuth during the growth of the first unit crystal. The RHEED pattern of the MgO substrate after cleaning is shown in Fig. 2(a). After the evaporation of (Bi-Sr-Cu-Sr-Bi) × 2, a halo appeared, as shown in Fig. 2(b). Immediately after the oxidation, the halo still remained, as shown in Fig. 2(c). When the temperature reached 500°C, the RHEED pattern changed from halo to rings, as shown in Fig. 2(d). When the temperature rose to 700°C, the RHEED pattern became spotlike, as shown in Fig. 2(e). After the temperature was raised to 750°C and kept there for one hour, the RHEED pattern changed to clear streaks which indicate the twin structure,[12,13] as shown in Fig. 2(f). The RHEED pattern gradually changed with increase of the total layer thickness. After growth of the first unit, the RHEED pattern showed the twin structure; however, its intensity was very weak.

Figures 3(a) and 3(b) show the RHEED patterns of the films from the MgO[100] and [110] azimuths, respectively, after growth of ten units. The lattice parameter calculated from Fig. 3(b) was 0.543 nm, which is in good

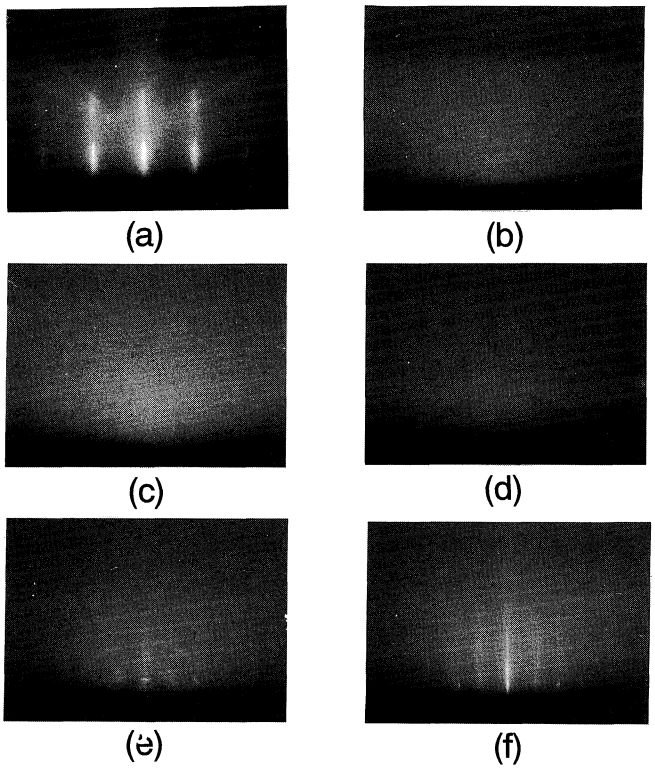

Fig. 2. RHEED pattern change during the growth of the first unit crystal. (a) After cleaning. (b) After evaporation. (c) After oxidation. (d) After substrate temperature was raised to 500°C. (e) After substrate temperature was raised to 750°C. (f) After crystallization.

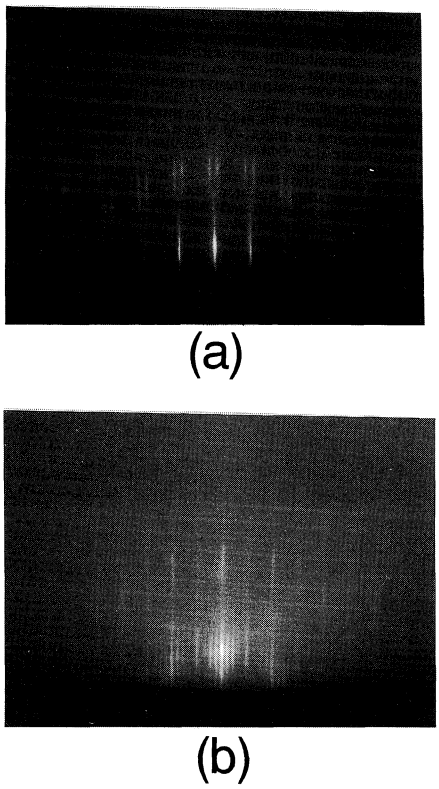

Fig. 3. RHEED patterns after crystallization of ten-units growth in vacuum. (a) MgO substrate [100] azimuth, (b) MgO substrate [110] azimuth.

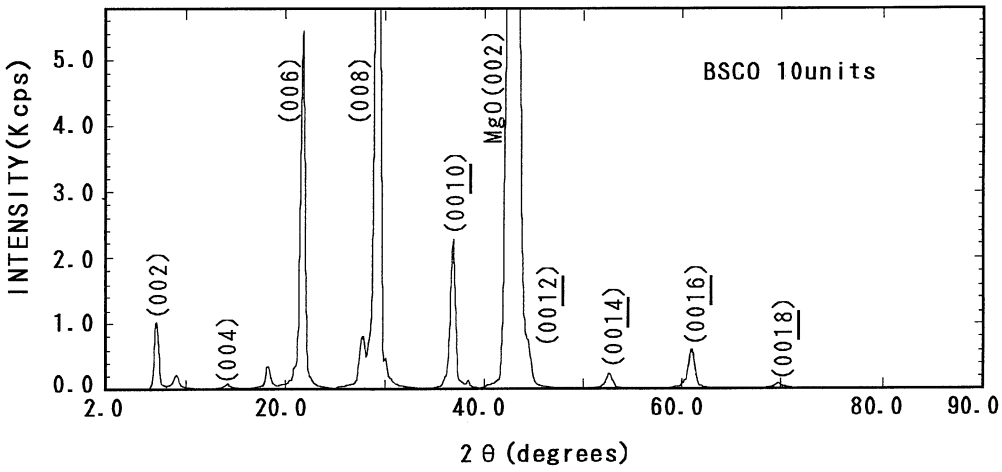

Fig. 4. X-ray diffraction pattern of the films with ten-unit growth.

agreement with the *a*-axis of $Bi_2Sr_2CuO_y$. The satellite peaks of the MgO[110] azimuth shown in Fig. 3(b) indicate the long-period structure of $b=4.8a$. These clear RHEED patterns indicate flat and good crystal growth of a perovskite structure. Hence, vacuum crystallization is effective in improving the crystal quality.

Figure 4 shows the X-ray diffraction pattern of the films with ten-unit growth. The estimated lattice constant of the *c*-axis from these peaks was about 2.4 nm. The large peak of 42.9° was diffraction of MgO(002). There were small peaks around 9.2°, 18.4° and 28.0°. These peaks indicate that the *c*-axis length is 1.8 nm. Without the crystallization process, these peaks were not observed. The peak widths at half-height of (006) and (008) were 0.56° and 0.59°, respectively. Although these values are inferior to results in another paper,[6] better films will be realized through process optimization. The chemical composition of the films, which was indicated by multiplication of the area of XPS signal intensity and the sensitivity coefficient, was $Bi_{2.0}Sr_{1.2}Cu_{0.6}O_{3.5}$. Superconductive characteristics were not observed in these films. Further optimization will be attempted in the fabrication of superconducting films.

In conclusion, we proposed the separated evaporation/oxidation/crystallization technique using MBE on a MgO (100) substrate. The main features of this process are unit-by-unit growth, low-temperature oxidation (in low-concentration O_3 atmosphere) and crystallization in an atmosphere different from that of the oxidation step. Good RHEED patterns were observed after ten-unit growth. These patterns indicate the flat-layer growth of $Bi_2Sr_2CuO_y$. Also, a fairly fine X-ray diffraction pattern was observed.

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