

Synthesis of Superconducting Thin Film by Molecular Beam Epitaxy

M. Ogiwara, N. Toda, T. Yamada and H. Abe

Research and Development Group, Oki Electric Industry Co., Ltd.
550-5 Higashiasakawa-cho, Hachioji-shi, Tokyo 193, Japan

BiSrCaCuO and BiBaRbO superconducting thin films were prepared by molecular beam epitaxy using distilled ozone. Growth temperature of the BiSrCaCuO thin film was decreased to 600 °C by sequential evaporation with shutter control in average growth rate of ~ 0.15 Å/s. Growth of BiSrCaCuO by sequential control of distilled-ozone-feeding in sequential evaporation was tested. The BiBaRbO thin film with superconducting transition temperature ~25K was synthesized on MgO(100) at substrate temperature ~370 °C.

1. INTRODUCTION

Heteroepitaxial growth of the oxide superconductor on the semiconductor is one of interesting techniques for device application. In this respect, growth temperature of the superconducting thin film should be as low as possible. Formation of the BiSrCaCuO (BSCCO) superconducting thin films by molecular beam epitaxy (MBE) has been studied extensively [1]. Decrease of the growth rate of coevaporation is one possibility to decrease growth temperature (T_s). Sequential evaporation technique is suitable for growth of a layered structure such as BSCCO and would be useful for device application [1]. This technique controlled on a layer by layer basis would be also suitable for low temperature growth. Growth of BSCCO at 300 °C was carried out by Watanabe et al. by oxidation with NO₂ after sequential evaporation of metal monolayers [2]. Timing of oxidation is one of important factors for low temperature growth of a crystal structure [2]. This gives us motivation to carry out sequential control of oxidation-gas-feeding in sequential evaporation of metal layers. The BaRbBiO (BRBO) is one of the promising materials because of much lower T_s compared to BSCCO [3]. In this paper, we report synthesis of the BSCCO thin films at $T_s < 700$ °C by MBE coevaporation and sequential evaporation using distilled ozone (O₃). A preliminary results in sequential control of O₃-feeding in sequential evaporation is also described. Preparation of the BRBO superconducting thin film at $T_s \sim 370$ °C by MBE was reported.

2. EXPERIMENTAL

2.1 Decrease of T_s for BSCCO growth

The BSCCO superconducting thin films were formed on MgO(100) substrates by MBE using O₃. The growth rate was 2 ~ 1 Å/s for

coevaporation at $T_s < 700$ °C. The BSCCO thin films were also grown by sequential evaporation. Sequence of Bi/Sr/Cu/Ca/Cu/Sr/Bi was repeated (60 times). The evaporation period and the period between each evaporation was 5 s. Beam flux intensity for sequential evaporation was the same as that for coevaporation with the growth rate of ~ 1 Å/s. This intensity leads roughly to a monolayer evaporation for each metal and the average growth rate of ~ 0.15 Å/s.

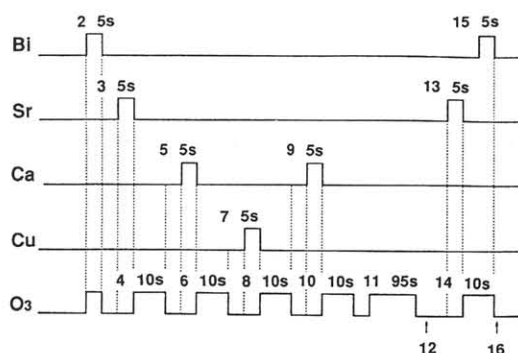


Figure 1 Diagram of sequential control of O₃-feeding in sequential evaporation.

2.2 Sequential control of O₃

Figure 1 shows a diagram of sequential control of O₃-feeding in sequential evaporation. Sequence of Bi/O₃/Sr/O₃/Cu/O₃/Ca/O₃/Cu/O₃/Sr/O₃/Bi/O₃ was carried out at $T_s \sim 650$ °C. O₃ and Bi flux were simultaneously introduced onto the SrTiO₃(100) (STO) substrate. Beam flux intensity of the metal sources was the same as that for coevaporation with the growth rate of ~ 1 Å/s. The patterns of reflection high energy electron diffraction (RHEED) during one sequence were observed.

2.3 BRBO preparation

The BRBO thin films were formed on the MgO(100) substrates at $T_s \sim 370^\circ\text{C}$ by MBE using O₃, Bi, Ba and Rb₂O sources were used. T_s was calibrated at the melting points of Bi ($\sim 271^\circ\text{C}$) and In ($\sim 156^\circ\text{C}$). The average growth rate of the BRBO thin film was $\sim 20 \text{ \AA/min}$, and film thickness was $\sim 700 \text{ \AA}$. The X-ray diffraction (XRD) patterns of the thin films and the resistance-temperature ($R(T)$) curves were measured.

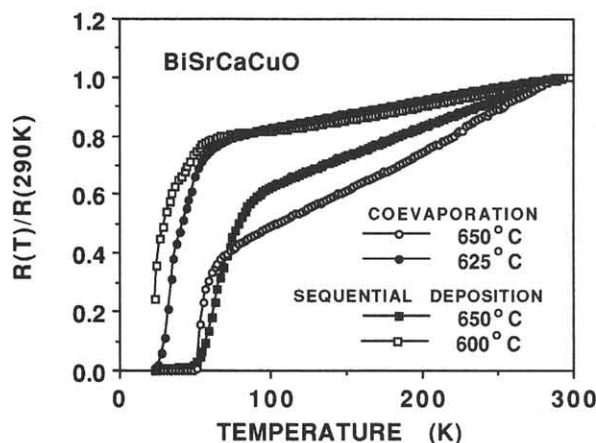


Figure 2 $R(T)$ -curves of the BSCCO thin films formed by coevaporation and sequential evaporation.

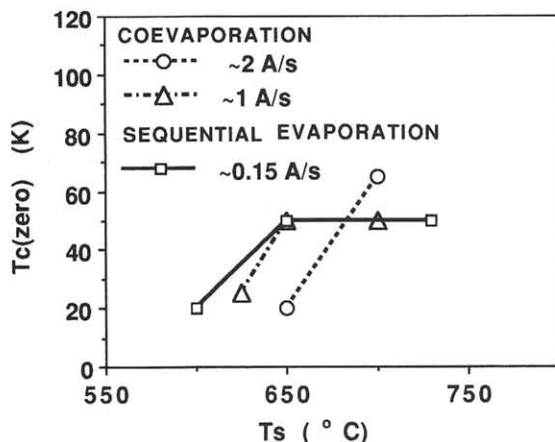


Figure 3 $T_c(0)$ as a function of T_s .

3. RESULTS

3.1 BSCCO superconducting thin film

The XRD patterns of the BSCCO thin films show that they are mainly c-axis oriented thin films of 30 Å-phase. Figure 2 shows $R(T)$ curves of the BSCCO thin films formed at $T_s \sim 650^\circ\text{C}$ and 625°C by coevaporation and $T_s \sim 650^\circ\text{C}$ and 600°C by sequential evaporation. The onset temperature of superconducting transition of the thin film grown at 650°C by sequential evaporation is higher than that by coevaporation although superconducting transition temperatures for zero resistance ($T_c(0)$) are identical ($T_c(0) = 50\text{K}$). $T_c(0)$ as a function of T_s was summarized in Fig. 3. Circles, triangles and squares were indicate $T_c(0)$ for the growth rates of $\sim 2 \text{ \AA/s}$, $\sim 1 \text{ \AA/s}$ and $\sim 0.15 \text{ \AA/s}$. Decreasing the growth rate from $2 \text{ \AA/s}$ to $1 \text{ \AA/s}$ lead to decreasing T_s by 625°C . T_s was reduced to 600°C by sequential evaporation with ~ 0.15

Å/s. Both factors of different growth process of sequential evaporation from coevaporation and the reduced growth rate would contribute to decrease T_s .

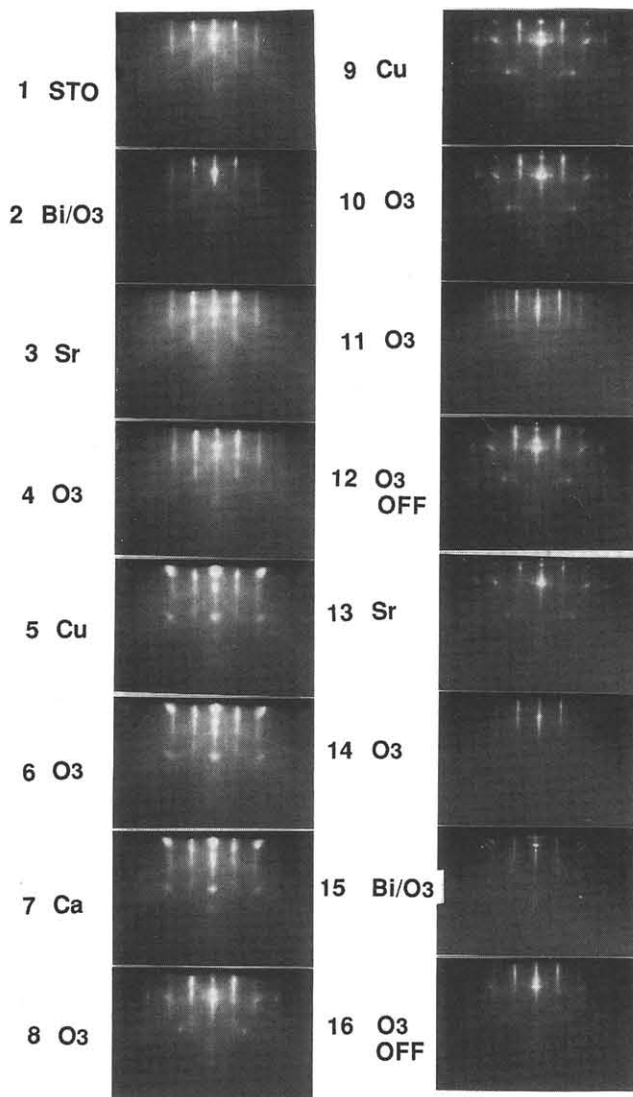


Figure 4 Photographs of the RHEED patterns at each periods indicated in Fig. 1 .

3.2 Sequential control of O₃

Figure 4 shows the photographs of the RHEED patterns at each period indicated in Fig.1. The pattern of streaks was obtained at O₃-feeding after evaporation of each metal layer. Long period of O₃ feeding after evaporation of the metal layer made the pattern of sharper streaks (compare photographs 10 to 11 in Fig. 1). After final layer of Bi, the RHEED pattern became the pattern of streaks. This implies that epitaxial growth of the BSCCO thin film would be also performed by sequential control of O₃-feeding in sequential evaporation. Further investigation is required for low temperature growth of the BSCCO superconducting thin film by this method.

3.2 BRBO superconducting thin film

Figure 5 shows the ratio of peak intensity of the (100) plane to the (110) plane in the XRD pattern of the BRBO thin film ($I(100)/I(110)$) as a function of $\text{Rb}/(\text{Bi}+\text{Ba})$. Figure 6 shows the XRD

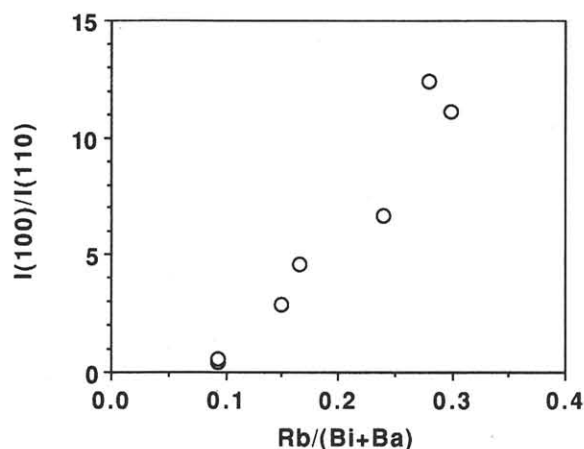


Figure 5 $I(100)/I(110)$ as a function of $Rb/(Bi+Ba)$.

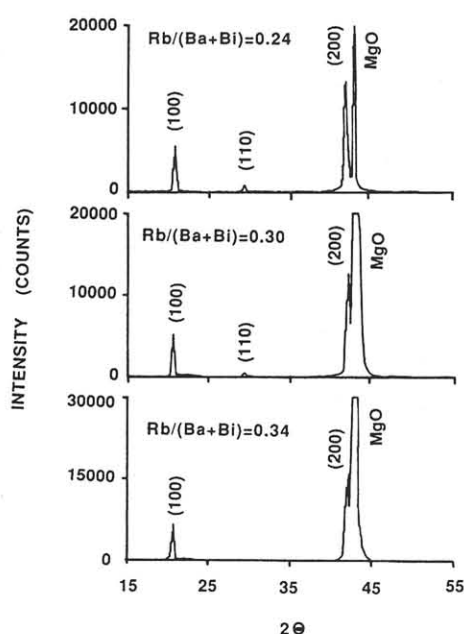


Figure 6 XRD patterns of the BRBO thin films for $Rb/(Bi+Ba) \sim 0.24, 0.30$ and 0.34 .

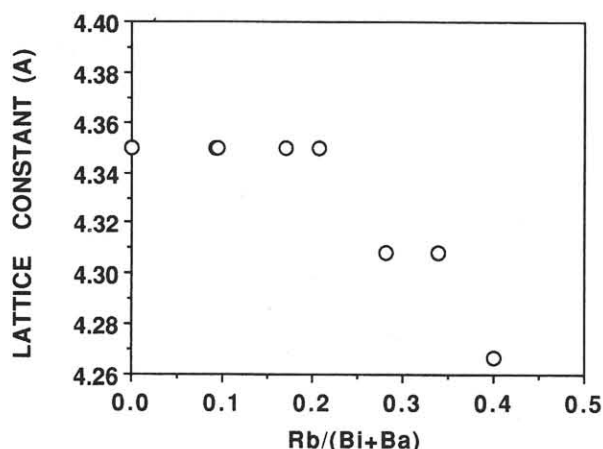


Figure 7 Lattice constant as a function of $Rb/(Bi+Ba)$.

patterns of the BRBO thin films at $Rb/(Bi+Ba) \sim 0.24, 0.3, 0.34$ (in this experiment, beam fluxes of Bi and Ba were constant and only Rb flux was

varied). The XRD patterns of the BRBO thin film indicates that (100) plane mainly grows on the MgO(100) substrate at $T_s \sim 370$ C. Small peak of the (110) plane was also observed. $I(100)/I(110)$ increases with increasing $Rb/(Bi+Ba)$ in the measured range. Figure 7 shows the lattice constant (d) as a function of $Rb/(Bi+Ba)$. d was deduced from the peak of the (100) plane in the XRD pattern. d decreases with increasing $Rb/(Bi+Ba)$ in the measured range. Those results shown in Figs. 5, 6 and 7 are consistent to those in Ref. 3. Figure 8 shows the $R(T)$ -curve of the BRBO thin film ($Rb/(Bi+Ba) \sim 0.3$). As seen in Fig. 8, the onset of the superconducting transition was obtained at ~ 25 K.

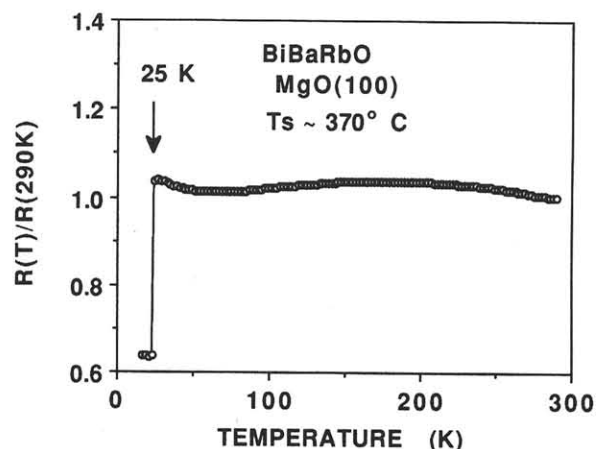


Figure 8 $R(T)$ -curve of the BRBO thin film formed at $T_s \sim 370$ C.

5. CONCLUSIONS

The growth temperature of the BSCCO thin film by coevaporation was reduced to 625 C by decreasing the growth rate from ~ 2 A/s to ~ 1 A/s. The growth rate of ~ 0.15 A/s by sequential evaporation resulted in decreasing growth temperature of the BSCCO superconducting thin film to 600 C.

The BRBO superconducting thin film with $T_c \sim 25$ K was synthesized at $T_s \sim 370$ C on MgO(100) substrate. Growth temperature of 370 C is low enough for BRBO growth on semiconductors [4,5]. Fabrication of junctions using BRBO thin film is now in progress.

Acknowledgement

This work was supported by NEDO under the management of FED.

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