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# Layer by Layer Growth of Bi-Sr-Ca-Cu-O by Molecular Beam Epitaxy

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Layer-by-layer growth of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ films by molecular beam epitaxy has been confirmed by the observation of intensity oscillations in reflection high-energy electron diffraction patterns. The films were prepared by a coevaporation method, where Bi, Sr, Ca and Cu metals were evaporated simultaneously with Knudsen cells under an oxygen/ozone mixture (ozone content of 10%) atmosphere. The 2212 and 2223 phases exhibited critical temperatures below 70K.

## 1. Introduction

Bi-Sr-Ca-Cu-O is a promising candidate as a practical high-temperature superconducting material because of its superior properties such as high critical temperature (Tc ~ 110K), resistance to humidity, and controllability of the number of layers of copper oxide by which the critical temperatures can be changed. Recently, layered structure of Bi-Sr-Ca-Cu-O has been succeeded by sequential deposition where each component is deposited sequentially by shutter control of Knudsen cells[1]. Previously, we have shown that in the sequential deposition of $Bi_2Sr_2CaCu_2O_x$ the reflection high-energy electron diffraction (RHEED) pattern becomes spotty gradually during the first unit cell deposition but just after the deposition of one half of a unit cell a streaky and reconstructed RHEED pattern is recovered[2].

These results indicate that the sequential deposition of each constituent is not necessary for layer-by-layer growth at least for the small layer number compounds. Actually, in case of YBCO deposition RHEED oscillations have been observed during the growth of $YBa_2Cu_3O_{7-x}$ superconductor prepared by coevaporation[3]. It has been shown that layer-by-layer growth of the oxide superconductors are practically possible. This is an important feature if we want to fabricate heterostructures.

In this paper we report a successful control of the Bi-Sr-Ca-Cu-O layered structure by coevaporation method. The layer-by-layer growth was confirmed by RHEED oscillations. To our knowledge this is the first observation of RHEED oscillations of the Bi-Sr-Ca-Cu-O systems by molecular beam epitaxy (MBE) coevaporation.

## 2. Experimental

Coevaporated Bi-Sr-Ca-Cu-O films were prepared on $SrTiO_3(100)$ and MgO(100) substrates by molecular beam epitaxy. Bi, Sr, Ca and Cu metals were evaporated with independent Knudsen cells. The growth rate was about 0.5 ~ 1A/sec. Oxygen/ozone mixture (ozone content of ~ 10%) generated by an ozonizer was introduced into the vacuum chamber close to the substrate (1 ~ 2cm) through a stainless steel tube. We used a diluted ozone because of safety and simple construction. The pressure near the vacuum pump was maintained at $2.5 \times 10^{-3}$Pa. Before the growth, the beam flux was measured individually by using a beam monitor (ionization guage) at the substrate position.

The substrate temperature was varied between 600 ~ 680 ℃. The chemical composition of the film was measured by induction-coupled plasma atomic emission (ICP). The beam monitor was calibrated by the ICP results. To achieve the expected phase, we adjusted the beam intensities of metals by controlling the K-cell temperatures.

We have fabricated 2201, 2212 and 2223 phases by coevaporation and observed RHEED oscillations during the growth of 2201 and 2212 phases on $SrTiO_3(100)$ substrates.

## 3. Results and discussion

### 3.1 Superconducting films prepared by coevaporation

Figure 1 shows the X-ray diffraction pattern of (a)2201, (b)2212 and (c)2223 phases on $SrTiO_3(100)$ substrates. Clearly each X-ray diffraction pattern is of single phase. Each of the c-axis length was calculated as 24.6, 30.7 and 37.3A, respectively.

Figure 2 shows the substrate temperature dependence of critical temperatures Tc(zero) and Tc(onset) of the films for the as-grown 2212 phases prepared on MgO(100) substrates.

Higher substrate temperatures result in higher Tc. Tc(zero) was 63K at 670 ℃. However $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ structures were not formed over 700 ℃ because of reevaporation of Bi from the film surface.

### 3.2 RHEED oscillations

Figure 3(a) shows the RHEED oscillation during the growth of 2201 phase prepared at 630 ℃. Figure 3(b) is the result for 2212 phase prepared at 650 ℃. Tc(zero) of this 2212 film whose thickness was about 2000A was 50K. The observation of RHEED oscillations for $YBa_2Cu_3O_{7-x}$ was reported by Bando et al, who claimed that the oscillation period corresponds to the height of the minimum unit [3]. In the case of Bi-Sr-Ca-Cu-O as well, the oscillation period corresponds to the time required for a half unit cell by calculating from Scherrer's formula[3], which is the full width at half maximum of X-ray diffraction of the thin films of 5nm, and also by the results of ICP measurements. The oscillation period of the first cycle is small compared with the other. The origin of this short periods is

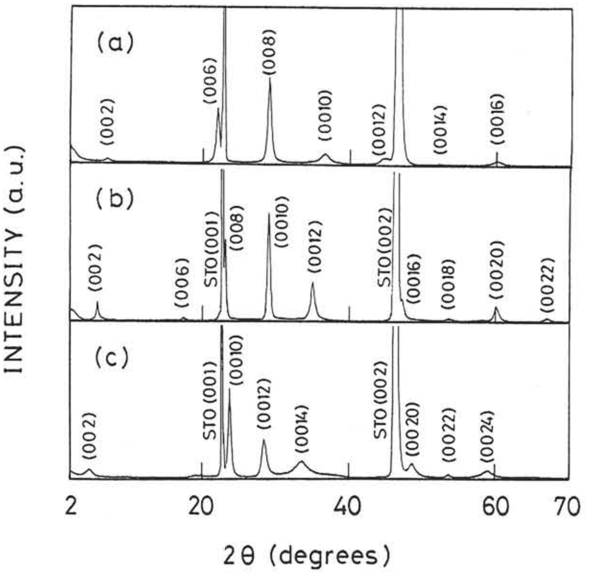


Fig.1 X-ray diffraction patterns measured for (a)2201, (b)2212 and (c)2223 phase prepared on $SrTiO_3$ (100) substrates, respectively.

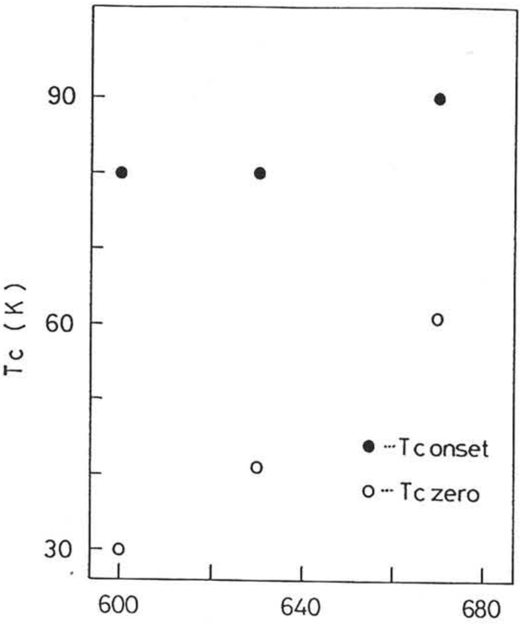


Fig.2 Dependence of the critical temperatures, Tc(zero) and Tc (onset), on substrate temperature for the as-grown 2212 phases prepared on MgO(100) substrates.

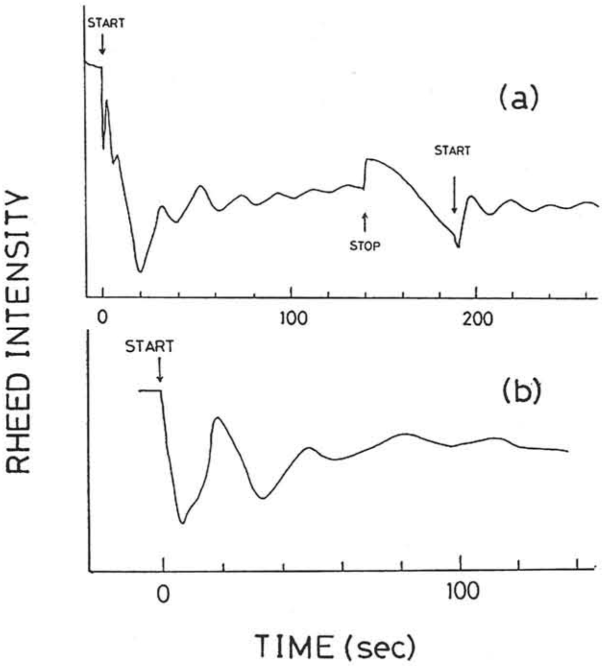


Fig.3 RHEED oscillations measured during the growth of (a)2201 phase prepared at 630 ℃ and (b)2212 phase at 650℃, respectively.

not clear at the moment. They might be due to the growth of a simple metal oxide as a first layer or surface roughness of the starting substrate surface which is usually observed in GaAs MBE.

As shown in Fig.4(a) and (b) the oscillation dumps gradually. This is due to the increase of surface roughness as the film grows. After the growth interruption for several tens of second by closing the substrate shutter, a clear oscillation recovers. This effect also suggest the growth surface is roughened during growth and smoothed by growth interruption. During the growth interruption the RHEED intensity shows unusual behavior as shown in FIb.4(a). The intensity increases abruptly at first and then decrease gradually. One possible explanation of their behavior in due to the leaked magnetic field from the coils which are used to drive the substrate shutter. During the growth on $SrTiO_3(100)$ substrates RHEED patterns show main streaks and satellite streaks due to the b-axis structure modulation. And it shows the twinned structure like these was reported in the growth of Bi-Sr-Ca-Cu-O films[4]. In the case of the 2212 phase, however, streak patterns and oscillations were not observed when substrate temperature was higher than 680 ℃ and below 630 ℃. RHEED patterns were spotty at 680 ℃ and dimly at 630 ℃.

## 4. Conclusion

We have observed RHEED oscillations during the growth of the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ films by coevaporation method for n=1, 2. It shows that a layer-by-layer growth has occurred during the growth of Bi-Sr-Ca-Cu-O systems. It can be concluded from these observations that a control of epitaxial growth by unit basis is possible by coevaporation at least for small n.

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## References

1) Y. Nakayama, I. Tsukada, A. Maeda and K. Uchinokura: Jpn. J. Appl. Phys. 28, (1989) L1890.

2) S. Yokoyama, T. Ishibashi, M. Yamagami and M. Kawabe: Jpn. J. Appl. Phys. 30, (1990) L106.

3) T. Terashima, Y. Bando, K. Iijima, K. Yamamoto, K. Hirata, K. Hayashi, K. Kamigaki and H. Terauchi: Phys. Rev. Lett. 65, 2684 (1990).

4) J. N. Eckstein, I. Bozovic, K. E. von Dessonneck, D. G. Schlom, J. S. Harris, Jr., and S. M. Baumann: Appl. Phys. Lett. 57, 931 (1990).

5) B. D. Cullity: Elements of X-ray diffraction, Addison-Wesley Series (Massachusetts, 1978).