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Atomic Layer Growth of BiSrCaCuO by Molecular Beam Epitaxy Using Ozone under UV Irradiation

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Molecular beam epitaxy technique in an ozone and oxygen mixture ambient under irradiation of ultraviolet light has been used to grow BiSrCaCuO superconducting thin film. The enhanced oxidation reaction is confirmed by this method. Layer by layer growth has been employed to control the complicated layered structure of this material. In situ Reflection High Energy Electron Diffraction (RHEED) measurement reveals a new insight for the growth mechanism of this perovskite type crystal. The reconstruction takes place just after completing the deposition of single unit cell.

1. INTRODUCTION

A high critical temperature (Tc∿110 K), no inclusion of expensive rare earth metals, no need of strongly toxic materials, high resistivity against humidity, and controllable copper layer number, by which the Tc is changed, are the attractive features of BiSrCaCuO superconductor.[1,2] For applying this material to the electronic devices and for investigating the intrinsic nature, it is strongly required to synthesize a single crystal film whose structure is highly controlled. Molecular Beam Epitaxy (MBE) and layer by layer growth technique, which is quite suitable to contol such a complicated layered structure, are employed. For studying the mechanism of the atomic layer growth, in situ RHEED measurement has been carried out. Ozone and ultraviolet (UV) irradiation are used to enhance the oxidation of metals.

2. EXPERIMENTAL

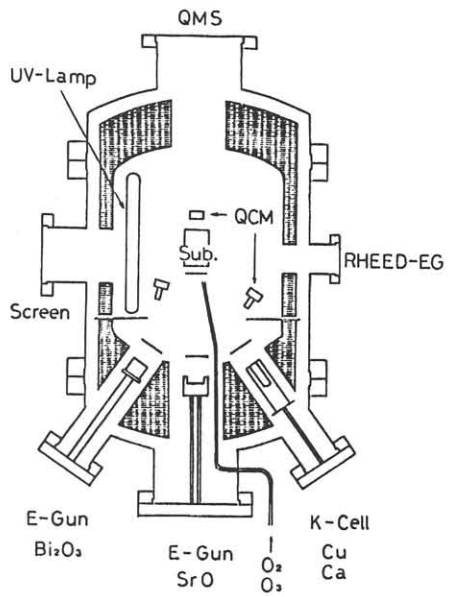

Fig. 1 Schematic diagram of the growth chamber. The load lock chamber, pumping system and RHEED system are omitted for the clairty.

Figure 1 shows the growth chamber. Bi_2O_3 and SrO are evaporated by the electron beam heating. Cu and Ca are evaporated by using the Knudsen cells. Oxygen and ozone (∿10% in content) mixture generated by the ozonizer is introduced into the chamber through the stainless steel tube. The pressure near the vacuum pump is maintained at 5×10^{-6} Torr. Near the sample surface it is

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estimated to be about two order of magnitude higher than this. A low pressure mercury lamp (mainly 253.7 nm in wavelength) is set in the chamber. The photon flux is $\sim 6\times10^{14}/cm^2 \cdot s$ at the sample surface. Ozone is esasily dissociated by this UV light, generating oxygen atom which is quite effective to enhance the oxidation reaction.[3] The molecular beam fluxes are monitored by the quartz crystal oscillators. The amount of the deposits is controlled by the evaporation rate and the shuttering time, which are controlled by the computer. The substrate temperature is 680°C. The atomic composition of the film is measured by the ICPAE (Induction Coupled Plasma Atomic Emission) and XMA (X-ray Micro Analysis). In order to test the performance of the experimental set up, co-evaporation method[4] is applied to grow $Bi_2Sr_2Ca_1Cu_2O_x$ film. Next, the atomic layer growth experiment is carried out. In situ RHEED measurement is employed for studying the growth mechanism.

3. RESULTS AND DISCUSSIONS

3. 1 Effect of Ozone and UV

Figure 2 shows the O/Cu Auger peak height ratio of the copper oxide (~20 nm in thickness) deposited on the MgO substrate at various conditions. For the samples with high O/Cu ratio (>1) Mg signal is detected, while no Mg signal is detected for low O/Cu ratio (<1). Therefore the high O/Cu ratio can be attributed to the reduction of the copper oxide thickness. The vapor pressure of Cu_2O is about 4 order of magnitude larger than that of Cu (7.5×10^{-9} Torr) at 600°C. By using ozone and UV irradiation the oxidation of copper must be enhanced, resulting in the reduction of the film thickness through the increase of reevaporation rate of the copper oxide. The merit of this method is the safety compared with pure ozone.[5,6] This technique should be noticed as a new method for making oxide film by MBE.

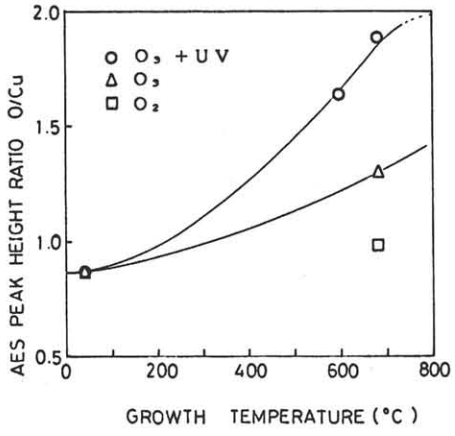

Fig. 2 O/Cu Auger signal ratio for various samples.

3. 2 Superconducting Film by Co-evaporation

$Bi_2Sr_2Ca_1Cu_2O_x$ (2212 phase) film is formed on the MgO substrate by co-evaporation method. Although only a small fraction of 2212 phase is observed for as grown film (Fig. 3(a)), annealing at 845°C for 2h results in almost single 2212 phase (Fig.

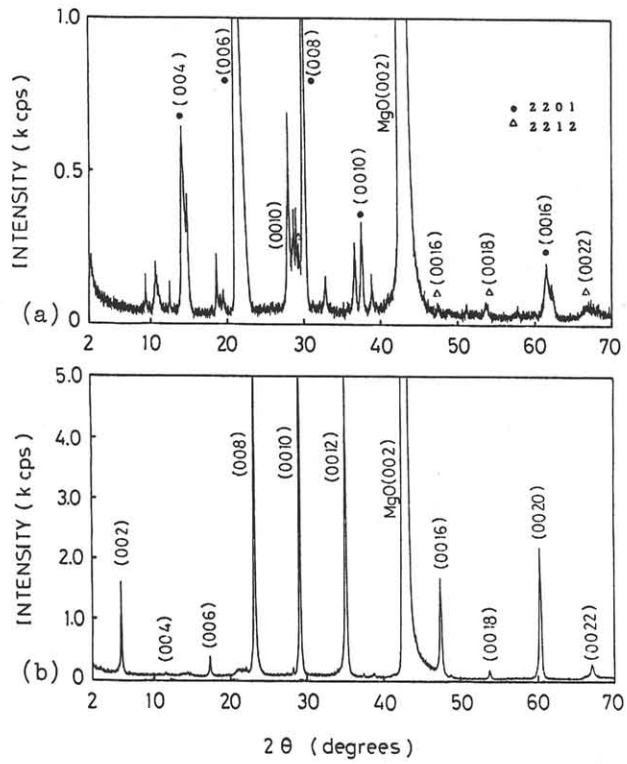

Fig. 3 X-ray diffraction spectra for (a) as-grown and (b) annealed samples grown by co-evaporation method. The growth temperature is 680°C. Annealing has been done at 845° for 2h in $Ar:O_2$(12:1) at atmospheric pressure.

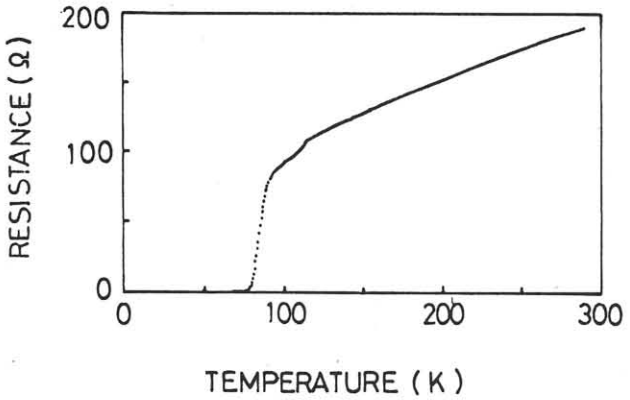

Fig. 4 Resistance-temperature characteristics for the annealed sample.

3(b)). Figure 4 shows the resistance-temperature curve of the annealed sample, in which Tc=76 K is achieved.

3. 3 Atomic Layer Growth

Figure 5 shows RHEED patterns at each step of the atomic layer growth on MgO and STO ($SrTiO_3$) substrates mounted on the same holder (680°C). The atomic layer growth for the 2212 phase has been carried out by sequentially depositing single atomic layer of BiO, SrO, CuO_2, ···. The deposition of single atomic layer is controlled by monitoring the quartz crystal oscillator calibrated by the ICP. For the MgO substrate, which has a large mismatch to BiSrCaCuO (>9%), the RHEED pattern changes from streak to spot after deposition of the 2nd SrO layer. After one unit cell (from the 1st BiO to the 7th BiO layer) deposition no remarkable improvement of the crystal quality has been achieved. For the STO substrate, however, the RHEED pattern remains streaky after the 4th Ca layer deposition. Spots appear after the 5th CuO_2 layer deposition. The most interesting point is that for the STO substrate the RHEED pattern with many spots and rings changes to streak like again after one unit cell deposition. Since the space between the streak lines is not changed, the azimuth of the lattice of the BiSrCaCuO may be rotated by 90 degree with respect to the substrate azimuth. The mismatch between the lattice constant of BiSrCaCuO (5.4 A) and that of STO (3.9 A) in this situation is only 2%. From these results, the epitaxial growth is not layer by layer growth, but three dimensional growth such as island formation and/or intermixing may take place during the growth. After one unit cell deposition the reconstruction takes place, forming the perovskite type single crystal which has minimum energy. Then the surface becomes smooth. The similar result is observed in the growth of YBaCuO by activated reactive evaporation.[7]

4. CONCLUSION

Ozone and UV irradiation are proposed as a new method for making oxide film by MBE. Atomic layer growth and in situ RHEED find out that the reconstruction takes place after deposition of the unit cell for BiSrCaCuO.

5. REFERENCES

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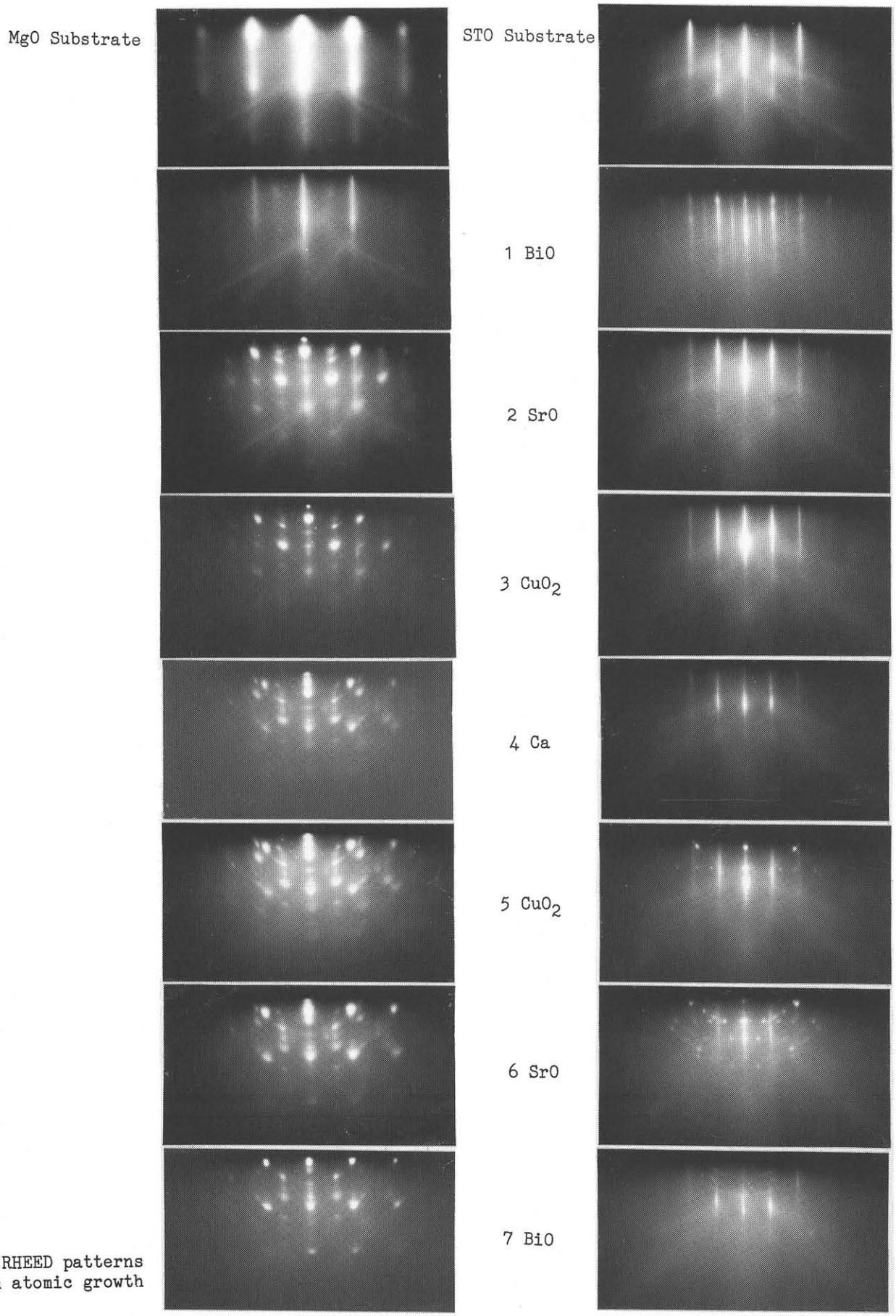

Fig. 5 RHEED patterns at each atomic growth step.