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Formation of Single Phase of $Bi_2Sr_2CaCu_2O_x$ Film by Plasma Assisted Organometallic Chemical Vapor Deposition Method

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A film of single phase of $Bi_2Sr_2CaCu_2O_x$ is prepared on a single crystalline $SrTiO_3$ (100) at 923 K by the method of plasma assisted organometallic chemical vapor deposition. The c axis of the resulting film is oriented in the direction perpendicular to the substrate surface.

The new superconductor in the system of Bi-Sr-Ca-Cu-O recently found by Maeda[1] has a higher critical temperature(T_c=110 K) and higher chemically stability against water in comparison with $YBa_2Cu_3O_{7-\delta}$. These properties of the superconductor are preferable from the viewpoint of application. For application of superconducting devices, uniformity, durability and high critical current are required for materials of superconductor. To satisfy these conditions, films of superconducting oxides have been prepared by various techniques such as magnetron sputtering,[2] molecular beam epitaxy,[3] reactive evaporation[4] and organometallic chemical vapor deposition(OMCVD).[5-7] It was reported that a single crystalline $YBa_2Cu_3O_{7-\delta}$ film is epitaxially grown on single crystalline $SrTiO_3$ and Al_2O_3 by reactive evaporation[8] and OMCVD [9] methods. Because of easy handling, OMCVD is particularly a promising method for preparation of high quality films, if suitable gas sources are available. For superconductive oxides in the Bi-Sr-Ca-Cu-O system, however, single crystalline films have not been prepared by the OMCVD method.

In this work, in order to promote the rate of decomposition and oxidation of organometallic compounds, plasma of O_2 and Ar is produced in a reaction chamber by applying r.f. power to a coil surrounding a reactor. This plasma assisted OMCVD method (POMCVD) enable us to prepare superconducting Bi-Sr-Ca-Cu-O films at fairly low temperature. In this letter, we describe procedure for the preparation of the $Bi_2Sr_2CaCu_2O_x$ film by the POMCVD method, and characteristics of the film are discussed on the basis of X-ray diffraction patterns.

Chelates of Cu, Sr, Ca with a ligand of 2,2,6,6-tetramethyl-3,5-heptanedione(thd) were used as source materials. Ligand of (thd) was synthesized according to published procedure.[10] Triphenyl bismuth, $Bi(phy)_3$, as a source material was synthesized with the grignard reaction.[11] Organometallic compounds of $Bi(phy)_3$, $Sr(thd)_2$, $Ca(thd)_2$, and $Cu(thd)_2$ were sublimed in 1 Pa at temperates of 357, 448, 428 and 367 K, respectively. A schematic diagram of experimental apparatus is shown in Fig. 1. The deposition was carried out in a quartz reactor held in an image furnace. A substrate of $SrTiO_3$(100) was placed on a Si single crystal which was heated effectively by absorbing light from image furnace. Deliver lines and a mixing tube were wrapped with heating tapes and were maintained at 470 K, being higher than the sublimation temperature of $Sr(thd)_2$. The deposition rate is controlled by sublimation temperatures of chelates and the flow rate of Ar carrier gas passed over chelates. Plasma was produced by applying r.f.(13.56 MHz) power to a coil surrounding a reaction chamber. After the deposition of a film by the POMCVD method was completed, substrate temperature was cooled at a rate of 4 K/min to 673 K, and then a film was further annealed at 673 K for one hour in 1 atm O_2.

Yamane et al.[5] reported that films in the Bi-Sr-Ca-Cu-O system were prepared by the OMCVD method in which alkoxide of Bi was used as a source material. In general the usage of alkoxide sensitive to moisture is unsuitable from the viewpoint of reproducibility, so that we employed triphenyl bismuth as a source material. According to preliminary experiments concerning thermal decomposition of $Bi(phy)_3$, the thermal decomposition of $Bi(phy)_3$ did not almost proceed at 923 K and produced $Bi_2O_2(CO_3)$ on a quartz glass even at 1173 K. This indicates low rate of the thermal decomposition of $Bi(phy)_3$. In the presence of plasma, $Bi(phy)_3$ was easily decomposed into Bi_2O_3 at 923 K. Thus, there is a possibility that superconducting oxides in the Bi-Sr-Ca-Cu-O system are formed even at low temperature by the POMCVD method.

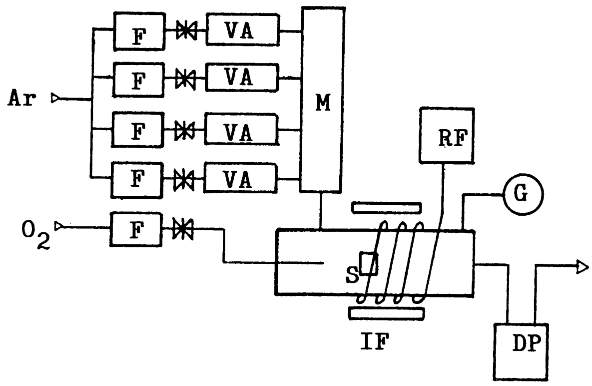

Fig. 1. Schematic diagram of experimental apparatus. F: mass flow controller; VA; vaporizer; M: mixing tube; RF: r.f. power; IF: image furnace; G: vacuum gauge; S: substrate; DP: diffusion pump.

Figure 2 shows a X-ray diffraction pattern of a film grown on a substrate of $SrTiO_3(100)$ at 923 K by the simple OMCVD method. In Fig. 2, there are no peaks originating from superconducting oxides in the Bi-Sr-Ca-Cu-O system, besides an unknown peak at 41.5 degree(this peak is different from a reflection of $Bi_2O_2(CO_3)$). This result is consistent with the anticipation deduced from the low rate of thermal decomposition of $Bi(phy)_3$. On the other hand, in the presence of plasma, a black film with electric conductivity was

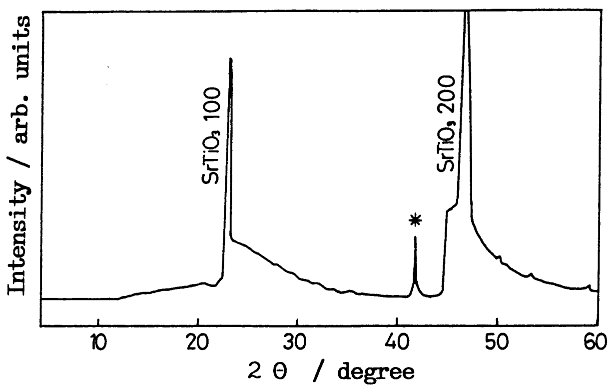

Fig. 2. X-Ray diffraction pattern of film prepared by OMCVD method. Asterisk is unknown peak. X-Ray is Cu(k α).

Table 1. Deposition conditions of $Bi_2Sr_2CaCu_2O_x$ film

Source material	$Bi(phy)_3$	$Sr(thd)_2$	$Ca(thd)_2$	$Cu(thd)_2$
Temperature of vaporizer (K)	387	450	452	386
Flow rate of Ar (sccm)	3.0	7.3	1.7	1.0
Substrate	$SrTiO_3$ (100)			
Temperature of substrate (K)	923			
Total gas pressure (Pa)	1.0			
Flow rate of O_2 (sccm)	20			
Deposition rate (nm/min)	16.3			
R.f. power (W)	20			

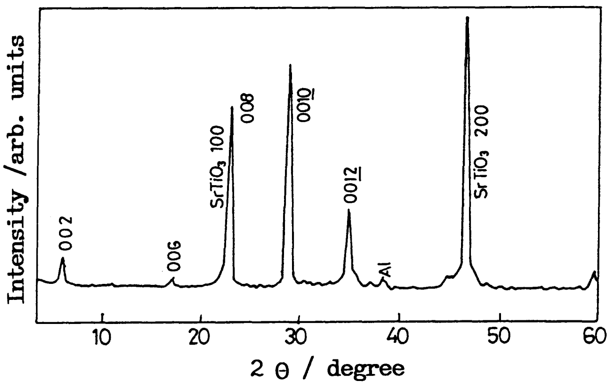

Fig. 3. X-Ray diffraction pattern of film prepared by POMCVD method. X-Ray is Cu(kα).

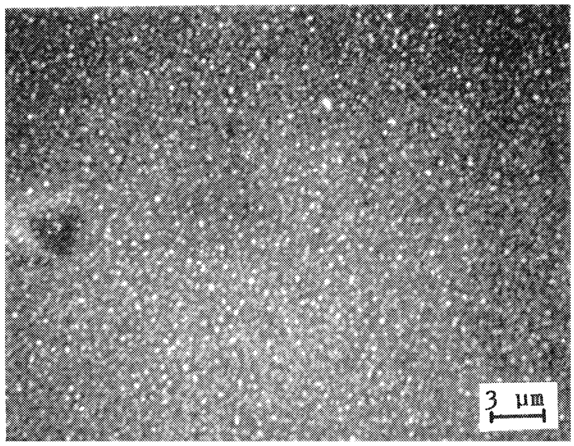

Fig. 4. Scanning electron micrograph of film prepared by POMCVD method.

grown on a single crystalline $SrTiO_3$ (100). The deposition conditions are listed in Table 1. By assuming that the density of the film is equal to that of single crystal, the film thickness is estimated to be 980 nm from the total amount of Bi, Cu, Sr and Ca contained in the film. A X-ray diffraction pattern of the film prepared by the POMCVD method is shown in Fig. 3. As seen in Fig. 3, there are only (00ℓ) reflections originating from $Bi_2Sr_2CaCu_2O_x$ in this diffraction pattern(Al peak arises from an Al-sample holder used in X-ray diffraction measurements). This indicates that the film consists of a single phase of $Bi_2Sr_2CaCu_2O_x$ of which c axis is preferentially oriented in the direction perpendicular to the substrate surface. It seems that the decomposition rate of $Bi(phy)_3$ is enhanced in the presence of plasma. Therefore, the POMCVD method has a advantage that films of superconducting oxides in the Bi-Sr-Ca-Cu-O system can be synthesized at considerably low temperature. A scanning electron micrograph shown in Fig. 4 reveals that a film is composed of grains ca. 0.3 μm or less in size.

Besides $Bi_2Sr_2CaCu_2O_x$ phase, $Bi_2Sr_2CuO_x$ phase with c axis oriented preferentially perpendicular to the substrate surface is synthesized by lowering vaporizer temperatures of $Ca(thd)_2$ and $Cu(thd)_2$. At the substrate temperature of 923 K, however, films of $Bi_2Sr_2Ca_2Cu_3O_x$ phase were not formed by changing temperatures of vaporizers of $Ca(thd)_2$, $Cu(thd)_2$, $Sr(thd)_2$, and $Bi(phy)_3$. The substrate temperature and total pressure of a reactor may be important factors for the preparation of $Bi_2Sr_2Ca_2Cu_3O_x$. The detailed discussion will be made in a forthcoming paper, together with the superconducting properties of these films .

References

1) H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys., 27, L209 (1988).
2) H. Adachi, S. Kohiki, K. Setsune, T. Mitsuyu, and K. Wasa, Jpn. J. Appl. Phys., 27, L1883 (1988).
3) J. Kwo, T.C. Hsieh, R.M. Fleming, M. Hong, S.H. Liou, B.A. Davison, and L.C. feldman, Phys. Rev. B,36, 4039(1987).
4) T. Aida, A. Tsukamoto, K. Imagawa, T. Fukuzawa, S. Saito, K. Shindo, K. Takai, and K. Miyauchi, Jpn. J. Appl. Phys., 28, L635 (1989).
5) H. Yamane, H. Kurosawa, and T. Hirai, Chem. Lett., 1988, 939, 1515; H. Yamane, H. Kurosawa, T. Hirai, H. Iwasaki, N. Kobayashi, and Y. Muto, Jpn. J. Appl. Phys., 27, L1495 (1988).
6) H. Abe, T. Tsuruoka, and T. Nakamori, Jpn. J. Appl. Phys., 27, L1473 (1988).
7) K. Shinohara, F. Munakata, and M. Yamanaka, Jpn. J. Appl. Phys., 27, L1683 (1988).
8) T. Terashima, K. Iijima, K. Yamamoto, Y. Bando, and H. Mazaki, Jpn. J. Appl. Phys., 27, L91 (1988);
9) S. Oda, H. Zama, T. Ohtsuka, K. Sugiyama, and T. Hattori, Jpn. J. Appl. Phys., 28, L427 (1989).
10) K.R. Kopecky, D.C. Nonhebel, G. Morris, and G.S. Hammond, J. Org. Chem., 27, 1036 (1962).
11) G.O. Dork and L.D. Freedman, Synthesis, 1974, 328

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