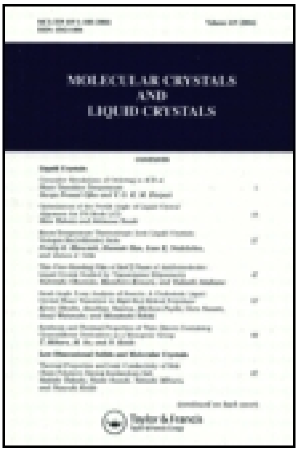

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Deposition of Bi, Sr, Ca, and Cu Oxide Films by RF Glow Discharge Generated at Relatively High Pressure

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DEPOSITION OF Bi, Sr, Ca, AND Cu OXIDE FILMS BY RF GLOW DISCHARGE GENERATED AT RELATIVELY HIGH PRESSURE

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Abstract Low temperature deposition of oxide films related to Bi-Sr-Ca-Cu-O superconductors has been investigated by using an apparatus originally designed for plasma chemical vapor deposition at moderately high pressures. Crystalline Bi_2O_3 film was obtained at a substrate temperature of 400°C from triphenylbismuth. Amorphous films as-deposited at 400°C from $Ca(DPM)_2$, $Sr(DPM)_2$, and $Cu(DPM)_2$ were annealed at 400°C in air to be crystalline films of $CaCO_3$, $SrCO_3$, and CuO, respectively. The effect of oxygen partial pressure on the crystallization of as-deposited films was examined with respect to $CaCO_3$ film to verify the effectiveness of elevated oxygen partial pressure for improving the film crystallinity. Linear relationships were obtained between the deposition time and film thickness. Preliminary data for the preparation of superconducting film by annealing a layered oxide film are also presented.

INTRODUCTION

Preparation of high-T_c superconducting oxide films by CVD were already reported,[1] but most of the reports employed thermal CVD using substrate temperatures higher than 700°C. For decreasing the film deposition temperature, we tried to use rf and microwave plasmas which could facilitate the decomposition of source gases and activate the oxygen.[2] Recently, Kobayashi and coworkers reported the construction of $Bi_2Sr_2CaCu_2O_x$ crystal structure by a plasma assisted chemical vapor deposition at 650°C.[3] In these experiments except for ours, mixtures of source materials were introduced into the reactors to produce homogeneous superconducting films and the layer-by-layer deposition of component oxides has scarcely been attempted. This paper describes a low temperature (<400°C) synthesis of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO films using our originally designed CVD apparatus. Bi-Sr-Ca-Cu-O superconducting system was reported to have a structure of several numbers of Ca/CuO_2 bi-layers sandwiched by two Bi_2O_2/SrO stacked layers.[4] For the artificial construction of these structures, we need to establish such a process technology as to enable the formation of as-grown crystalline film from each one of the sources at a low temperature and at a constant deposition rate.

EXPERIMENTAL

The setup of the apparatus used in the present study was reported elsewhere.[5] The condenser type electrodes structure was modified so that rf glow discharge could be sustained at a pressure even as high as 1atm; the cathode was tungsten needles with a diameter of 0.2mm and the anode was covered with a quartz plate of 0.2mm thick. The substrate MgO(100) was heated at 400°C. A mixture of plasma excited O_2 and Ar gases was introduced above the substrate to be mixed with the source materials carried on helium flow. Helium was indispensable for sustaining the glow discharge at pressures higher than 10Torr. Rf plasma in a high oxygen partial pressure was expected to facilitate the preparation of oxide films efficiently. Source materials employed were $Bi(C_6H_5)_3$, $Sr(DPM)_2$, $Ca(DPM)_2$, and $Cu(DPM)_2$, where DPM represents $(CH_3)_3CCOCHCO(CH_3)_3$, supplied from Tri-chemical Co., Ltd. They were heated separately in oil baths and carried into the reaction chamber by helium. The evaporation temperatures were determined by TG measurement under Ar 100Torr atmosphere using a Sinku-Riko TGD-7000RH model. To prevent the source materials from condensation, the gas lines were heated up to 250°C. The film thickness was determined by the stylus method using a Taylor-Hobson Talystep. The crystal structure was analyzed by X-ray diffraction (XRD: MAC Science MXP^3).

RESULTS AND DISCUSSION

Film deposition and crystal structure

Table 1 lists representative film preparation conditions and results. The as-deposited film prepared at 400°C from $Bi(C_6H_5)_3$ has a crystal structure of Bi_2O_3. Amorphous films were obtained from $Sr(DPM)_2$, $Ca(DPM)_2$, and $Cu(DPM)_2$ at a reaction pressure of 3Torr. XRD Peak of CuO(111) appeared by annealing the film prepared from $Cu(DPM)_2$ at 400°C in air. Clear XRD patterns of $CaCO_3$ was observed in the film prepared from $Ca(DPM)_2$ after annealing in air at 500°C. Annealing at a temperature of 400°C also gave $CaCO_3$ pattern. Annealing the film prepared from $Sr(DPM)_2$ at 400°C also produced crystalline $SrCO_3$. Sharper XRD pattern of $SrCO_3$ was observed by elevating the annealing temperature up to 600°C. Rather than CaO and SrO films, $CaCO_3$ and $SrCO_3$ films were preferentially formed probably because the carbonates were more stable thermodynamically under the experimental conditions and carbon was present in the source. Deposition at a higher oxygen partial pressure was effective to prepare as-grown crystalline films. Figure 1 shows the XRD patterns of the as-grown films prepared from $Ca(DPM)_2$ at pressures of 3Torr and 10Torr. The film prepared at 10Torr showed $CaCO_3$ crystal structure without post-annealing.

Deposition rate

Figure 2(a)-(d) shows the relationship between the film thickness and reaction time. Fairly good linear relationships were obtained for all of the plasma CVD reactions to give the deposition rates of 1.30, 1.67, 1.25, and 1.50A/s for Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO films, respectively. Since the thickness of each oxide layers in Bi-Sr-Ca-Cu-O superconductor is 2∿3A[4], the thickness of each oxide film must be controlled at that order for layer-by-layer as-grown superconductor. The deposition rates we obtained (1.25∿1.67A) appear to be a little too high for the purpose of such layer-by-layer deposition.

Preparation of a superconducting film

Four films were deposited successively under the conditions of Runs 1, 2, 3, and 4 in Table 1 from $Bi(C_6H_5)_3$, $Sr(DPM)_2$, $Ca(DPM)_2$, and $Cu(DPM)_2$. Each layer was designed to have a thickness of 1000A. The stacked film was annealed at 850°C in air for 30min. Low temperature resistivity was measured by the conventional four probe method. T_c^{onset} was observed at 80K. Peaks of $Bi_2Sr_2CaCu_2O_x$ appeared in XRD pattern of the film. Further study is in progress for better control of film deposition using a computer controlled gas supplying system.

Conclusion

Crystalline Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO films were prepared by rf plasma assisted CVD at a temperature of 400°C. Increase of oxygen partial pressure was effective to prepare as-grown crystalline films. The accumulation of these four layers of about 1000A thick each at

400°C and subsequent annealing at 850°C gave a film indicating a superconductivity at 80K.

Acknowledgment
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Table I Representative preparation conditions and results

	Source material	Evaporation temperature (°C)	Carrier flow (sccm)	Reaction pressure (Torr)	Depo. rate. (A/s)	Crystal structure as-grown	Crystal structure 400°C anneal
#1	$Bi(C_6H_5)_3$	130	40	3	1.30	Bi_2O_3	-
#2	$Sr(DPM)_2$	240	6	3	1.67	amorphous	$SrCO_3$
#3	$Ca(DPM)_2$	220	6	3	1.25	amorphous	$CaCO_3$
#4	$Cu(DPM)_2$	140	40	3	1.50	amorphous	CuO
#5	$Ca(DPM)_2$	220	6	10	1.25	$CaCO_3$	-

rf power: 100W Substrate temperature: 400°C Ar: 2sccm O_2: 2sccm

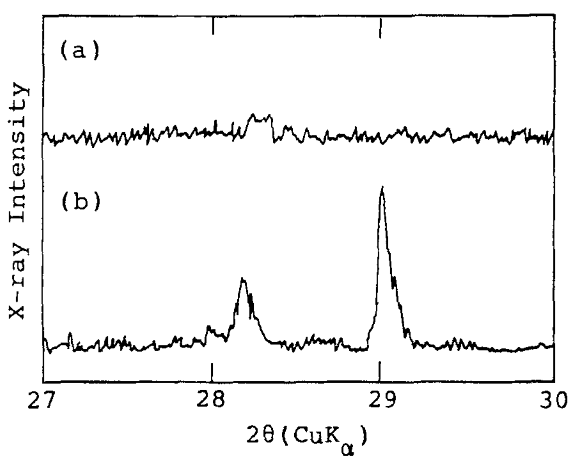

Fig. 1 X-ray diffraction patterns of the as-grown films prepared from $Ca(DPM)_2$ at a reaction pressure of (a) 3Torr and (b) 10Torr.

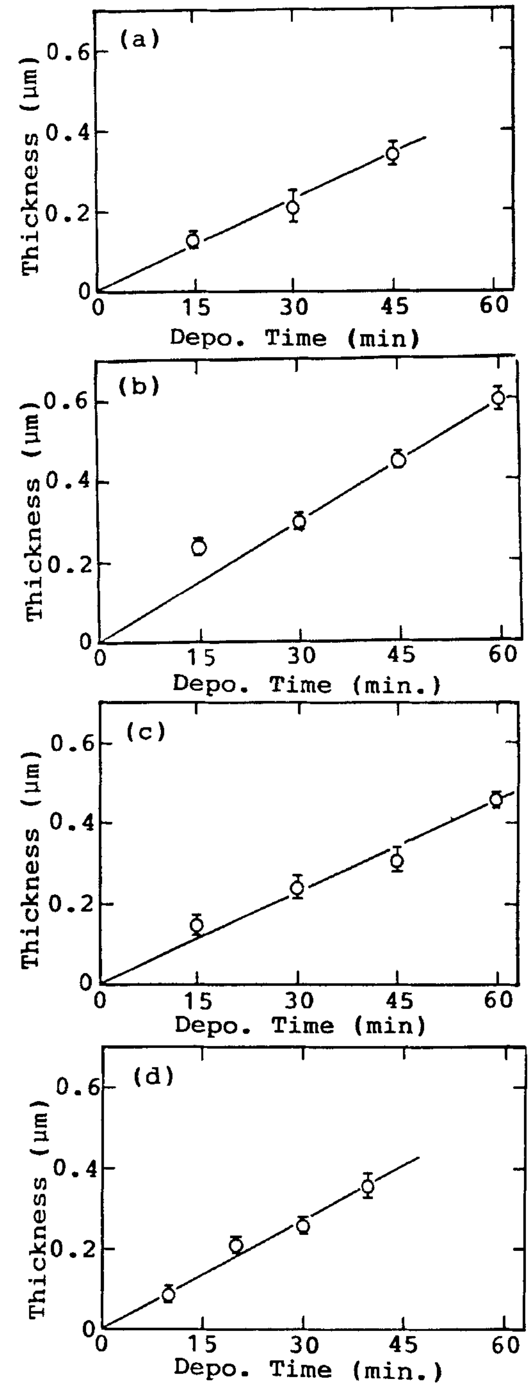

Fig. 2 Time dependence of film thickness prepared from (a) $Bi(C_6H_5)$, (b) $Sr(DPM)_2$, (c) $Ca(DPM)_2$, and (d) $Cu(DPM)_2$.