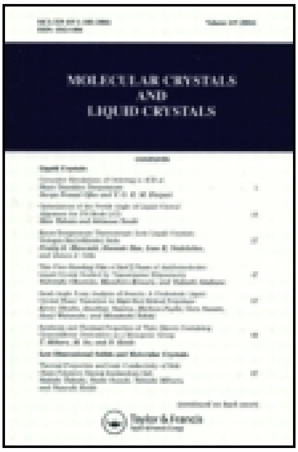

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Microwave Plasma CVD of Oxide Films Relating to High-T_c Bi-Sr-Ca-Cu-O Superconductor

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Version of record first published: 22 Sep 2006.

Mol. Cryst. Liq. Cryst., 1990, vol. 184, pp. 207–211
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Printed in the United States of America

MICROWAVE PLASMA CVD OF OXIDE FILMS RELATING TO HIGH-T_c Bi-Sr-Ca-Cu-O SUPERCONDUCTOR

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Abstract As a low temperature preparation method of Bi, Sr, Ca, and Cu oxide and fluoride films, microwave plasma of Ar and O_2 gases was applied to decompose $Bi(C_6H_5)_3$ and metal β-diketone complexes. As-deposited crystalline Bi_2O_3, CuO, SrF_2, and CaF_2 films were obtained at a substrate temperature of 400°C and below. The film thickness was nearly proportional to the deposition time for each film. These Bi_2O_3, SrF_2, CuO, and CaF_2 crystalline films designed to have a 2000Å thickness each were stacked and annealed at 850°C for 30min to show a superconductivity with T_c^{onset} at 65K.

Introduction

Low temperature preparation of metal oxide films is required for the construction of artificially designed crystal structure including high-T_c superconductor related compounds. As low temperature processes for fabricating high-T_c superconducting films, various methods such as activated reactive evaporation[1], plasma assisted laser evaporation[2] and light irradiation during sputtering[3] have been reported. Besides these physical vapor deposition (PVD), chemical vapor deposition (CVD) can also be a low temperature process under moderately high oxygen partial pressure. However, reported CVDs were mostly thermal CVDs and substrate temperatures required to achieve the superconductivity of the films were above 700°C.[4] As a fundamental study toward the artificial construction of layered structure, we examined the low temperature synthesis of metal oxide films assisted by the rf or microwave plasma.[5,6] This paper reports the as-grown synthesis of Bi_2O_3, SrF_2, CaF_2, and CuO films by using microwave plasma CVD apparatus. Preliminary data for the preparation of superconducting film by accumulating CVD layers are also presented.

Experimental

The CVD sources used were $Bi(C_6H_5)_3$, $Sr(PPM)_2$, $Ca(PPM)_2$, and $Cu(HFA)_2$, where PPM and HFA represent $C_2F_5COCHCOC(CH_3)_3$ and $CF_3COCHCOCF_3$, respectively. These sources supplied from Tri-Chemical Co., Ltd. were separately heated in oil baths and carried into the reaction chamber with helium at a total pressure of 100Torr. The evaporation temperatures were determined in view of the TG data of the sources measured under Ar 100Torr atmosphere using a Sinku-Riko model TGD-7000RH. To avoid the condensation of source materials, the gas lines were heated at a temperature of about 250°C. The configuration of the microwave plasma CVD apparatus is shown in Fig. 1. A 2.45GHz microwave was applied at the double quartz tubing, inner for introduction of Ar and outer for O_2, to generate excited argon and oxygen for decomposing source materials efficiently. An MgO(100) substrate was placed in the quartz flask and heated at a temperature between 200°C and 400°C by a focused IR lamp. In the deposition of CaF_2 films, Si(100), Si(111), and GaAs(100) substrates were also used. The film thickness was measured by the stylus method using a Taylor-Hobson Talystep. The crystal structures of the films were analyzed by X-ray diffraction measurement (XRD: MAC Science MXP^3). X-ray photoelectron spectroscopy (XPS: JEOL JPS-80) was measured on some of the films to determine the elemental composition.

Results and Discussion

Preparation of CuO film from $Cu(HFA)_2$

Powderly $Cu(HFA)_2$ was heated at 80°C and the evaporated vapor was carried in a stream of 80sccm helium. The reaction pressure and microwave power were 1.5Torr and 90W, respectively. With the aid of microwave plasma generated at various O_2/Ar ratios, films were prepared on MgO(100) substrate heated at a temperature of 400°C. The X-ray diffraction patterns of prepared films are shown in Fig. 2. The film was amorphous when prepared at an O_2/Ar ratio of 5/50. Peaks of both CuF_2 and CuO were detected in the film prepared by increasing the O_2/Ar ratio to 10/50. Further increase of the O_2/Ar ratio up to 15/50 increased the intensity of CuO peaks and decreased that of CuF_2.

Preparation of Bi_2O_3 film from $Bi(C_6H_5)_3$

$Bi(C_6H_5)_3$ was evaporated by being heated at 120°C and carried in a stream of 80sccm helium. The reaction pressure and O_2/Ar ratio were 1.5Torr and 5/50, respectively. Figure 3 shows the X-ray diffraction pattern of the film prepared from $Bi(C_6H_5)_3$ on MgO (100) substrate at a temperature of 200°C. The microwave plasma power was 60W or 90W. When 60W microwave power was applied, the obtained film was amorphous. The film prepared at a microwave power of 90W showed X-ray diffraction peaks all of which could be identified to be β-Bi_2O_3. Increase in the amount of excited oxygen species is considered to work effectively for the formation of crystalline oxide film. The deposition rate was constant at about 0.56A/s throughout the reaction time of 60min to give a film of 2000A thick. Carbon contamination in the film was not observed by XPS measurement.

Synthesis of oriented CaF_2 and SrF_2 films

From the TG analysis, the evaporation temperatures of $Sr(PPM)_2$ and $Ca(PPM)_2$ were determined to be 240°C and 200°C, respectively. The flow rates of He, Ar, and O_2 gases were 80, 50, and 10sccm, respectively. Films were deposited at a pressure of 1.5Torr under a microwave power of 90W. The substrate temperature was 400°C. Figure 4 shows X-ray diffraction patterns of the films prepared on MgO(100) substrate. The CaF_2 and SrF_2 films strongly oriented to (001) direction were prepared from $Ca(PPM)_2$ and $Sr(PPM)_2$, respectively. The orientation of CaF_2 film could be controlled by the substrate. Films oriented to (001) were obtained on Si(100) and GaAs(100) substrate, while (111) oriented film was on Si(111) substrate. XPS measurement indicated that the ratio of Ca/F came between 0.4 and 0.5. A little contamination of carbon and oxygen in the film was also observed.

Synthesis of superconducting film by annealing layered film

A layered film was prepared by successive deposition of Bi_2O_3, SrF_2, CaF_2, and CuO films of about 2000A each. Annealing the film at 850°C for 30min in air yielded a T_c^{onset} at 65K as shown in Fig. 5. However, zero resistivity was not achieved. The interdiffusion required for the construction of superconducting phase should be difficult between such thick layers. Accumulation of thinner layers would facilitate the preparation of superconducting films at a low temperature.

Conclusion

As-grown Bi_2O_3, SrF_2, CaF_2, and CuO films were obtained at 400°C or below by using a microwave plasma CVD apparatus. Superconducting film with T_c^{onset} of 65K was prepared by annealing a film accumulating four layers of Bi_2O_3, SrF_2, CaF_2, and CuO at 850°C for 30min in air.

Acknowledgment

The authors acknowledge Mr. A. Kishi (Sinku-Riko) for the TG measurement. The part of this work is supported by Grant-in-Aid for Scientific Research on Chemistry of New Superconductors from Ministry of Education, Science and Culture.

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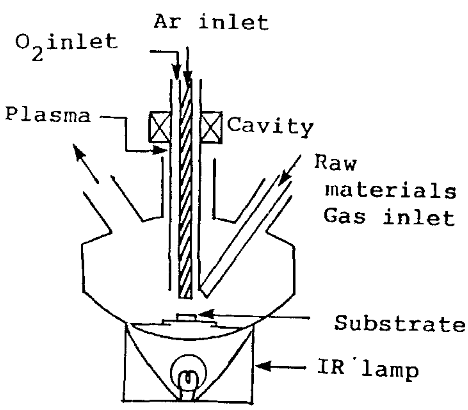

Fig. 1 Schematic diagram of microwave CVD system.

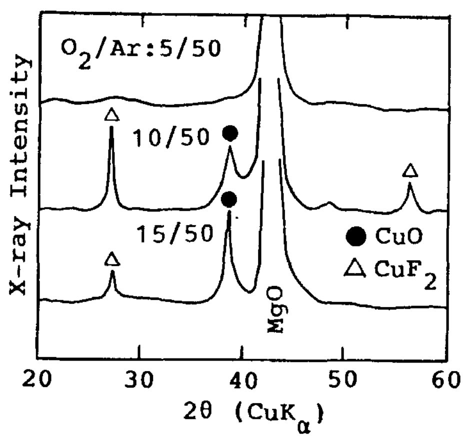

Fig. 2 X-ray diffraction patterns of the films prepared at 400°C from $Cu(HFA)_2$ at various O_2/Ar ratio.

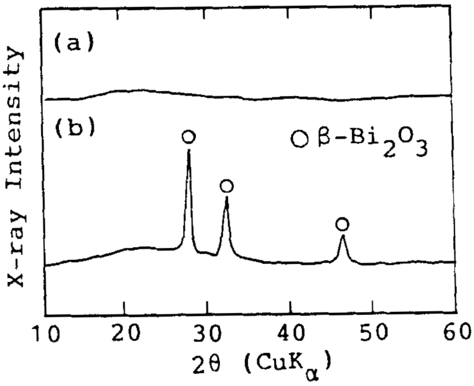

Fig. 3 X-ray diffraction pattern of the film prepared from $Bi(C_6H_5)_3$ at microwave power of (a)60W and (b)90W. The substrate temperature was 200°C.

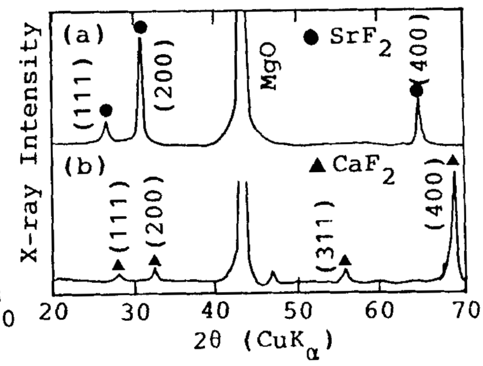

Fig. 4 X-ray diffraction patterns of the films on MgO (100) prepared at 400°C from (a)$Sr(PPM)_2$ and (b)$Ca(PPM)_2$.

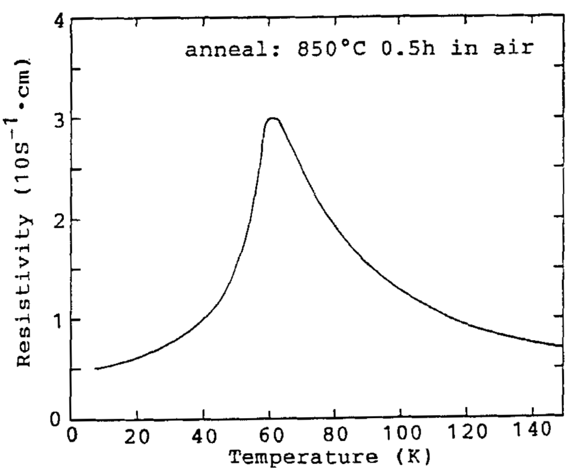

Fig. 5 Temperature dependence of resistivity of the layered film after being annealed at 850°C for 30min.