APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 325–330 (1991)

Photo-absorption and photochemical decomposition of copper and alkaline-earth β-diketonates as source gases of high-T_c superconducting films

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For low-temperature deposition of oxide films relating to Bi–Sr–Ca–Cu–O superconductors, photo-absorption and -decomposition properties were examined with respect to copper and alkaline-earth β-diketonates. It was confirmed that all β-diketonates examined were promising as source materials for photochemical vapour deposition (photo-CVD) using a low-pressure mercury lamp, in view of their large light absorption coefficients at wavelength 254 nm. The light irradiation was effective for the formation of highly crystalline oxide films at temperatures below 600 °C. By combining two sources, Ca_2CuO_3 and $SrCuO_2$ films were prepared. Photo-CVD of *c*-axis oriented $Bi_2Sr_2CuO_x$ film was achieved by the irradiation of ternary sources of $Bi(C_6H_5)_3$ and strontium and copper β-diketonates at 500 °C.

Keywords: Thin film, photo CVD, metal β-diketonates, complex oxide, high-T_c superconductor

1 INTRODUCTION

Ceramic multilayered films attract much interest in relation to the layered perovskite structure of high-T_c superconductors.[1] For the construction of artificially designed layered structures, low-temperature deposition is essential to prevent interdiffusion between the layers. Chemical vapor deposition (CVD) is one of the promising methods for this purpose due to the high energy state of source materials and high process controllability. However, most of the CVD films of high-T_c superconductors have so far been prepared at substrate temperatures higher than 700 °C.[2] A few studies have been reported on the utilization of plasma excitation for decreasing CVD temperature.[3,4] Another potentially low-temperature process, photo-CVD, had not been reported until our recent study.[5] Using the purified source materials,[6] we presented our preliminary results on the deposition of some oxide and/or carbonate films by light irradiation from a low-pressure mercury lamp.

The present study has been carried out to evaluate the light absorption properties of copper and alkaline-earth β-diketonates and to fabricate various oxide films relating to Bi–Sr–Ca–Cu–O superconductors by a low-temperature photo-CVD process.

2 EXPERIMENTAL

Source materials used were $Sr(DPM)_2$, $Ca(DPM)_2$, and $Cu(DPM)_2$ complexes (DPM: dipyvaloylmethane, $(CH_3)_3CCOCH_2COC(CH_3)_3$, i.e. 2,2,6,6-tetramethyl-3,5-heptanedione according to IUPAC nomenclature). They were supplied from Tri-chemical Co. Ltd, Nihonsanso Co. Ltd, and Nihon Kagaku Sangyo Co. Ltd, and purified by sublimation and recrystallization as described previously.[6] The absorption coefficients of the sources were determined from the UV–VIS spectra measured on n-hexane solutions of concentration of (1, 2, 5, 7 and 10) ×

0268-2605/91/040325-06$05.00

Received 8 April 1991
Revised 25 April 1991

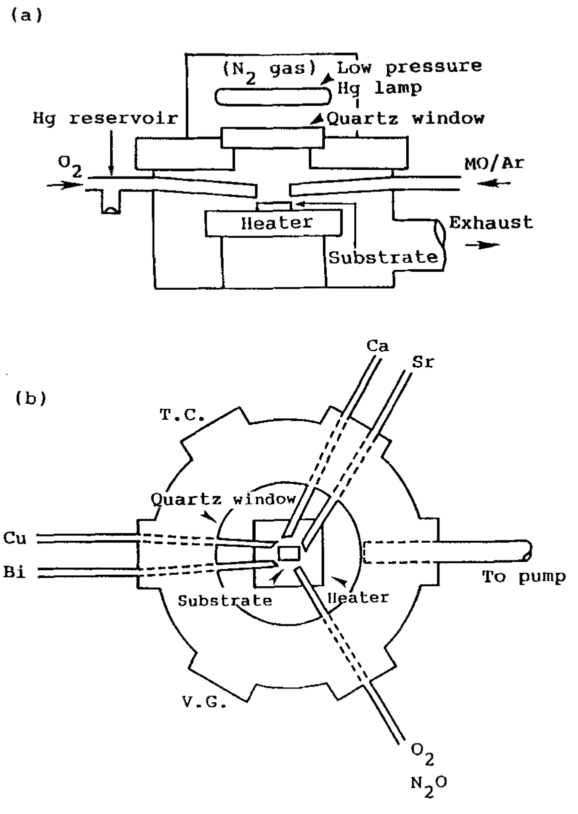

Figure 1 Photo-CVD apparatus used in this study. (a) Cross-sectional view; (b) top view. Abbreviations: T.C., Thermocouple; V.G., Vacuum gauge.

10^{-5} mol dm^{-3} in the wavelength range 190–900 nm using a Hitachi 200-20 spectrometer.

The purified $Cu(DPM)_2$, $Ca(DPM)_2$ and $Sr(DPM)_2$ complexes were placed in glass flasks and heated in separate oil baths at 90–120 °C, 180–200 °C and 200 °C, respectively. The evaporated sources were carried by argon (50 sccm (standard cubic centimeter per minute)) through heated stainless-steel pipes into the CVD chamber illustrated in Fig. 1. An oxidant gas (O_2, N_2O, or NO_2: 20 sccm) was introduced to the chamber independently. The reaction pressure and time were 20 Torr and 2 h, respectively. The substrate, MgO(100) or $SrTiO_3$(100), was placed 2 cm below the quartz window and heated at a temperature between 300 °C and 600 °C. A low-pressure mercury lamp (Orc Co. Ltd, 110 W) was used as UV light source. The film thickness was measured by the stylus method using a ULVAC Dektak-3010. Crystal structure and composition of the films were analyzed by X-ray diffraction (XRD, MAC Science: MXP^3) using CuK$_\alpha$ and X-ray photoelectron spectroscopy (XPS; JEOL, JPS-80), respectively. The temperature dependence of resistivity of the films was measured by the conventional four-probe method.

RESULTS AND DISCUSSION

3.1 Photo-absorption properties

Figure 2 shows UV–VIS (190–900 nm) spectra of hexane solutions of (A) $Ca(DPM)_2$, (B) $Sr(DPM)_2$, and (C) $Cu(DPM)_2$. Hexane was employed as solvent to minimize solvation effect. For all of the sources, strong light absorption was observed in the range 190–320 nm but not in the range 320–900 nm. The light absorption obeyed the Lambert–Beer's law for all the sources in this concentration range to enable the determination of molar light absorption coefficients. Table 1 lists the absorption coefficients of Sr $(DPM)_2$, $Ca(DPM)_2$, and $Cu(DPM)_2$ at various wavelengths frequently used in photo-CVD. The absorption coefficients at 249 nm (KrF excimer laser) and 254 nm (low-pressure mercury lamp) are in the range of 10^4–10^5 dm^3 mol^{-1} · cm^{-1}. The concentration range 10^{-5}–10^{-4} mol dm^{-3} should correspond to 0.2–2 Torr partial pressure in the gas phase, which is generally employed in CVD. Thus, the source materials examined have a high potential as sources for photo-CVD excited with a low-pressure mercury lamp or KrF excimer laser.

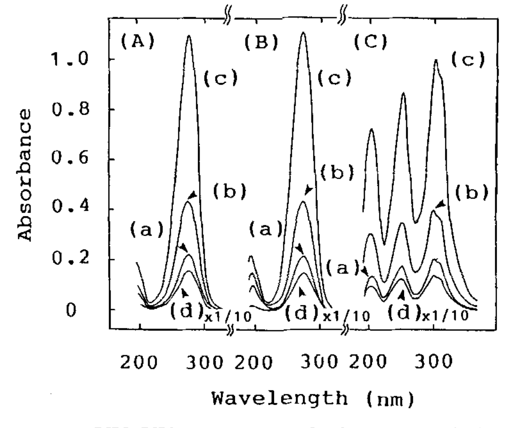

Figure 2 UV–VIS spectra of hexane solution of (A) $Ca(DPM)_2$, (B) $Sr(DPM)_2$, and (C) $Cu(DPM)_2$. The concentration was (a) 1×10^{-5} mol dm^{-3}; (b) 2×10^{-5} mol dm^{-3}; (c) 5×10^{-5} mol dm^{-3}, and (d) 7×10^{-5} mol dm^{-3}.

Table 1 Molar absorption coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) of hexane solutions of source materials at various wavelengths

Material	ArF excimer laser (193 nm)	KrF excimer laser (248 nm)	Low-pressure Hg lamp (254 nm)	XeCl excimer laser (308 nm)
$Sr(DPM)_2$	4.0×10^3	5.8×10^3	9.5×10^3	1.3×10^3
$Ca(DPM)_2$	3.9×10^3	6.8×10^3	1.0×10^4	1.2×10^3
$Cu(DPM)_2$	1.1×10^4	1.7×10^4	1.7×10^4	1.9×10^4

3.2 Photochemical decomposition of copper and alkaline earth β-diketonates

First, the preparation of oxide films from a single source was examined. From $Cu(DPM)_2$, black films were obtained at substrate temperatures of 300 °C and 400 °C. The presence of copper in the divalent state, together with oxygen and carbon, in the films was confirmed by X-ray photoelectron spectroscopy (XPS). Figure 3 shows X-ray diffraction (XRD) patterns of the films prepared under various conditions. No XRD peak was observed in the films deposited at a substrate temperature of 300 °C, either with or without the light irradiation from a low-pressure mercury lamp. By increasing the substrate temperature to 400 °C, the film showed XRD peaks due to CuO crystals. The peak intensities were 1.3–3 times higher for the film prepared with the light irradiation than for the film prepared without, showing the improvement of film crystallinity by UV light irradiation.

Figure 4 shows XRD patterns of the films prepared from $Ca(DPM)_2$. The film prepared at 300 °C was amorphous [Fig. 4(a)]. By increasing the substrate temperature to 400 °C, (001)-oriented $CaCO_3$ film was prepared. The peak intensities of the film prepared with the UV irradiation [Fig. 4(b)] were more than three times higher than those of the film without light irradiation [Fig. 4(c)]. Further increase of the substrate temperature to 500 °C produced CaO films with strong (001) orientation irrespective of light irradiation [Fig. 4(d)]. Thermal processes should be predominant at this temperature. It is noteworthy that $CaCO_3$ formation at 400 °C was suppressed and CaO formation was promoted by using N_2O as an oxidant instead of O_2, as shown in Fig. 4(e); the CaO (200) peak is observed and no peak assignable to $CaCO_3$ is present in the film prepared in the presence of N_2O at 400 °C. The result suggests a variation of intermediate species of reaction depending on the oxidant gas.

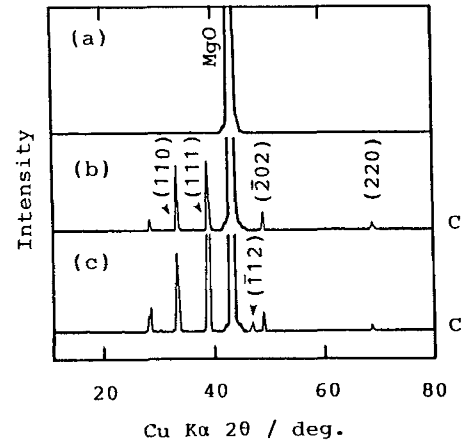

Figure 3 X-ray diffraction patterns of the films [about 3000 Å (300 nm) thick] prepared from $Cu(DPM)_2$ at a substrate temperature of (a) 300 °C with UV light irradiation; (b) 400 °C without UV light irradiation; and (c) 400 °C with UV light irradiation. Intensity

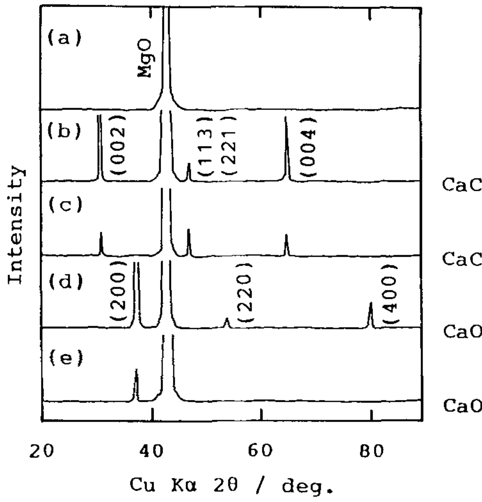

Figure 4 X-ray diffraction patterns of the films [about 5000 Å (500 nm) thick] prepared from $Ca(DPM)_2$ at (a) 300 °C with UV light irradiation; (b) 400 °C with UV light irradiation; (c) 400 °C without UV light irradiation; (d) 500 °C with UV light irradiation; and (e) 400 °C with UV light irradiation in the presence of N_2O. $CaCO_3$ $CaCO_3$ CaO CaO

Figure 5 shows the XRD patterns of films prepared from Sr(DPM)$_2$ under various conditions. Peaks assigned to $SrCO_3$ were observed in the XRD patterns of the films prepared at 400 °C and 500 °C with UV irradiation. Without UV irradiation, no XRD peak was observed. At a temperature of 600 °C, SrO film was formed irrespective of UV irradiation. Judging from the enthalpy and entropy of formation for the reaction $MCO_3 \rightarrow MO + CO_2$, the temperature required for the formation of oxide rather than carbonate is expected to be higher for M = Sr than for M = Ca. The result is qualitatively consistent with this thermodynamic prediction.

3.3 Photo-CVD of complex oxides

Synthesis of $MCuO_2$ (M = Ca,Sr) films attracts our special interest because it can contain a CuO_2 plane which is considered to be the supercurrent layer in high-T_c cuprates.[7] Low-temperature synthesis of Ca–Cu–O and Sr–Cu–O systems by photo-CVD was examined by simultaneous supply of two source materials. By supplying supposedly equimolar Ca(DPM)$_2$ and Cu(DPM)$_2$ concurrently to the chamber, a black crystalline film was obtained by UV irradiation at a substrate temperature of 400 °C. XPS analysis of the film showed the presence of calcium and oxygen as well as of the divalent state of copper which was evidenced by the appearance of clear satellite peaks of Cu$2p_{1/2}$ and Cu$2p_{3/2}$ (Fig. 6).[8] The XRD peaks shown in Fig. 7 are assignable to Ca_2CuO_3. No peak assignable to $CaCuO_2$, which we wished to make, was observed in the XRD spectrum of the film. It must be noted that $CaCO_3$ was not detected. The film deposited in the absence of UV light was amorphous.

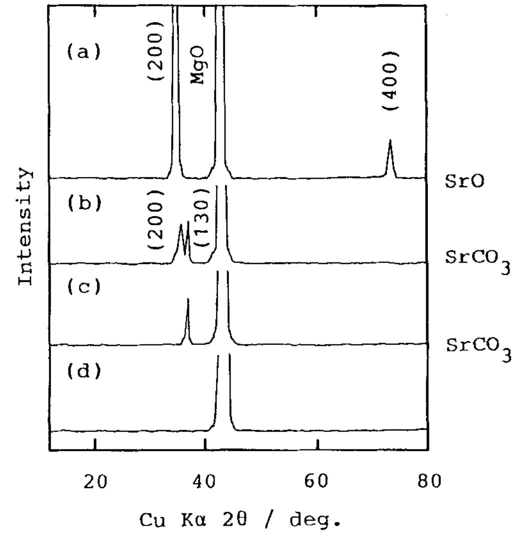

Figure 5 X-ray diffraction patterns of the films prepared from Sr(DPM)$_2$. The preparation conditions are (a) 600 °C with UV light irradiation; (b) 500 °C with UV light irradiation; (c) 400 °C with UV light irradiation; and (d) 500 °C without UV light irradiation.

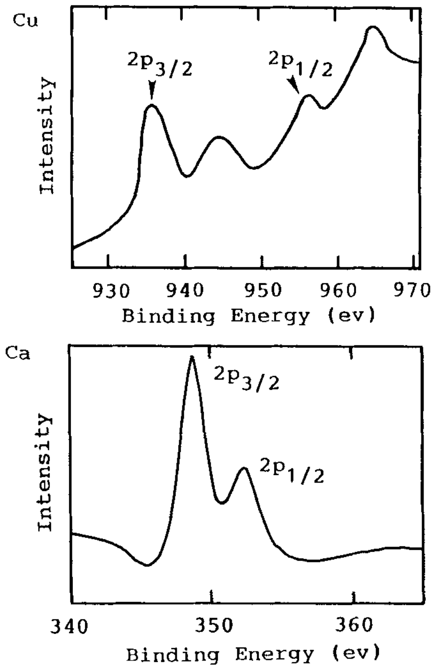

Figure 6 X-ray photoelectron spectra of the film prepared at 400 °C from Ca(DPM)$_2$ and Cu(DPM)$_2$.

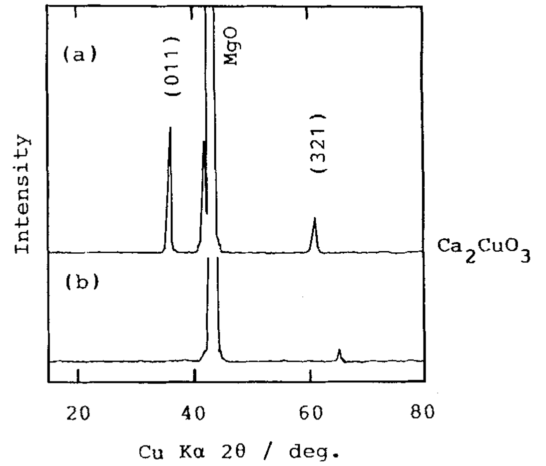

Figure 7 X-ray diffraction patterns of the films (about 3000 Å thick) prepared at 400 °C by simultaneous supply of Ca(DPM)$_2$ and Cu(DPM)$_2$. (a) With UV light irradiation; (b) without UV light irradiation.

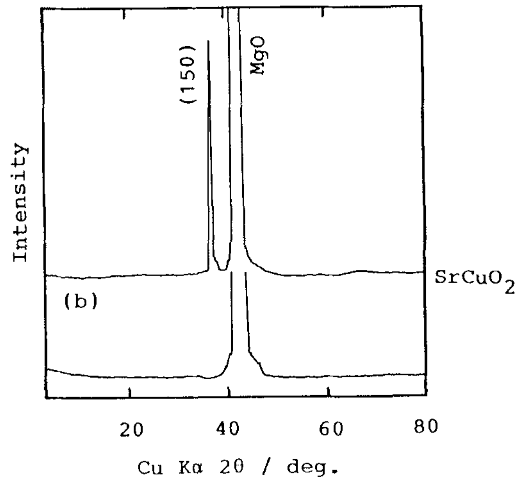

Figure 8 X-ray diffraction patterns of the films prepared at 400 °C from the mixture of $Sr(DPM)_2$ and $Cu(DPM)_2$. (a) With UV irradiation; (b) without UV light irradiation.

Figure 8 shows the XRD patterns of the films prepared from an equimolar supply of $Sr(DPM)_2$ and $Cu(DPM)_2$ at a substrate temperature of 400 °C. Film prepared without UV irradiation was amorphous, whereas UV irradiation induced the formation of orthorhombic $SrCuO_2$. XPS spectra of this photo-CVD film verified the divalent state of copper, strontium and oxygen. Again it should be noted that no carbonate peak was observed in the XRD of the film prepared from $Sr(DPM)_2/Cu(DPM)_2$ under the conditions that $SrCO_3$ was formed preferentially from $Sr(DPM)_2$ alone.

3.4 Photo-CVD of $Bi_2Sr_2CuO_x$ film

The preparation of $Bi_2Sr_2CuO_x$ film, so-called (2201) phase with 20 K class superconductivity,[9] was investigated by supplying ternary source materials of $Bi(C_6H_5)_3$, $Sr(DPM)_2$, and $Ca(DPM)_2$. The temperatures for evaporating the sources were 90 °C, 200 °C and 90 °C for $Bi(C_6H_5)_3$, $Sr(DPM)_2$, respectively. The substrate, $SrTiO_3(100)$, was kept 500 °C. Figure 9 shows the XRD pattern of the photo-CVD film. Almost single-phase $Bi_2Sr_2CuO_x$ with (001) orientation was obtained. The presence of bismuth, strontium and copper in divalent state in the film was confirmed by XPS. The temperature dependence of resistivity of the film was semiconductive. Further optimization of preparation conditions and oxygen stoichiometry is in progress to obtain superconducting films.

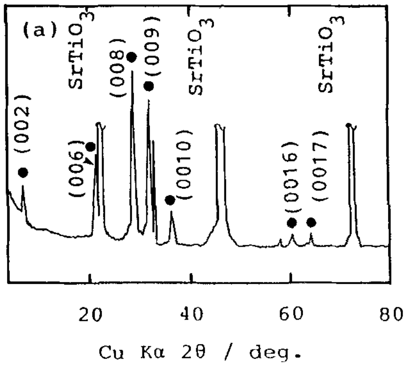

Figure 9 X-ray diffraction pattern of the film prepared at 500 °C with UV irradiation by supply of $Bi(C_6H_5)_3$, $Sr(DPM)_2$, and $Cu(DPM)_2$ simultaneously; *c*-axis oriented $Bi_2Sr_2CuO_x$ was observed.

4 CONCLUSION

Copper and alkaline earth β-diketonates can be used as sources for photo-CVD of ceramic thin films due to their strong light absorption coefficients at the wavelength of a low-pressure mercury lamp. UV irradiation was effective to prepare crystalline Ca_2CuO_3 and $SrCuO_2$ films at a substrate temperature of 400 °C. Formation of a $Bi_2Sr_2CuO_x$ phase was also promoted by UV irradiation.

Acknowledgement The authors acknowledge Messrs S. Gonda (Tokyo Institute of Technology) and M. Matsuse (Tokai University) for XPS measurements. This study was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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