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Preparation of Bi-Sr-Ca-Cu-O Films by Chemical Vapor Deposition with Metal Chelate and Alkoxide

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Bi-Sr-Ca-Cu-O films were chemically deposited on yttria stabilized zirconia substrates at 1083 K and 130 Pa using a bismuth alkoxide and β-diketonate chelates with Sr, Ca, and Cu as source materials.

Recently, high temperature superconducting oxides were discovered in the system of Bi-Sr-Ca-Cu-O (BSCCO).[1] One of the compounds in this system shows a high Tc around 110 K. These compounds are relatively stable against moisture compared to the rare-earth barium cuprate superconductors. Films of BSCCO compounds have already been prepared by sputtering and "painting" techniques. According to one report,[2] the chemical vapor deposition (CVD) technique has also been applied to the preparation of BSCCO films. The source materials were metal halides (SrI_2, CaI_2, CuI, and $BiCl_3$). Temperatures of 773-1098 K were needed to obtain adequate vapor pressures of the alkaline earth metal halides. However, halogen gases generated by the decomposition of halides in the CVD processes are liable to etch substrates and reactor wall, and hence the use of halogen-free source materials is preferable. Moreover, the use of halides is not favorable for lowering the deposition temperature.

We previously succeeded in preparing $YBa_2Cu_3O_{7-x}$ films by CVD using metal chelates as source materials.[3] Reasonable vapor pressures of metal chelates for CVD can be obtained below 550 K.

We describe here the preparation of BSCCO films by CVD, using a bismuth alkoxide and metal β-diketonate chelates as source materials which do not contain halogen elements.

A bismuth alkoxide (triethoxybismuth $Bi(OC_2H_5)_3$; 99.99% purchased from TRI Chemical Laboratory) was evaporated at 410 K. The metal β-diketonate chelates used were bis-(2,2,6,6-tetramethyl-3,5-heptanediono(thd))-strontium, -calcium, and -copper(II). $Sr(thd)_2$, $Ca(thd)_2$, and $Cu(thd)_2$ were evaporated at 500, 450, and 400 K, respectively. These vapors were carried with Ar gas, while oxygen gas was separately introduced into the reactor. The total gas flow rate was 300 ml/min (O_2:Ar = 2:1). The gas pressure in the reactor was maintained at 130 Pa. Yttria (8 mol%) stabilized zirconia (YSZ) substrates were used. The deposition temperature was 1083 K.

Black, electrically conducting films were obtained on the substrate, with growth rates of about 4 μm/h. The presence of Bi, Sr, Ca, and Cu in the film was confirmed by qualitative analysis with a energy dispersive X-ray spectroanalyzer (Philips PV9100).

Figure 1 shows an X-ray diffraction pattern of a film with a YSZ substrate. Most of the diffraction peaks can be indexed by a tetragonal (or pseudotetragonal) cell of $Bi_2(Sr,Ca)_3Cu_2O_x$ with a = 5.40 and c = 30.64 Å.[4,5]

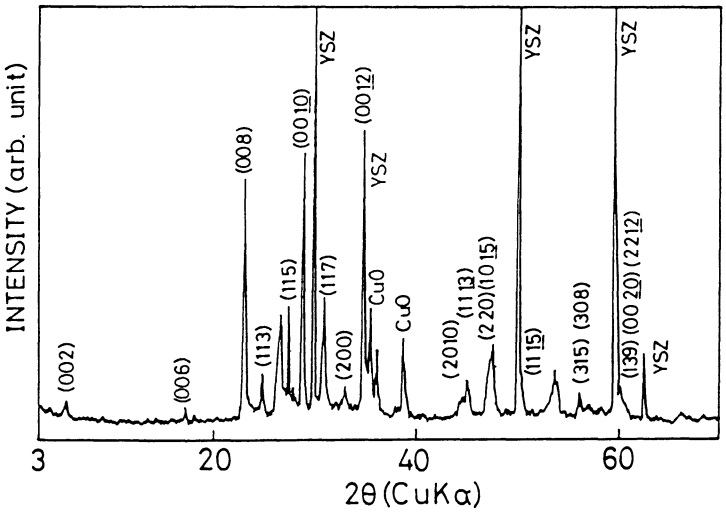

Fig. 1. X-Ray diffraction pattern of a film with a YSZ substrate. Indexed peaks were associated with $Bi_2(Sr,Ca)_3Cu_2O_x$.

Figure 2 shows a scanning electron micrograph of the cross section of a film on a YSZ substrate. The film was porous, especially near the surface.

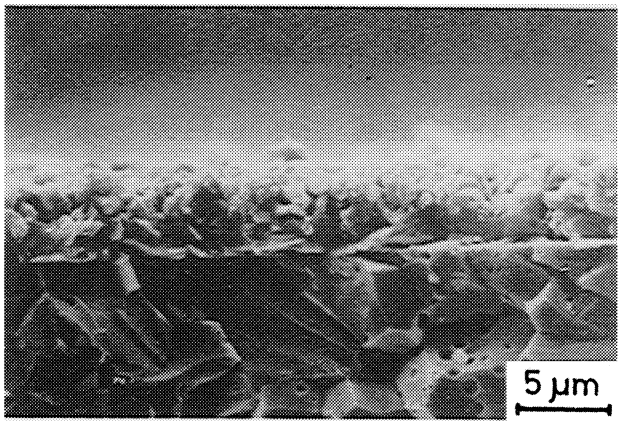

Fig. 2. SEM photograph of the cross section of a film.

In summary, we have successfully prepared Bi-Sr-Ca-Cu-O films by CVD using a bismuth alkoxide and metal β-diketonate chelates as source materials.

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