YBa₂Cu₃O_x superconducting thin films prepared by low temperature vacuum codeposition

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Abstract. Y–Ba–Cu–O films were prepared by low temperature codeposition of three components. The Y and Cu contents were evaporated from metallic sources, while Ba was vacuum-evaporated from Ba, BaO and BaF₂ sources in separate codeposition experiments. The lowest temperature at which superconducting YBa₂Cu₃O_x thin films (about 0.5 μm thick) prepared *in situ* was near 500°C. This process enables preparation of superconducting films on various substrates (SrTiO₃, MgO, Al₂O₃, Si) without a buffer layer. Zero-resistance critical temperature was as high as 88 K and the critical current density was 10⁴ A/cm² at 4.2 K. The morphology of the films was granular with disordered grain orientation, the average grain size being typically 0.5 μm.

Keywords. Superconductivity; thin films; vacuum coevaporation.

1. Introduction

High-quality polycrystalline and even single-crystal Y–Ba–Cu–O thin films were prepared at temperatures higher than 800°C using various vacuum deposition techniques (Li *et al* 1988; Bao *et al* 1987; Garzon *et al* 1989). However, some problems have to be solved before these films can be used in microelectronic or optoelectronic applications: (i) sufficiently low temperature process of superconducting thin film synthesis compatible with other microelectronic technologies, (ii) preparation of films on technological substrates and (iii) reproducibility and stability of thin films.

It was found that these requirements in the case of Y–Ba–Cu–O thin films prepared by coevaporation of three components can be solved (Chromik *et al* 1989a,b,c,d) but the parameters of technological process, the properties of thin films and the choice of substrates are influenced by the source of the Ba component. The aim of this work is to show the influence of BaO-, Ba- and BaF₂-evaporating sources on the technological process and properties of Y–Ba–Cu–O thin films.

2. Experimental

In the case of BaO-evaporating source (Chromik *et al* 1989a,b) the basic technology is vacuum coevaporation of three components. The vacuum chamber was first evacuated using an oil diffusion pump to an initial pressure of 10^{−4} Pa and then the vacuum was degraded by oxygen to the pressure of 10^{−2} Pa. The evaporation sources were two thermal evaporation boats (Y, Ba) and one electron gun (BaO). The total evaporation rate and thicknesses were nearly 1 nm/s and 1 μm respectively. The composition of our films was studied by energy-dispersive X-ray analysis (EDAX) which showed that most of the films did not have an exact composition 1:2:3 due to the spatial geometry of the evaporation sources. However, the films with a higher

copper content, according to the nominal stoichiometry and with the ratio Y:Ba near 0.5, showed good superconducting properties. The evaporation rate and thickness of three components were monitored separately by thickness monitors. The best results were obtained at a substrate temperature in the range 550–580°C during deposition.

In the case of evaporation of metallic Ba this process was modified (Chromik *et al* 1989c). We performed the coevaporation of three metallic elements Y, Ba, Cu in a vacuum of 5×10^{-3} Pa. The deposition process was divided into repetitive steps of evaporation separated by oxidation at an oxygen pressure of 10^{-2} Pa. The annealing between individual evaporation steps usually took 3 minutes. The minimum temperature of the substrate was 580°C and the film thickness was 900 nm.

BaF₂ evaporation source was used in deposition which was also divided into few coevaporating steps (Chromik *et al* 1989d). These steps were separated from each other by annealing steps. The total evaporation rate, film thickness and vacuum pressure used during each coevaporation step were less than 1 nm/s, 100–150 nm and 10^{-4} Pa respectively. The annealing step took usually 5 min at a partial pressure of oxygen of 10^{-2} Pa. The total film thickness and substrate temperature during evaporation and annealing steps were 700 nm and 580–650°C respectively. The process of final oxidation of the films in the case of BaO, Ba, BaF₂ evaporation sources was performed using the same procedure (Chromik *et al* 1989 a,b).

3. Results and discussion

In the case of BaO evaporating source polycrystalline thin films were prepared. The resistivity of the films measured by the dc four-probe method shows a metallic character of R–T dependence with the onset of temperature T_{con} near 92 K and the best zero resistance critical temperature T_{ce} near 88 K. A relatively small scattering of T_{ce} at different substrates is probably a consequence of the low-temperature procedure, i.e. small interdiffusion between substrate and Y–Ba–Cu–O film. This is in agreement with AES depth profile analysis (Chromik *et al* 1990a) of thin films prepared on different substrates. We have used (100) SrTiO₃, Al₂O₃ and silicon single-crystal substrate oxidized silicon and silicon with SrTiO₃ buffer layer, and polycrystalline Al₂O₃. The low temperature procedure enables us to prepare good superconducting Y–Ba–Cu–O thin films at a temperature of 530–550°C on silicon substrate without a buffer layer (Chromik *et al* 1989b). The oxygen from the BaO evaporating source can be directly incorporated into the film. However, the reproducibility of such films was not very good. An analysis of the composition of the films after each experiment was necessary. EDAX and atomic emission spectroscopy were used to determine the Ba content in the film which significantly depends on the state of BaO ingot. The problem arises due to different densities of Ba and BaO which are deposited during evaporation. Before each new deposition we have carried out necessary corrections concerning the evaporation of BaO.

In the case of the metallic Ba evaporating source the evaporation at good vacuum pressure ensured good reproducibility of the deposition process but the incorporation of oxygen, during annealing periods between coevaporation steps, was not sufficient if the same oxidation condition as in BaO was used. Besides increasing the film thickness it was necessary to increase the minimum temperature of the substrate up to 580°C during evaporation and annealing in order to obtain the same electrical properties as in

the BaO evaporation source. The thickness dependence of our thin films can be explained by the smaller influence of interface between the film and the substrate, and the higher probability of percolation conduction paths in the case of thicker films. We have observed the quality dependence of whole films on the thickness of individual films deposited during one evaporation step. The preliminary AES analyses show significantly higher diffusion of Si from Si-substrate into superconducting film compared to BaO indicating that substrate temperatures around 600°C are critical in the deterioration of properties of thin Y–Ba–Cu–O films by contamination with Si (Agarwal *et al* 1990). The main disadvantage of metallic Ba is its chemical instability because when exposed to air it oxidizes in a few minutes.

Relatively inert BaF₂ material was used as a source material of Ba (Garzon *et al* 1989). We have chosen as substrate material a poly- and single-crystalline Al₂O₃ and single-crystal SrTiO₃ (100) (Chromik *et al* 1989d). It was found that annealing is important for increasing the oxygen content in the preparation of thin films whereas coevaporation steps in good vacuum are necessary to release the fluorine from the film. This method enables us to prepare homogeneous polycrystalline superconducting thin films with critical temperature onset at 92 to 93 K. The maximum zero resistance critical temperature for single-crystal Al₂O₃ and SrTiO₃ substrates was 84.7 K and 88.4 K respectively. The critical current density at a temperature of 4.2 K was 40 K A/cm². Our analysis (Chromik *et al* 1989d) shows traces of fluorine in the film. Experiments with Si substrates were not very successful probably due to the higher temperature of the substrate (600°C) or the possible reaction of fluorine with substrate. A maximum T_{cc} in this case was only 30 K. The thin films prepared by BaF₂ as source material showed higher stability against moisture during photolithography process.

4. Conclusions

We have compared the influence of different materials as a source of Ba component in high Y–Ba–Cu–O thin films prepared by *in situ* low temperature coevaporation. The main advantage of BaO is the possibility of sufficiently low temperature process (530–580°C) to prepare high T_c Y–Ba–Cu–O thin films without buffer layer on Si substrates. However, the reproducibility of such films was not satisfactory due to instability of BaO source before evaporation. Metallic Ba enables good reproducibility of thin films, but the minimum temperature of substrate was 580°C. It was necessary to increase the film thickness to 900 nm. A significant diffusion of Si into film in the case of Si substrate was observed. Metallic Ba exhibits chemical instability in air. The application of BaF₂ was connected with good reproducibility of the film on the Al₂O₃ and SrTiO₃ substrates. The temperature of the substrate was near 600°C. The films showed higher stability against moisture and during photolithography processing.

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