PREPARATION STUDY OF Bi-Sr-Ca-Cu-OXIDES SUPERCONDUCTING
THIN FILMS BY RESISTIVE EVAPORATION

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ABSTRACT

A conventional vacuum system housing resistively heated sources only was used to study the evaporation conditions for Bi-Sr-Ca-Cu oxides thin film production. Thin film were prepared by sequential evaporation of CaF$_2$, SrF$_2$ and Bi pulverized mixture and Cu from the two separate sources. The starting materials were weighed to yield a stoichiometric Bi$_2$Sr$_2$CaCu$_2$ film of about 1µm thickness upon evaporation to completion. Well polished HgO Substrates kept at room temperature were used in this experiment.

The films were annealed in a quartz-tube furnace at 350°C for one hour for oxidation of the copper layers thus precluding any Bismuth escape, followed by 10 minutes at 725°C in flowing O$_2$ bubbled through water for defluorination and then at Ca. 870°C for 14 hours.

Typical results, using four-point probe method reveal a $T_c$ (R = 0) at 83K and critical current density of $10^7$ A/cm$^2$ at 66K.

This work presents one of the simplest vacuum deposition methods in which no thickness monitor or any other control system is required. The crucial point in the heating treatment was to overcome the problem of the Bismuth diffusing out of the film during the long annealing time at high temperature.

INTRODUCTION

Much effort has been expanded on preparation of the Bismuth family high $T_c$ superconductors since its first discovery by Maeda et al$^1$. By now the Bi-Sr-Ca-Cu-O family is known to have at least three different systems showing three different Phase-transition temperatures, Bi$_2$Sr$_2$CaCu$_2$O$_x$ (abbreviated 2223) with $T_c$ above 100K. Bi$_2$Sr$_2$CaCu$_2$O$_{0.9}$ (2212) with $T_c$ = 80K and Bi$_2$Sr$_2$CuO$_{3.1}$ (2201) with $T_c$ = 20K. Reports on film preparation of the (2223) Phase point out that it is rather difficult to get really Single Phase Polycrystalline samples. It seems to be process dependent since this phase tends to crystallize only in small unconnected grains separated by the lower $T_c$ phases (mostly 2212)$^2$, thus precluding zero resistance at 110K. It was recently reported$^3$. 
that partial substitution of Bi by Pb atoms helps to increase the proportion of the (2223) Phase.

Several methods, such as magnetron sputtering, ion beam sputtering and laser ablation, have been used to prepare the Bi-Si-Ca-Cu-O thin film system. However they require many elaborated expensive peripheral facilities such as controllers, thickness monitoring systems, etc. In this communication we present a study of Bi-Si-Ca-Cu-O Superconducting thin film preparation utilizing a simple inexpensive evaporation system and post annealing procedure.

EXPERIMENTAL AND DISCUSSION

A conventional vacuum system with basic pressure of 10^{-5} torr equipped with resistively heated tungsten boats was used for the evaporation. The desired film thicknesses were obtained by predetermination of the material amount considering the substrate to boat distance and by its evaporation to completion. No thickness monitor or any other control or monitoring systems were used.

After having tried a variety of starting materials, such as oxides and carbonates, it was realised that only fluorides which evaporate readily best meet our purposes. SrF₂, CaF₂, Bi and Cu were weighed in the atomic proportion to yield stoichiometric Bi₂Sr₂Ca₁Cu₂ Phase. The Cu and the well grounded pulverized mixture of Bi, SrF₂, CaF₂ were introduced in two separate boats at 6 cm distance below the substrate holder. Films were prepared by a sequential evaporation of the mixture and the copper in this order onto well polished MgO substrates kept at room temperature. In our early depositions we used only one boat into which the mixture of all the constituents was placed and evaporated all together. Auger depth profile analysis of films prepared by this evaporation method revealed strong diffusion of Bismuth atoms out of the sample surface, which presumably evaporated during the long annealing treatment. Therefore we have subsequently used the sequential evaporation method. Films thus obtained were then annealed in quartz-tube furnace at 350°C for an hour for oxidation of the most upper copper layers, thus precluding the Bismuth constituent escape. This stage was followed by 10 minutes at 725°C in wet O₂ atmosphere for defluorination and then at 870°C for 14 hours crystallization, after which it was quenched to room temperature.

Electrical characterization has been carried out using a standard four-probe DC method in a zero magnetic field with a typical supercurrent of 3 mA. Voltage values were averaged for both direct and reverse current direction to eliminate any possible thermal EMF effects. Temperature dependence of the resistance is depicted in Fig.1 where zero resistance was detected at 83K. In Fig.2 the I-V curve at 65°K of the same sample is shown, from which a critical current density of 1000 A/cm² was deduced. SEM examination of the annealed film revealed a porous polycrystalline structure consisting of randomly oriented needles like crystallites similar to previous observation.

The same evaporation method and post heating treatment were used to get the (2223) Phase with a nominal composition aimed to Bi₂Sr₂Ca₃Cu₄. The R vs. T result shown in Fig.3 strongly indicates that some portion of the higher Tc Phase is already fabricated, as can be deduced from the clear 20% step onset at about 115K. Reannealing of this sample to a higher temperature and longer duration time resulted in a higher room temperature resistance without any improvement in Tc.

From crystal studies it is well established by now that the (2212) Phase has an ideal composition of Bi₂Sr₄Ca₂Cu₂O₈ which can be described as a packing of (2212) layers along the c axis shifted with respect to each other.