Thin films of Y–Ba–Cu–O by rf sputtering and study of Josephson effect

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Abstract. Thin films of Y–Ba–Cu–O material have been prepared by rf diode sputtering using a single oxide target on strontium titanate substrates kept at an ambient temperature. It was found difficult to attain stoichiometry of the films identical to that of the target due to resputtering of the films. The influence of sputtering parameters such as target-substrate distance, rf power, gas pressure and substrate temperature in attaining a particular stoichiometry of the film has been studied. The I–V characteristics of the bridges show Shapiro steps when the bridges are irradiated with microwave radiations. The thin film bridges have the dimensions larger than coherence length; thus all the Josephson effect features are understood to arise due to intergranular junctions.

Keywords. RF sputtered film; Y–Ba–Cu–O film; Josephson effect; microwave irradiation; effects.

1. Introduction

Amongst various techniques of preparation of Y–Ba–Cu–O thin films, rf sputtering with single composite target has been considered quick, simple and relatively inexpensive in comparison to coevaporation or cosputtering processes. However, realizing the right stoichiometry has often been a problem due to change in nature of the target surface during subsequent sputtering cycles, resputtering of the deposited film, sensitivity of stoichiometry to the sputtering geometry and to the substrate material used, besides its orientation. Overall the annealing procedure plays a vital role in attaining optimum superconducting properties.

In case of composite oxide targets it is now well known that due to different sputtering yields of the constituents there are changes in the composition (Bigniew and Kowalski 1983) and topography (Greene *et al* 1978) of their surface layer. These dynamic changes of the target surface accompanies sputtering till the formation of an equilibrium-altered layer on the target. Resputtering due to negative ion formation has often been reported to occur particularly in targets of alkali metal and alkaline earth containing oxides and also for those based on fluorides and chlorides targets (viz. BaTiO₃—Shintani *et al* 1975; Ba(Pb, Bi)O₃—Gilbert *et al* 1980; and TbF₃—Hanak and Pellicane 1976). This has been studied by Saito *et al* (1988) in great detail specially for targets containing barium and oxygen as constituents.

2. Experimental

Thin films of Y—Ba—Cu—O were deposited by rf diode sputtering from a single-mixed oxide target of approximately 100 mm diameter. The planar target has been prepared by the conventional solid-state reaction method. Sputtering was performed in pure argon atmosphere. The influence of significant sputtering parameters such as rf power,

target-substrate distance and gas pressure was studied and accordingly optimized to get films of required 123 stoichiometry. The composition of the films has been determined by energy-dispersive X-ray analysis both in pre- and post-annealing stages. X-ray diffraction patterns helped in identifying the structure. The conventional four-probe method was used for R-T and I-V measurements. Keeping all necessary sputtering parameters, as well as constituents and configuration of the target unchanged, the ageing of the target during sputtering has been investigated systematically by analysing the changes in films deposited after different durations. The substrate temperature was recorded during a sputtering cycle. After thirty cycles of sputtering at very high rf power, a small part of the target was cut and its micrographs were taken both for planar and transverse cross-sections.

In subsequent experiments targets of 135 stoichiometry were fabricated to compensate for the deficiency of Ba and Cu occurring in case of 123 targets. We also studied the target-substrate distance effect on the film stoichiometry with 135 targets. The sputtering parameters were maintained throughout along with a gas pressure of 20 mtorr and an rf power of 100 Watt.

The typical films after annealing in oxygen atmosphere were found to be superconducting at 73 K. A microbridge with constriction of dimensions $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ was patterned by the standard photolithographic process using Shipley 1450 J positive photoresist. This sample was annealed at 950°C for 1 h in oxygen atmosphere and allowed to cool slowly. The annealed sample was mounted inside the waveguide holder for microwave studies.

3. Results and discussion

The films deposited, using single target with nominal composition 123 of Y:Ba:Cu, usually showed in the films deficiency of Ba on substrate surface immediately below the centre of the target. The composition of the first few films, deposited from a freshly made unresputtered target, was found to depend on the target-age (i.e. number of sputtering cycles or total sputtered time of the target) as shown in figure 1. This change is understood to arise due to formation of altered layers. It has been seen that after some sputtering cycles the colour of the sputtered side of the target changes from black to brown. Further, the sheet resistivity of the sputtered side of the target decreased and stabilized to some lower value. All these observations indicate the changes in phase and/or loss of an element of any constituent component due to preferential sputtering. Further the ion bombardment leads generally to surface enrichment of the component having a lower sputtering yield. In this case we expect that the nature of the target surface changes from insulating to metallic behaviour mainly due to (preferential) loss of oxygen. Such type of preferential loss of oxygen has already been reported in CuO targets as well (Behrisch 1983). In figure 1 the atomic weight percentage of Cu decreased initially and later stabilized to a lower value. This is expected because atomic weight percentage of Cu in the altered layer decreases due to high sputtering yield of Cu.

It has been observed that the film deposition rate increased first and then stabilized with the aging of the target. This also involves the changes in electrical conduction behaviour of the target. The loss of oxygen may change the target from semi-conducting or insulating-to-metallic character.

Figure 1. Change in the atomic compositions of Y, Ba and Cu in the thin film with target age.

Figure 2 shows the SEM micrographs of the cross-sectional view of the sputtered part of the target. Figure 3a,b show the SEM micrograph of the sputtered and unsputtered surfaces. A lot of microcracks are visible even on the sputtered surface. This is attributed to low thermal conductivity and differential heating of the target. The possible solution to this problem is to increase power as slowly as possible so that thermal stabilization could take place. The second solution is to make the target by joining the rods of YBaCuO with the help of some epoxy or silver paste.

Figures 4a,b show the change in grain size of the sputtered and unsputtered sides of the target. The former is smaller than that of the unsputtered side. This is an indication of the heating effect or segregation of some elements to provide the required composition and conditions for the formation of smaller grain size.

It has been observed that usually the sputtered films are Ba and Cu-deficient due to resputtering effect. There may be so many possible reasons for this effect and it is difficult to isolate any one of them. The formation of O^- during sputtering from an oxide target was reported by Hanak and Pellicane (1976) who suggested that O^- has a tendency to contribute to the resputtering of the films. From figure 1, it seems that the O^- has some effect on the atomic ratio of Ba because there is a very small increase in its value with target age. The second cause of resputtering is the production of secondary electrons. Lau *et al* (1972) have shown that the rise in substrate temperature mainly occurs due to bombardment of secondary electrons. We have also observed rise in substrate temperature which causes loss of the Ba adatoms. Another possibility is the preferential sputtering of Ba from films or the formation of Ba^+ ions (Gilbert *et al* 1980) which are expected to be recaptured by the cathode and hence the films get deficient in barium. All the above effects seem to contribute cumulatively to the deficiency of Ba and Cu in films. This leads to the conclusion that increasing the target-substrate distance results in deficiency of Ba concentration. Figure 5 shows the nature of target-substrate distance vs atomic weight percentage of Y, Ba and Cu curves.

Figures 2 and 3. 2. SEM micrograph of the cross-sectional view of the sputtered target.
3. SEM micrographs of the surfaces of the target (**a**) sputtered side, (**b**) unsputtered side.

Figure 4. SEM micrographs presenting the changes in grain size on the surfaces of the target (a) sputtered side, (b) unspattered side.

After annealing of the patterned microbridge, the effect of microwave irradiation on its I-V curve was studied. Shapiro steps have been clearly observed (Kumar *et al* 1989). This effect is interpreted to arise due to the presence of a network of grain boundary Josephson junctions.

Figure 5. Change in atomic composition of Y, Ba and Cu in the film as a function of target-substrate distance.

4. Conclusions

Thin films of Y-Ba-Cu-O material have been prepared by rf sputtering. The behaviour of the target along with its aging and associated resputtering effects have been studied. On irradiation with microwave the Shapiro steps have been observed in I-V curves of the patterned thin film microbridges. The weaklink area of the bridge consists of a random network of large number of Josephson junctions. This cumulative effect is regularly observed despite the high temperature superconductor being a short coherence length material and the pattern being quite wide.

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