Synthesis of sequentially-deposited Cu/BaF₂/Y films on SrTiO₃ and buffered Si substrates

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Abstract. Sequentially-deposited layers of Cu/BaF₂/Y on buffered Si and SrTiO₃ substrates have been synthesised to produce YBa₂Cu₃O_{7- δ} thin film. An attempt has been made to see the effect of the ZrO₂ and Al buffer layers on Si of the annealing of the layered structure. X-ray diffraction studies reveal that on ZrO₂-buffered Si the annealing of the layered structure leads to formation of 211 phase while on Al-buffer layer 123 phase is obtained. Noticeable effect in annealed-layered structure of oblique deposition of BaF₂ from a Knudson Cell is seen in X-ray diffraction.

Keywords. Buffer layers; layered structure.

1. Introduction

The synthesis of bulk superconducting ceramics La/Ba/Cu/O (Bednorz and Muller 1986) and Y/Ba/Cu/O (Wu *et al* 1987) with high transition temperatures of 30 and 90 K respectively spurred a great deal of enthusiasm to produce these materials in thin film form. Attempts have been made to produce these high T_c materials on Si substrates. Some success has been obtained in this regard but the materials synthesized on buffered Si substrates have been by far more promising in yielding T_c at 80 K (Mogso Campero *et al* 1988). Recently, it has been shown that Al acts as a very good buffer layer for a screen-printed YBa/Cu/O film due to inhibiting Cu from precipitating at film substrate interface (Asano *et al* 1989). In preparing the thin film of the material, the constituents YBaCu have been used either as oxides of metals or in a few cases BaF₂ has been found to be more effective in the sense that the 123 material synthesized using the fluoride gives a moisture-resistant substance (Mankewich *et al* 1987). On the other hand the barium component while using as a fluoride has been deposited either by thermal evaporation (Hilton *et al* 1988) or by means of Knudson cell (Allen *et al* 1988). To address the problem of effect of substrate, the buffer layer and the deposition of the BaF₂ by oblique incidence we have carried out the sequential deposition of Cu-BaF₂-Y on buffered Si and SrTiO₃ substrates and report the results of the study in the present work.

2. Experimental

The substrates used were (100) or (111) P-Si and (100) SrTiO₃. The Si wafers were cleaned thoroughly by RCA process while SrTiO substrates were cleaned ultrasonically in organic solvents. All the substrates were given thorough deionized water rinse and blown dry with pure N gas before loading into the Varian VT118A UHV system. The Si wafers were precoated with e-beam deposited ZrO₂ and Al films for use as buffer layers. The layered structure of Cu/BaF₂/Y was obtained by sequential deposition of the materials without breaking the vacuum. Cu, Y were deposited by e-beam and BaF₂

Table 1. Table showing annealing sequence of the deposited samples of substrates.

Parameter	Ramp parameter	Soaking time	Oxygen
Ramp up 650°C–930°C	5°C/min		Dry
Annealing temp. 930°C	—	$\frac{1}{2}$ h	Wet
Ramp down 930°C–750°C	2°C/min		Dry
Intermediate temp 750°C	—	3 h	Dry
Ramp down 750°C–550°C	2°C/min	—	Dry
Intermediate temp II 550°C	—	1 h	Dry
Final cool down to ambient	Natural cooling (3°C/min)	—	Dry

was deposited by Knudson cell (K-cell). The rates for Cu and Y were chosen as 2 Å/s and the thicknesses were 1000 Å, 4500 Å and 3000 Å for Y, Cu and BaF₂ respectively. The base pressure in all the deposition was 2×10^{-8} mbar and the deposition pressure was 4×10^{-7} mbar. The substrates were not heated and no oxygen was bled during deposition. A thin cap of 100 Å of Cu was given on the completed layered structure to avoid any atmospheric contamination. All the deposited samples were then annealed in a Tempress, Omega Junior-I microprocessor-controlled furnace having a stability of $\pm 0.10^\circ\text{C}$ at all temperatures used ($150 \leq T \leq 930$). The annealing was done in dry/wet/dry oxygen. The annealing sequence is as shown in table 1. The ramp up or down parameters though fixed at 5°C/min or 2°C/min in the present case, can be changed to any value between 0 and 100°C in steps of 0–1°C.

To evaluate the effect of the substrates, the buffer layer and the annealing recipes the annealed samples were subjected to X-ray diffraction (XRD), scanning electron microscopy (SEM) and R–T measurements by the four-probe method.

3. Results and discussion

Figure 1 shows the XRD pattern of the annealed layered structure on Al-coated Si wafer. We clearly see that 123 peaks are obtained at (004) and (112). The sample was annealed as per recipe given in table 2. In contrast to this the sample deposited on ZrO₂-coated Si wafer did not yield any observable 123 phase for the same annealing recipe. The films were deposited without breaking the vacuum and to achieve this BaF₂ was deposited from the K-cell resulting in oblique incidence (45°) of the vapour beam to the wafer. XRD does not show the presence of peaks associated with (211) phase. To ascertain the effect of the annealing recipe on the Si/Al interface a bare Al-coated wafer was also subjected to the same heat-treatment conditions and XRD was taken. The resultant pattern is as shown in figure 2. The SEM picture of the samples on Al buffered substrate as in figure 1 is shown in figure 3.

In contrast to the case of 123 synthesized on Si/Al substrate the formation of the material on SrTiO₃ with BaF₂ at normal incidence is very marked. As seen in the XRD of figure 4, more peaks seem to appear in the pattern than in buffered Si substrates. However, in obliquely deposited BaF₂ in the layered structure the XRD pattern of annealed sample is slightly different with peaks appearing at (112), (020) as shown in figure 5. However, in both cases there is no indication of formation of (211) phase. The

Figure 1. X-ray diffraction pattern of annealed Y-BaF-Cu layers on Al-buffered Si substrate.

Figure 2. X-ray diffraction pattern of dry-wet-dry oxidation of Al-Si structure. The annealing recipe is the same as in table 1.

SEM picture (figure 6) of the same sample shows formation of large-oriented crystallites which was also observed earlier.

The reason for the absence of substantial amount of 123 phase in films on ZrO_2 -buffered Si substrates may be because there could be a noticeable reaction of the material with the film used as buffer. The possibility of such a reaction occurring has been reported earlier (Cima *et al* 1988). In the particular case under discussion the ZrO_2 film was deposited by e-beam with the base pressure $\sim 10^{-7}$ mbar without any substrate heating or oxygen bleeding during deposition. The loss of 123 could thus occur only if there are voids or cracks in the film to facilitate diffusion of Si to react with the layered structure. The reason why we have been able to produce 123 film on buffered Al substrate clearly demonstrates that there is no significant reaction of the layered structure. It agrees well with the findings of Asano *et al* (1989) on screen-printed 123 films on Al-coated Si substrates. This result clearly indicates that Al film can be easily used as an effective buffer layer for synthesis of 123 on Si wafer.

A variety of annealing recipes have been reported, used in the final synthesis of the 123 material, the main variant being the soaking time at annealing temperature (850–930°C) ($\frac{1}{2}$ hr:5hr) and during cooling down phase at 750°C. However, wet oxidation has been used when BaF_2 has been taken as one of the constituents in the as-deposited

Figure 3. SEM picture of annealed Y-BaF-Cu layer on Al-buffered Si substrate. Annealing temperature 930°C, time 30 min.

Figure 4. X-ray diffraction pattern of 123 material on SrTiO single crystal. The BaF₂ component in the layered structure was deposited at normal incidence by e-beam.

films. Wet oxidation is essential for converting $\text{BaF}_2 \rightarrow \text{BaO}$ to form the 123 material (Sui Waichen *et al* 1988). The change of annealing recipe is also expected to affect the reaction of the layered structure on buffered Si substrates. To actually see this, the annealing recipe used for Al-buffered Si was slightly altered. All other parameters were kept the same except for the soaking time at 750°C. This time was chosen as 1 h as against the usual 3 h. The result of this change was that the 123 phase did not form at all

Figure 5. X-ray diffraction pattern of 123 material on SrTiO_3 single crystal. The BaF_2 component in the layered structure was deposited obliquely using as K-cell.

Figure 6. R vs T curve for 123 film on SrTiO_3 substrate.

and instead the 211 phase was obtained. This could be because intermixing of the layers has not completed even though Y and BaF_2 would have been oxidized. However, this 211 phase can at least be used as a fresh substrate for subsequent deposition of the constituents to get the desired 123 phase.

The preparation of 123 high T_c material has been well established on SrTiO_3 and a variety of process variations have been used. Notable amongst these is the use of BaF_2 as the source for Ba and in particular using an effusion cell for the deposition. As shown in earlier figures we see that the oblique deposition of the BaF_2 component also yields the 123 material with slightly changed orientations in contrast to the case when BaF_2 is deposited at normal incidence by using an e-gun for its evaporation. This slight difference in the XRD peaks can at least be qualitatively understood on the basis of the

reasoning that the nucleation of the BaF_2 on the predeposited Cu layer will be different in the two cases. This changed nucleation is thus responsible for an entirely changed microstructure thus leading to different solid-state reaction between the layers upon annealing. This changed mechanism could also explain the formation of the surface microstructure as observed in SEM.

5. Conclusion

It has been observed that Al buffer layer acts as a better barrier compared to ZrO_2 film when using Si as substrate. The angle of deposition of BaF_2 in the particular case has been found to lead to a slightly different orientation of the synthesized 123 material on SrTiO_3 .

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