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Deposition of yttria-stabilized zirconia buffer layer on Si and its suitability for Y–Ba–Cu–O thin films

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Abstract. The deposition of yttria-stabilized zirconia (YSZ) as buffer layer on (100) silicon has been studied by rf sputtering with a view to subsequently preparing superconducting films of $YBa_2Cu_3O_x$ on it. As-deposited films were found to be (100) oriented. The thermal mismatch and reaction between Si and YSZ at high temperatures were found to give rise to cracks in the films. Grain growth of buffer layer on annealing helped in the formation of superconducting phase.

Keywords. YSZ buffer layer; thin films; high temperature superconductivity; silicon.

1. Introduction

Deposition of Y–Ba–Cu–O on silicon is of technological importance. Though direct deposition of Y–Ba–Cu–O in Si has been tried, the quality of the film produced is quite poor (Berberich *et al* 1988). This is presumably due to (i) reaction between film and substrate and (ii) the mismatch between the thermal and lattice parameters. Intermediate buffer layers have been studied with a view to overcome these difficulties (Mogro-Campero and Turner 1988).

The present investigation was carried out with a view to studying the suitability of yttria-stabilized zirconia as a buffer layer. The presence of cracks and the formation of $ZrSiO_4$ was observed when the buffer layers were annealed above 600°C. Subsequently deposition of Y–Ba–Cu–O on such buffer layers yielded barium-deficient films on post-deposition annealing. The loss of barium has been confirmed to be due to the formation of Ba_2SiO_4 at the elevated temperatures.

2. Experimental

Thin film deposition of both YSZ buffer layer and Y–Ba–Cu–O was carried out by rf sputtering. A 40 mm diameter target of nominal composition $Y_{0.1}Zr_{0.9}O_x$ was used for buffer layer deposition. Sputtering was carried out at 0.05 torr argon pressure. Films of about one micron thickness were deposited on (100) oriented silicon. Subsequently they were annealed for 4 h at various temperatures between 600°C and 1100°C. A uniform heating and cooling rate of 100°C/h was used.

Thin film deposition of Y–Ba–Cu–O on buffered silicon substrates was carried out using a stoichiometric target. Other deposition conditions were essentially the same as in

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the case of YSZ. Y–Ba–Cu–O films were post-annealed under oxygen for 30 min at various temperatures in the range 830–890°C.

3. Results

Both YSZ and Y–Ba–Cu–O films were investigated for the phase and microstructure. In addition resistivity was measured on Y–Ba–Cu–O films.

3.1 *YSZ films*

X-ray diffraction of the as-deposited YSZ film shown in figure 1 clearly reveals its highly oriented (100) nature. Similar result has been reported by Morita *et al* (1985) for zirconia deposition using electron beam evaporation. Weak (311) reflection is also present. Annealing of films between 600 and 975°C reduces the width and increases the

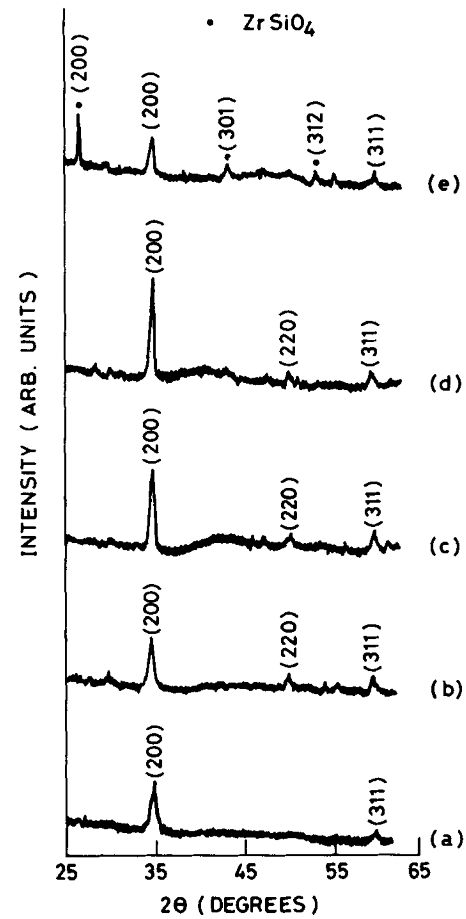

Figure 1. X-ray diffraction pattern for YSZ buffer layer on silicon (**a**) as-deposited and annealed at (**b**) 600°C (**c**) 800°C (**d**) 975°C and (**e**) 1100°C.

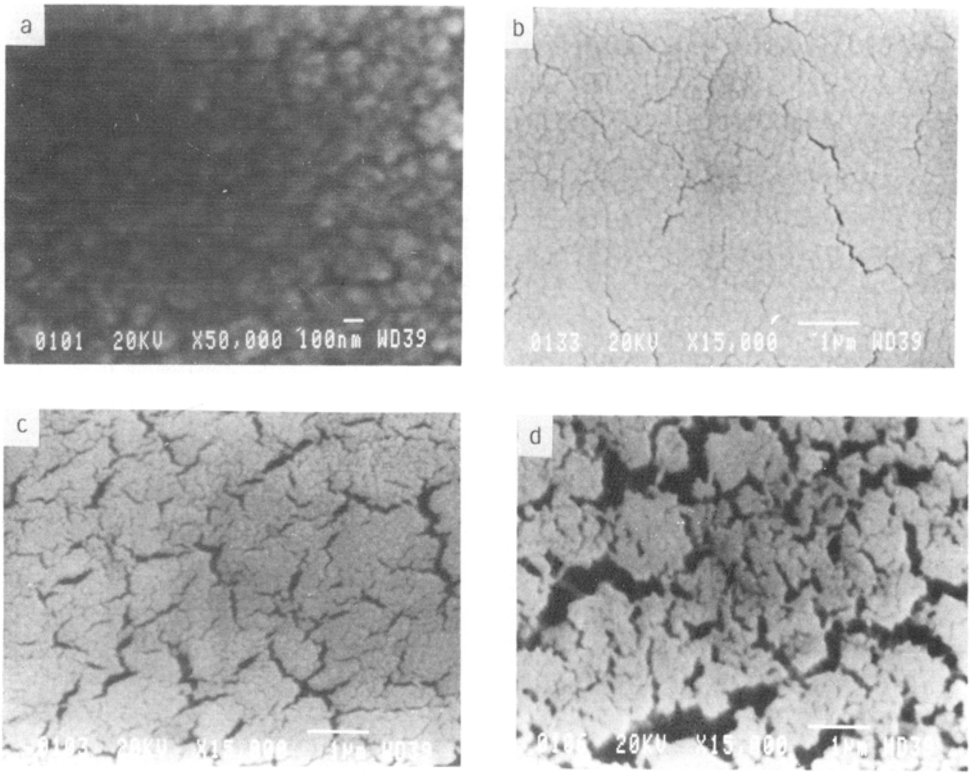

Figure 2. Scanning electron micrographs of YSZ buffer layer on silicon (**a**) as-deposited and annealed at (**b**) 600°C (**c**) 975°C (**d**) 1100°C.

height of (200) peak indicating grain growth. Small peak corresponding to (220) is also seen on annealing. In contrast to our observations YSZ films earlier reported by Lee *et al* (1988) by sputtering were randomly oriented. In YSZ films annealed at 1100°C, the height of (200) reflection is seen to have reduced. Reflections corresponding to $ZrSiO_4$ are also seen. This suggests that at high temperatures YSZ reacts with silicon to yield $ZrSiO_4$.

SEM photographs obtained for as-deposited and annealed films are shown in figure 2. The micrographs clearly show the grain growth on annealing as also revealed by the XRD data. Further on annealing films are seen to develop cracks. We attribute this to the enhanced reaction between silicon and YSZ at high temperature and also to the thermal mismatch. Although XRD data show reaction only in films annealed at 1100°C, SEM in figure 2 suggest the onset of reaction even at much lower temperatures. This is further supported by the observation that films turned from transparent to whitish on annealing above 800°C.

3.2 *Y–Ba–Cu–O films*

YSZ films annealed at 975°C which showed sharp (200) peak and good grain growth were used for depositing Y–Ba–Cu–O films during our initial trials. The composition of the as-deposited film was close to $YBa_{1.75}Cu_{3.1}O_x$. On subsequent annealing loss of barium

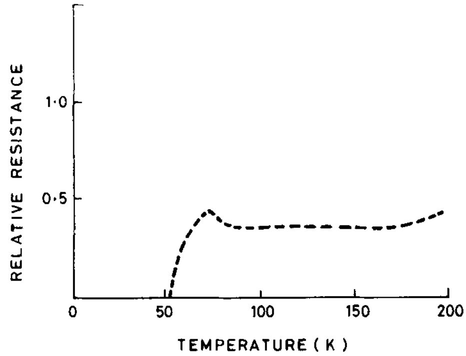

Figure 3. Resistance vs temperature plot for a typical Y–Ba–Cu–O film on silicon with YSZ buffer layer.

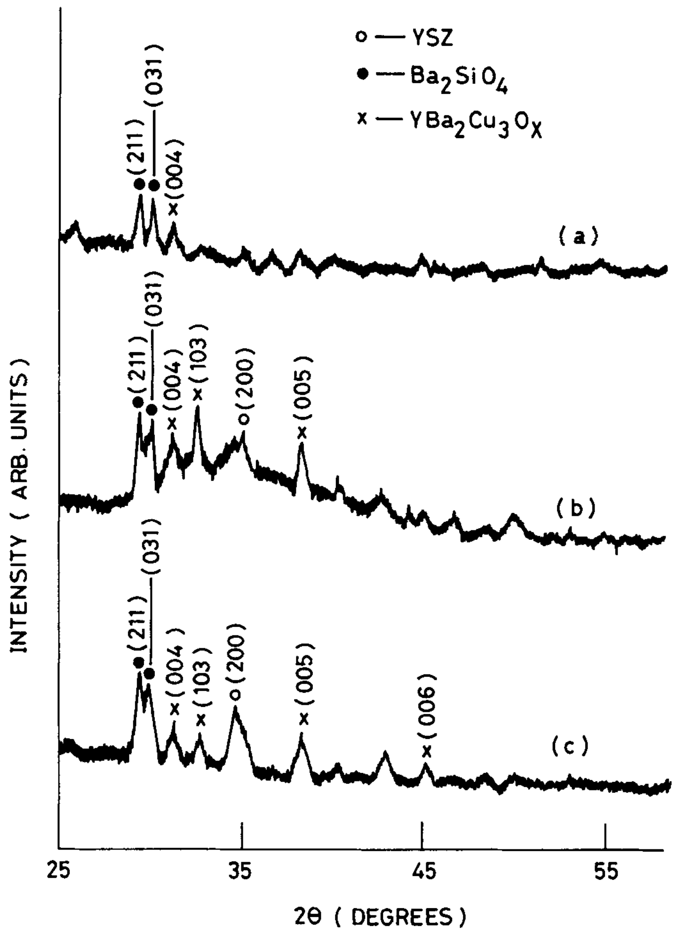

Figure 4. X-ray diffraction pattern for Y–Ba–Cu–O film deposited on (a) silicon (b) unannealed buffer layer and (c) 975°C annealed buffer layer.

from the film was observed. Room temperature resistance of films annealed between 830 and 890°C was measured and those annealed between 845 and 860°C were found to have minimum value. R vs Tcurve for a film annealed at 845°C is reproduced in figure 3. Transition to superconducting state ($R = 0$) is seen to occur at 52 K in this case.

In order to investigate the loss of barium on annealing, XRD of the Y–Ba–Cu–O film deposited on bare silicon as well as with buffer layer was studied. The plots are shown in figure 4. It is seen from figure 4a that Si reacts with Y–Ba–Cu–O to yield Ba_2SiO_4. The formation of Ba_2SiO_4 was also confirmed in this case when silicon with YSZ layer was used (figure 4c). This is presumably due to crack formation in the film through which Y–Ba–Cu–O reacts with Si. This also explains the observation made by Greve *et al* (1989). As a consequence Y–Ba–Cu–O films on Si with YSZ buffer layer should be annealed at much lower temperatures compared to those for YSZ substrate as reported by Aswal *et al* (1989). However in low temperature-annealed buffer layer the crystallite size is very small. The large number of grain boundaries yield poor quality Y–Ba–Cu–O films (figure 4b). High temperature annealing on the other hand though yields large size YSZ crystallites, it also leads to the formation of cracks through which Y–Ba–Cu–O film reacts with Si. Therefore in our opinion the deposition of YSZ buffer layer at room temperature cannot yield good quality film and the YSZ layer should also be formed *in situ* at high temperature.

4. Conclusion

The YSZ film deposited on Si when subjected to high temperature anneal develops cracks. The formation of $ZrSiO_4$ and thermal mismatch are found to be responsible for this. In Y–Ba–Cu–O films deposited on YSZ buffered Si substrate the loss of barium observed on annealing is attributed to the reaction between film and the substrate.

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