JOURNAL OF MATERIALS SCIENCE 28 (1993) 781–784

P^+ implantation and annealing effects on the T_c in BiSrCaCuO films

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The T_c changes related to the microstructure as a function of annealing temperature for the BiSrCaCuO (BSCCO) film implanted with 170 keV P^+ at two different doses were studied. The BSCCO films were prepared by d.c. sputtering on MgO substrates. For the film implanted at a dose of $5\times10^{15}\,cm^{-2}$ post-implantation annealing at 600–800 °C enabled the T_cs of the film to be completely recovered. For the film implanted at a dose of $1.0\times10^{17}\,cm^{-2}$ the T_cs were only partly recovered after 600 °C annealing. On further annealing at 700 °C the superconductivity of the film disappeared. TEM examination showed that significant amount of CaP, Ca_3P_2, and some unknown phases were formed. It is considered that the significant amounts of these phases formed during post-implantation annealing renders the recovery of the superconductivity of the P^+-implanted BSCCO film difficult.

1. Introduction
Radiation effects on the superconducting properties of the YBaCuO and BiSrCaCuO (BSCCO) systems have been extensively studied in both fundamental and technological research [1–7]. In general, T_c is reduced as the radiation dose is increased. A quantum interference device fabricated on YBaCuO thin film using the patterning by oxygen or arsenic ion implantations has been reported [8]. It is well known that ion-implantation techniques have been applied to the fabrication of semiconductor devices. In view of the possible application of superconducting thin films in microelectronic devices [9] it is interesting to investigate the ion-implantation effect on the superconductivity of the high T_c films. In our previous results, B^+ implantation and annealing effects on the superconductivity and microstructure of the BSCCO film were studied [10]. It seems that the B^+ implantation technique is compatible with the BSCCO film in device application. In this work the T_c changes related to the microstructure as a function of the annealing temperature in the P^+-implanted BSCCO film were studied.

2. Experimental procedure
BSCCO films were deposited on (1 0 0) MgO substrate in 0.05 torr (1 torr = 133.322 Pa) of argon by d.c. sputtering from a sintered $Bi_2Sr_2CaCu_3O_x$ target. The target–substrate distance and plasma power were 3 cm and 50 W, respectively. During sputtering, the substrate temperature was kept at about 200 °C. The thickness of the as-deposited film was around 2 μm. After appropriate annealing, the as-deposited films became superconducting [11, 12]. The temperature dependence of the electrical resistance was measured by the four-probe method. Ion-implantation was performed at room temperature by 170 keV P^+, and with a beam current of 2 μA. The microstructure of the film was observed using transmission electron microscopy (TEM). The post-implantation annealing time for each thermal treatment was 15 min.

3. Results and discussion
3.1. $5.0\times10^{15}\,cm^{-2}$
For Sample A with the chemical compositions Bi:Sr:Ca:Cu = 30:24:16:30 the T_c (onset) and T_c (zero) were around 87 and 79 K, respectively. After being implanted with 170 keV P^+ at a dose of $5.0\times10^{15}\,cm^{-2}$ the T_cs of the film became 85 and 77 K, respectively, which were somewhat lower than those prior to ion implantation. Fig. 1 shows the P^+ implantation and annealing effects on the T_cs of the film. The penetration depth of the 170 keV P^+ in the BSCCO film was estimated to be about 0.15 μm using TRIM-90 code [13]. From TEM examination, amorphous zones were formed in the 2 2 1 2 grains due to ion implantation and most of the film still remained crystalline. One example is shown in Fig. 2. It is evident that the implantation-induced defects, such as the amorphous zones, produce a significant decrease in carrier mobility, resulting in the degradation of superconductivity of the film. After annealing at 600 °C the T_cs of the film were recovered to its original values before ion implantation, meanwhile the amorphous zones were recrystallized to the 2212 phase as shown in Fig. 3. On annealing at 800 °C the T_cs of the film still remained unchanged, indicating that phosphorus dopants at the level of $5\times10^{15}\,cm^{-2}$ have no significant effect on the T_c of the annealed film. A similar result was also observed in the B^+-implanted BSCCO films after 800 °C annealing, in

which the boron dopants resident in the film were 3.7×10^{15} cm^{-2} [10].

3.2. 1.0×10^{17} cm^{-2}

For Sample B with the chemical compositions

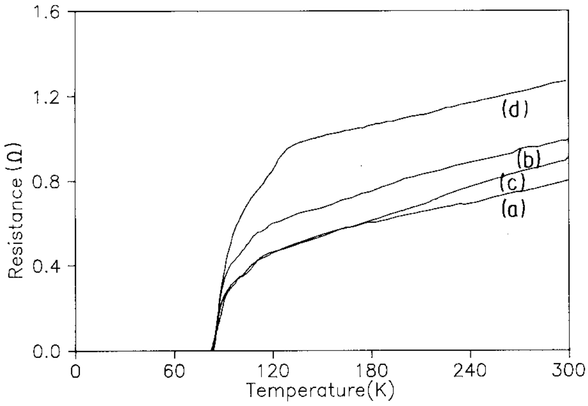

Figure 1 Resistance–temperature curves for the film implanted with 170 keV P^+ at a dose of 5×10^{15} cm^{-2}. (a) As-prepared, (b) as-implanted, (c) post-implantation annealing at 600 °C, (d) post-implantation annealing at 800 °C.

Bi:Sr:Ca:Cu = 23:30:16:31, the T_c (onset) and T_c (zero) were 85 and 72 K, respectively. After being implanted with 170 keV P^+ at a dose of 1.0×10^{17} cm^{-2}, the film was annealed starting from 500 °C. The changes in the resistance–temperature (R–T) curves are shown in Fig. 4. The R–T curve of the as-implanted film showed semiconductor behaviour. From TEM examination, the fraction of amorphous regions was larger than that in the film implanted at a dose of 5×10^{15} cm^{-2}. After 600 °C annealing, the T_c (onset) of the implanted film was significantly recovered but there was still residual resistance of about 14 mΩ below 70 K. It is worth noting that as the annealing temperature reached 700 °C the R–T curve of the film showed semiconductor behaviour again. These results are greatly different from those for Sample A implanted at a dose of 5×10^{15} cm^{-2}, in which post-implantation annealing at 600–800 °C enables the T_cs of the film to be completely recovered to the values prior to ion implantation.

It has been reported that phosphorus dopants have a tendency to decompose the 2 2 2 3 and 2 2 1 2 phases to the 2 2 0 1 and non-superconducting phases after

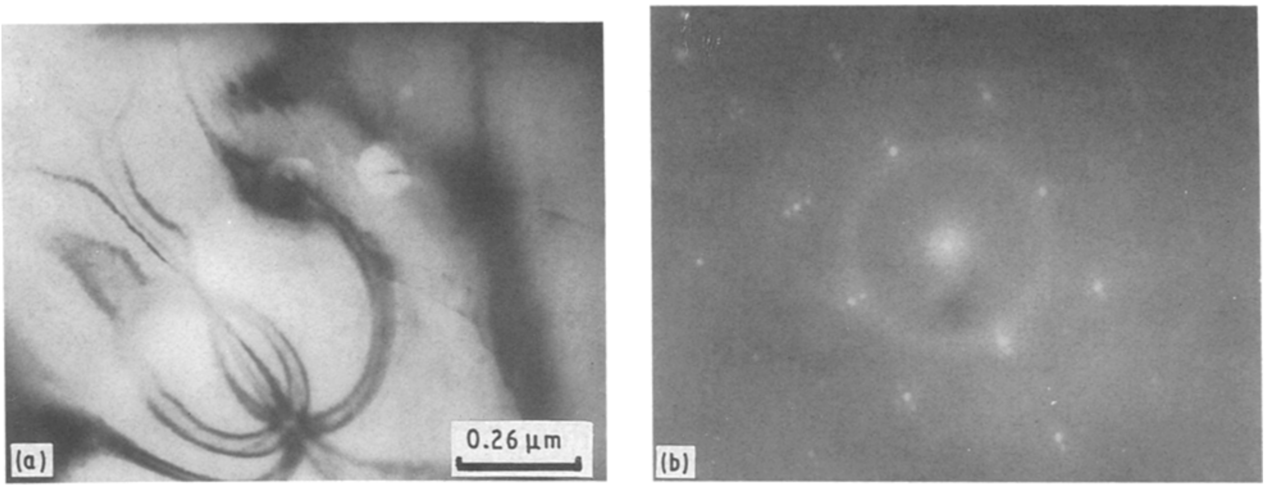

Figure 2 (a) Bright-field image of the film implanted with 170 keV P^+ at a dose of 5×10^{15} cm^{-2} showing that the amorphous zones were formed in the 2 2 1 2 grain. (b) Diffraction pattern of (a).

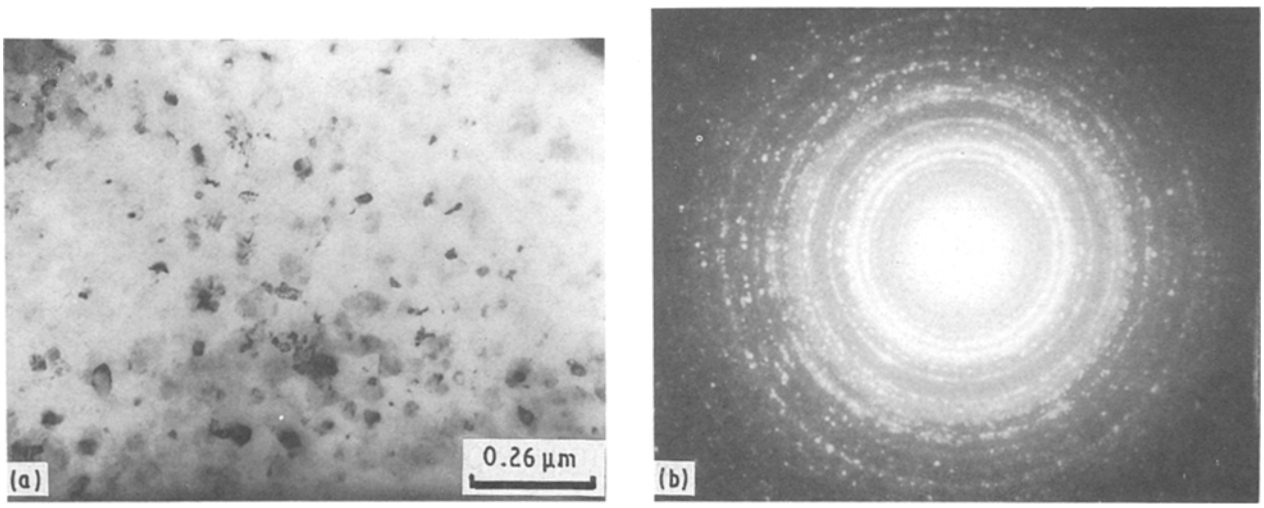

Figure 3 (a) Bright-field image of the film annealed at 600 °C after having been implanted with 170 keV P^+ at a dose of 5×10^{15} cm^{-2} showing the recrystallization of the 2 2 1 2 phase from the amorphous zones. (b) Diffraction pattern of (a).

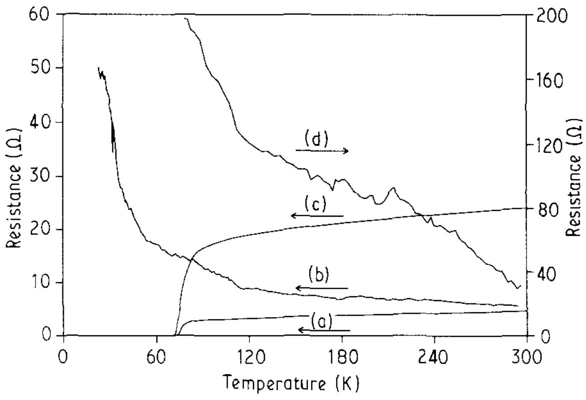

Figure 4 Resistance–temperature curves for the film implanted with 170 keV P^+ at a dose of $1.0 \times 10^{17}\,cm^{-2}$. (a) As-prepared, (b) as-implanted, (c) post-implantation annealing at 600 °C, (d) post-implantation annealing at 700 °C.

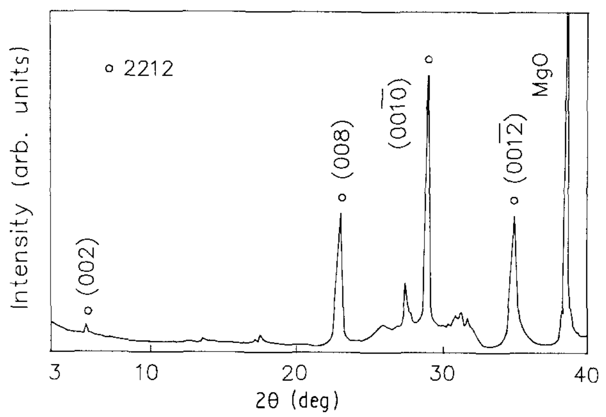

Figure 5 X-ray diffraction pattern showing that for the BSCCO film annealed at 700 °C after having been implanted with 170 keV P^+ at a dose of $1.0 \times 10^{17}\,cm^{-2}$, no significant amount of the 2 2 0 1 phase was formed.

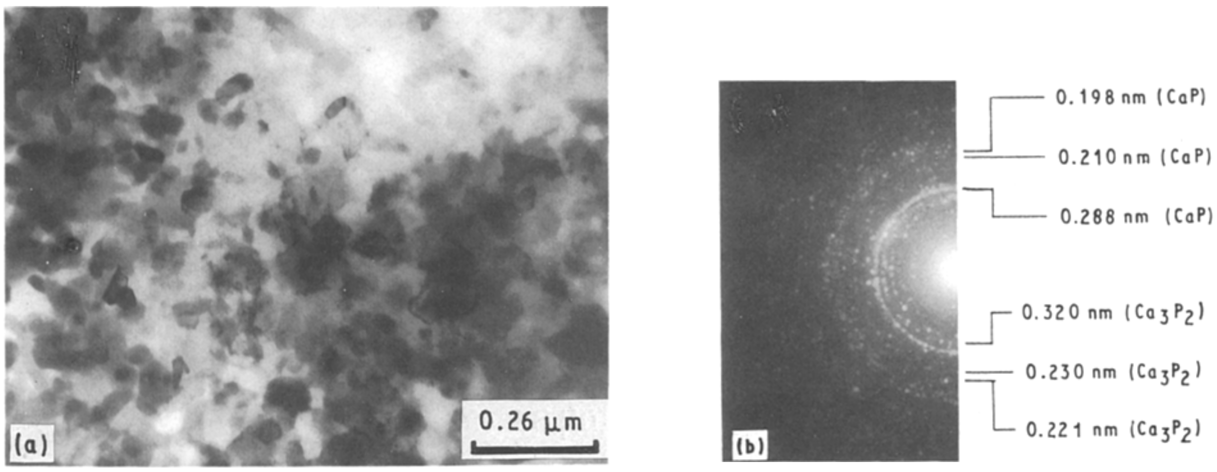

Figure 6 (a) Bright-field image showing that significant amount of CaP, Ca_3P_2, and unknown phases were formed in the film annealed above 600 °C after having been implanted with 170 keV P^+ at a dose of $1.0 \times 10^{17}\,cm^{-2}$. (b) Diffraction pattern of (a).

860 °C annealing [14]. In this study, for the film annealed at 600 and 700 °C after having been implanted with 170 keV P^+ at a dose of $1.0 \times 10^{17}cm^{-2}$, no significant amount of the 2 2 0 1 phase was formed, as seen from X-ray diffraction analysis in Fig. 5, while from TEM examination, a significant amount of CaP, Ca_3P_2, and some unknown phases were observed, as seen in Fig. 6. It is evident that the formation of these phases during post-implantation annealing plays an important role in degrading the superconductivity of the film. The degradation of the superconductivity due to the implantation-induced compounds was also observed in the H^+-implanted $YBa_2Cu_3O_x$ (1 2 3) superconductor, in which H^+ deoxidized the 1 2 3 compound to form H_2O which reacted with 1 2 3 compound to form Y_2BaCuO_5 and CuO [15].

4. Conclusion

For the BSCCO film implanted with 170 keV P^+ at a dose of $5 \times 10^{15}\,cm^{-2}$ post-implantation annealing at 600–800 °C enabled the T_cs of the film to be completely recovered to their original values prior to ion implantation. For the BSCCO film implanted with 170 keV P^+ at a dose of $1.0 \times 10^{17}\,cm^{-2}$, the T_cs were only partly recovered after 600 °C annealing, there still being a residual resistance of 14 mΩ below 70 K. On further annealing at 700 °C the superconductivity of the film disappeared. From TEM examination, significant amounts of CaP, Ca_3P_2, and some unknown phases were formed. It is considered that significant amounts of these phases formed during post-implantation annealing renders the recovery of the superconductivity of the P^+-implanted BSCCO films difficult.

Acknowledgement

This work was sponsored by the Republic of China National Science Council under contract NSC-80-0405-E-006-37.

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Received 8 November 1991
and accepted 25 June 1992