JOURNAL OF MATERIALS SCIENCE 26 (1991) 1321–1326

Influence of calcium content on the preparation of the high T_c (110 K class) Bi–Pb–Sr–Ca–Cu–O thin film

KEIZOU TSUKAMOTO, HIROMASA SHIMOJIMA, CHITAKE YAMAGISHI
Central Research Laboratory, Nihon Cement Co. Ltd, 1-2-23, Kiyosumi, Koutouku, Tokyo 135, Japan

The Bi–Pb–Sr–Ca–Cu–O thin films with various Ca/Sr ratios were prepared by r.f. magnetron sputtering using multi-targets ($Bi_{0.5}Pb_{0.5}O_x$, $CaCu_{0.75}O_x$, $SrCu_{0.75}O_x$). The high T_c phase (2223 phase) was obtained by firing these films. The film with the highest Ca/Sr ratio (Ca/Sr > 1.0) produced the largest amount of 2223 phase on firing at 850 °C. The highest Ca/Sr ratio ($= 1.17$) film contained 91% volume ratio of 2223 phase compared with the low T_c phase (2212 phase) after 15 h firing. However, the 2223 phase decreased with increasing long-term firing (65 h). The resistance curve of the film with the highest Ca/Sr ratio fired for 65 h showed tailing, until the temperature fell below 20 K, suggesting that this phenomenon was due to the segregation of excess calcium and copper components around the grain, in the amorphous state.

1. Introduction

Since the discovery by Maeda *et al.* [1] of the Bi–Sr–Ca–Cu–O system superconductor with a transition temperature above 100 K, many researchers world-wide have been investigating this compound. In the early studies, it was very difficult to prepare a 110 K class superconducting phase $Bi_2Sr_2Ca_2Cu_3O_x$ (2223 phase) without impurity phases, because a 80 K class superconducting phase $Bi_2Sr_2CaCu_2O_x$ (2212 phase) or a semiconducting phase $Bi_2Sr_2CuO_x$ (2201 phase) was simultaneously produced during firing. However, Takano *et al.* [2] and Endo *et al.* [3] reported that the 2223 phase without impurity phases could be easily obtained by the addition of PbO. In order to apply this superconductor to various electric devices, it is necessary to establish the preparation method of thin films of this compound. The sputtering technique is one of the many methods used for preparation of thin films. In the Bi–Sr–Ca–Cu–O [4–6] or Bi–Pb–Sr–Ca–Cu–O [7–12] systems, the sputtering method has been mainly used to prepare the thin films. However, PbO, which is necessary to stabilize the 2223 phase, vaporizes immediately from the thin film during firing to crystallize the amorphous film. Therefore, it was very difficult to control the vaporization of PbO. Previous methods used to prepare the 2223 phase in the PbO-doped system were (1) firing in air the thin film including excess PbO [7–10], (2) firing the thin film in a PbO atmosphere [11, 12]. However, as the preparation of the thin films with the 2223 phase but without impurity phases was very difficult, a stable preparation method has not yet been established. Here, the preparation of 2223 phase by firing the thin film with various Ca/Sr ratios in the Bi–Pb–Sr–Ca–Cu–O system is reported and the relation between the transition temperature and composition of the thin film prepared by the sputtering technique is investigated.

2. Experimental procedure

2.1. Preparation of the thin film

The Bi–Pb–Sr–Ca–Cu–O thin films were prepared on MgO (100) single crystal substrates by r.f. magnetron sputtering. The thin films were deposited on substrates from three targets which were simultaneously discharged while the substrates were circulated over each target. The three targets were the oxide powder and with the composition $Bi_{0.5}Pb_{0.5}O_x$ (mixed powders Bi_2O_3 and PbO), $CaCu_{0.75}O_x$ (pulverized powders of the oxides which were $CaCO_3$ and CuO fired at 950 °C), and $SrCu_{0.75}O_x$ (pulverized powder of the oxides which were $SrCO_3$ and CuO fired at 950 °C). The substrates were kept directly over each target for 8 to 63.5 sec. The total length of the three holding times was 100 sec. About 5 nm film was deposited by one circle of each target, and circling of each target was repeated 400 times to give a film thickness of 2 μm. It was possible to control precisely the chemical composition of the thin film by adjusting the holding time over each target. The sputtering conditions are shown in Table I. The deposition conditions are shown in

TABLE I Sputtering conditions

R.f. power	100 W
Sputtering gas	Ar 100%
Pressure	10 m torr
Substrate	MgO (100)
Substrate temperature	200 °C
Film thickness	2 μm

0022–2461/91 $03.00 + .12 © *1991 Chapman and Hall Ltd.*

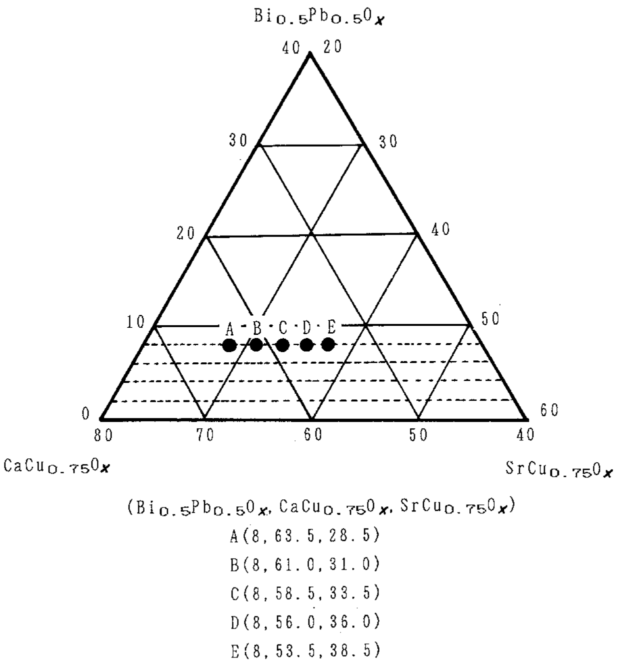


Figure 1 Deposition time diagram for each target.

Fig. 1, for the preparation of films A to E. The holding time of $Bi_{0.5}Pb_{0.5}O_x$ was fixed at 8 sec and those of $CaCu_{0.75}O_x$ and $SrCu_{0.75}O_x$ were varied in order to obtain films with various Ca/Sr ratios. In this experiment, the holding times of $CaCu_{0.75}O_x$ were 53.5, 56, 58.5, 61 and 63.5 sec.

2.2. Crystallization of the thin film

The deposited Bi–Pb–Sr–Ca–Cu–O thin films were amorphous because the substrate temperature was about 200 °C during deposition. These films were fired at 850 °C to achieve crystallization, the 2223 phase being easily synthesized at this temperature. The thin films were fired with about 1.0 g $Bi_{0.96}Pb_{0.24}SrCaCu_{1.6}O_x$ pellet (sintered at 850 °C) to prevent vaporization of PbO from the thin film. These thin films were fired for 15, 24 and 65 h and cooled in the furnace to room temperature.

2.3. Characterization of the thin film

The compositions of as-deposited and fired films on MgO single crystal substrates were determined by electron probe microanalysis (EPMA) and inductively coupled plasma (ICP). The crystalline analysis was measured by X-ray diffraction (XRD). The volume ratio of the 2223 phase compared with the 2212 phase was calculated from the ratio of the strengths of the (002) reflections:

$$\text{Volume ratio of the 2223} = \frac{H(0\,0\,2)}{H(0\,0\,2) + L(0\,0\,2)} \qquad (1)$$

where $H(0\,0\,2)$ is the strength of the (002) reflection of the 2223 phase ($2\theta = 4.7°$) and $L(0\,0\,2)$ is the strength of the (002) reflection of the 2212 phase ($2\theta = 5.8°$).

The *c*-axis lattice constant of the 2223 phase was calculated by (002), (008), (0010) and (0014) reflection angles corrected by (200) and (400) reflections of MgO. The electric resistance was measured during cryostat cooling at a rate of 2 °C min^{-1} using the four-probe method with a typical current of 10 μA. The morphology was observed using a scanning electron microscope (SEM).

3. Results and discussion

3.1. Composition analysis of the thin film

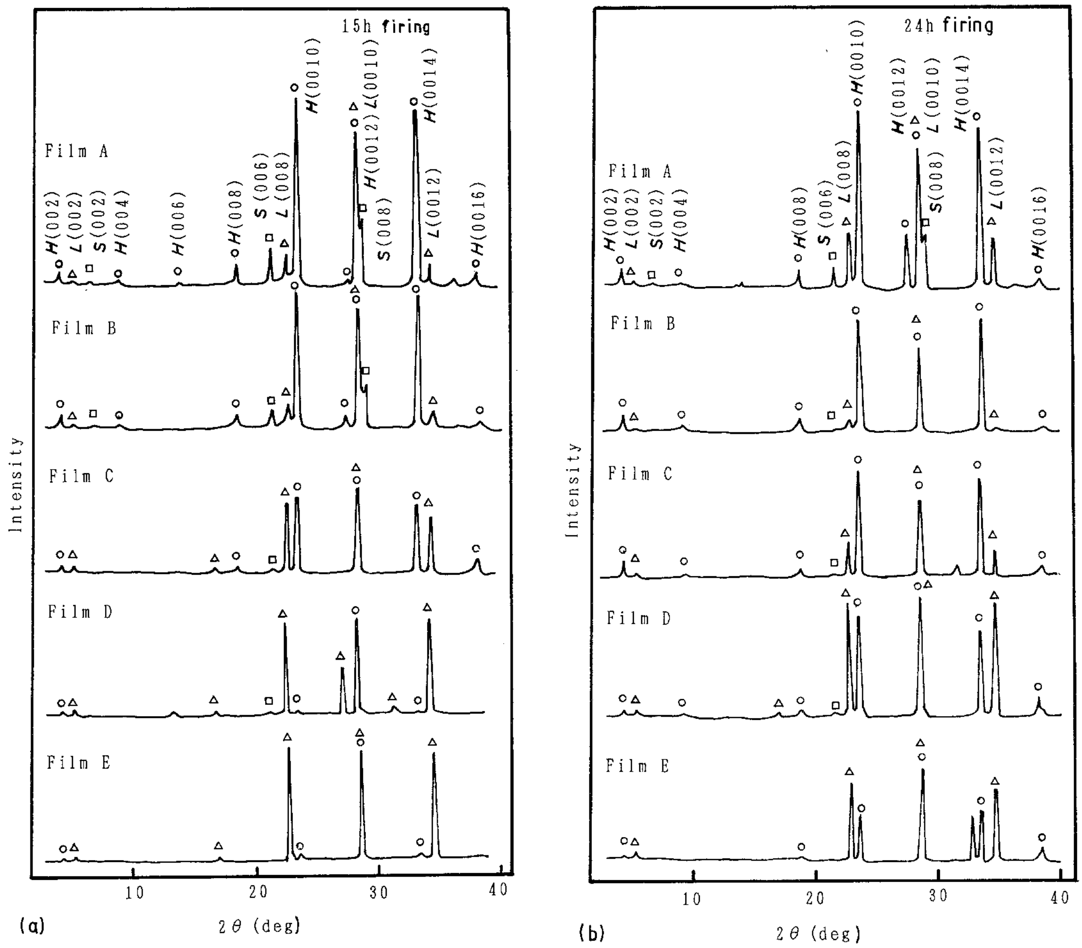
The compositions of films A to E as shown in Fig. 1 were determined by EPMA. The values of 2(Bi + Pb)/(Ca + Sr), 2Cu/(Ca + Sr) and Bi/Pb of all films were about 1.5, 1.8 and 1.0, respectively. The Ca/Sr ratio increased with increasing $CaCu_{0.75}O_x$ deposition time and its value for various films was A, 1.17; B, 1.09; C, 0.92; D, 0.90; E, 0.89.

3.2. XRD analysis of the thin film

Figs 2 a to c show XRD patterns of the thin films fired at 850 °C for 15, 24 and 65 h. All films were crystallized at 850 °C with the *c*-axis preferred orientation perpendicular to the (100) surface of the substrate. Of the films fired for 15 h, films A and B, having a Ca/Sr ratio more than 1.0, consisted of a large amount of 2223 phase. Films D and E were almost completely 2212 phase. The volume of the 2223 phase decreased with decreasing Ca/Sr ratio. A small amount of 2201 phase was simultaneously formed in the films. In higher calcium content films, the (006) reflection ($2\theta = 21.6°$) of the 2201 phase was strong. On the other hand, films C, D and E synthesized little 2201 phase, that is, the higher calcium content film increased the formation of the 2201 phase which contained no elemental calcium. As shown in Fig. 2b, a similar phenomenon was observed in the film fired for 24 h. The amount of 2223 phase increased with increasing Ca/Sr ratio. Film B, fired for 24 h, consisted of almost all 2223 phase. Film A produced the 2201 phase, as seen in the film fired for 15 h. From results from films C, D and E, the amount of 2223 phase was seen to increase with increasing firing time in the film with lower Ca/Sr ratios. Fig. 3 shows the (002) reflection strength ratio of the 2223 and 2212 phases calculated from the XRD pattern. The films fired for 24 h had more 2223 phase than with other firing times. In particular, the film having a Ca/Sr ratio greater than 1, produced the largest amount of 2223 phase on firing for 15 and 24 h. After firing for 65 h, the 2223 phase decreased. It appears that the 2223 phase was decomposed into 2212 phase by long-term firing. Fig. 4 shows the *c*-axis lattice constant of the 2223 phase of the films obtained under several firing conditions. The *c*-axis lattice constant was about 3.71 nm. This value was constant in films having various Ca/Sr ratios and films fired for various times.

3.3. Critical temperature of the thin film

Fig. 5 shows the critical temperature of the thin films fired for 15, 24 and 65 h. The temperature dependence of the resistance of film A is shown in Fig. 6. In the



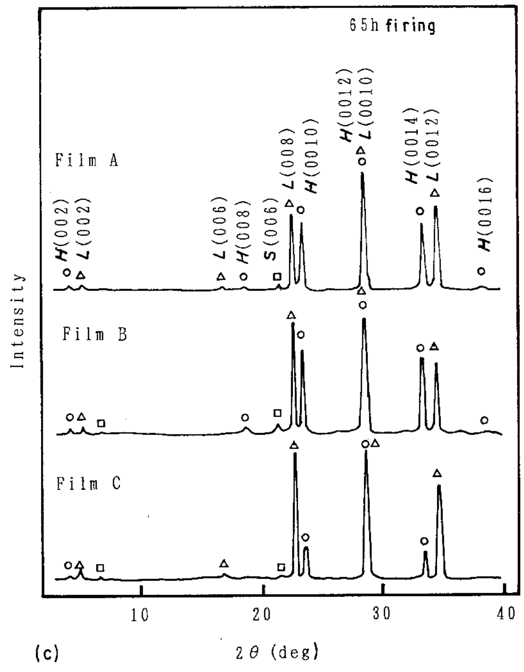


Figure 2 X-ray diffraction patterns of the thin film fired at 850 °C for (a) 15 h (b) 24 h (c) 65 h. (○) 2223 phase, (△) 2212 phase, (□) 2201 phase.

films fired for 15 h, the critical temperature of film A was 99 K. The critical temperature fell from 99 to 61 K in proportion to the decrease in Ca/Sr ratio. This also increased according to the volume of the 2223 phase calculated using the (002) reflection strength ratios in the XRD patterns. Although the films with higher calcium contents were found to contain the 2201 phase, this semiconducting phase did not have any detrimental influence on the critical temperature by segregation of the compound into grain boundaries or around the 2223 phase. In films fired for 24 h, the critical temperature had no influence on the Ca/Sr ratio and the volume of the 2223 phase. In particular, the critical temperature of film B was 60 K although the volume of the 2223 phase was 91%, while the volume in film C was 75% at a critical temperature of 100 K. In films fired for 65 h, the resistance of film A dropped at 110 K and tailed to below 20 K. As shown in Fig. 6, film A showed no superconductive state. However, the temperature dependence of the resistance in films B and C having a Ca/Sr ratio of ~ 1.0 did not tail to low temperature, as seen in Fig. 6, and showed critical temperatures of 78 K and 79 K, respectively. It seems that this result is anomalous considering the crystalline analysis by XRD.

3.4. EPMA analysis of the thin film

The compositions of the plate-like crystals of the 2223 phase in films A to E which were fired for 24 h were determined by EPMA. These plate-like crystals were approximately Bi:Sr:Ca:Cu = 2:2:2:3. The chemical compositions of all crystals were found to be: A, $Bi_{1.84}Sr_{2.00}Ca_{2.00}Cu_{3.14}O_x$; B, $Bi_{1.72}Sr_{2.00}Ca_{1.98}Cu_{2.96}O_x$; C, $Bi_{1.68}Sr_{2.00}Ca_{1.98}Cu_{3.04}O_x$; D, $Bi_{1.90}Sr_{2.00}Ca_{1.94}Cu_{2.94}O_x$; E, $Bi_{1.82}Sr_{2.00}Ca_{1.64}Cu_{3.16}O_x$.

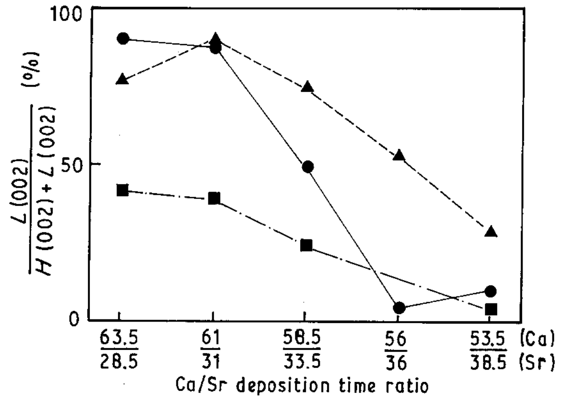


Figure 3 The relationship between the volume ratio of the 2223 phase and the Ca/Sr ratio of the film. Firing time: (●) 15 h, (▲) 24 h, (■) 65 h.

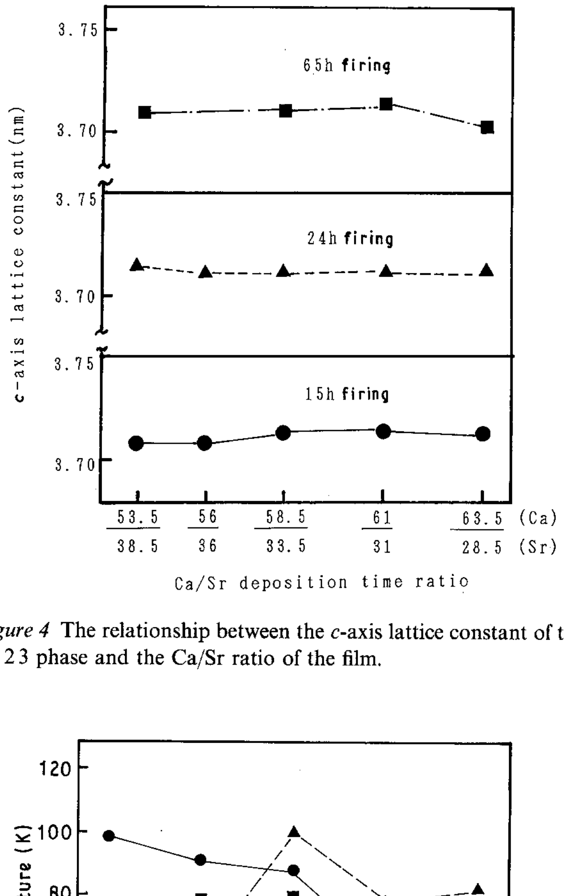


Figure 4 The relationship between the *c*-axis lattice constant of the 2223 phase and the Ca/Sr ratio of the film.

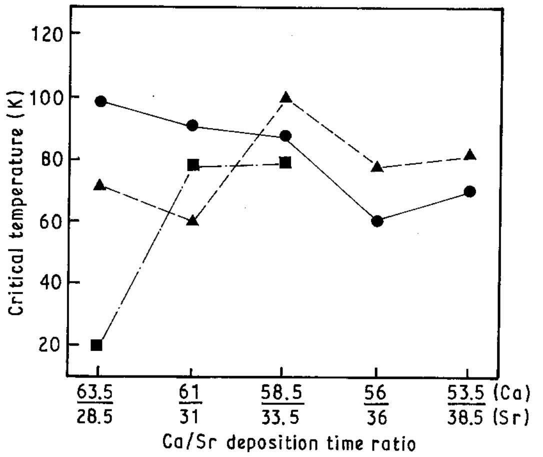


Figure 5 The relationship between the critical temperature and the Ca/Sr ratio of the film. Firing time: (●) 15 h; (▲) 24 h; (■) 65 h.

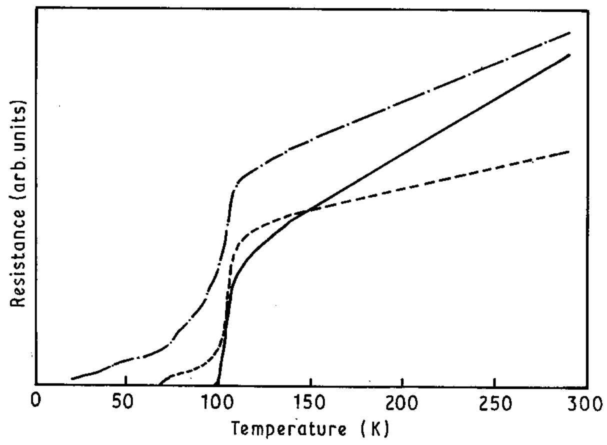


Figure 6 Temperature dependence of the resistance of film A. Firing time: (——) 15 h, (– – –) 24 h, (—·—) 65 h.

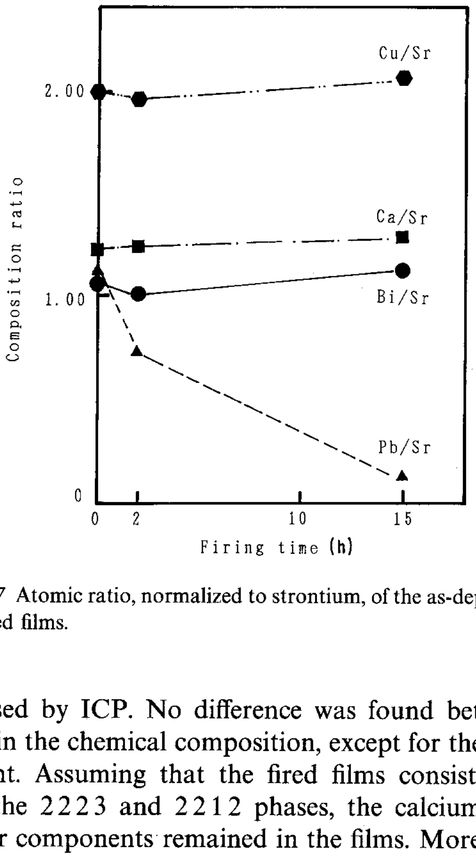


Figure 7 Atomic ratio, normalized to strontium, of the as-deposited and fired films.

These results indicated that the composition of the plate-like crystals had no relation to the Ca/Sr ratio of the as-deposited film. This also agreed with the *c*-axis lattice constant of the 2223 phase. Fig. 7 shows the chemical composition of as-deposited and fired films analysed by ICP. No difference was found between them in the chemical composition, except for the lead content. Assuming that the fired films consisted of only the 2223 and 2212 phases, the calcium and copper components remained in the films. Moreover, the film containing higher Ca/Sr ratios, retained the largest amount of calcium and copper components. As no Ca–Cu–O compounds corresponding to $CaCu_2O_3$ or Ca_2CuO_3 were detected by XRD analysis, it is likely that the Ca–Cu–O exists in the film in the amorphous state.

3.5. Morphology of the thin film

Fig. 8 shows scanning electron micrographs of the surface of films A to E fired for 24 h and film A fired for 15 and 65 h. These figures indicate that all films consisted of plate-like crystals perpendicular to MgO (100) and did not contain needle-like crystals corresponding to Sr–Ca–Cu–O compound. Compared with films A to E, the film containing the highest calcium content indicated an obscure grain boundary. The shape of the grain was clear in film A fired for 15 h but

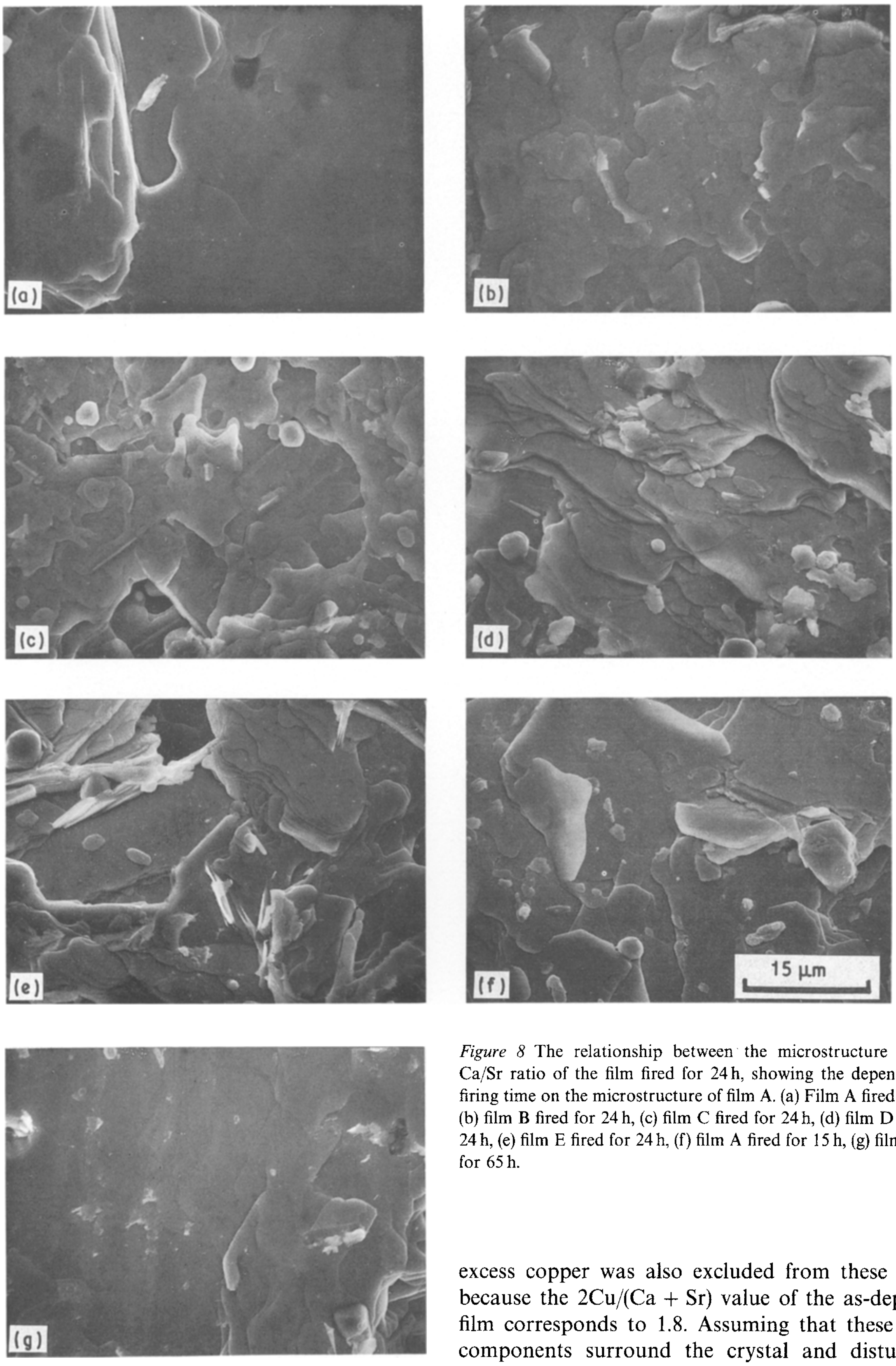


Figure 8 The relationship between the microstructure and the Ca/Sr ratio of the film fired for 24 h, showing the dependence of firing time on the microstructure of film A. (a) Film A fired for 24 h, (b) film B fired for 24 h, (c) film C fired for 24 h, (d) film D fired for 24 h, (e) film E fired for 24 h, (f) film A fired for 15 h, (g) film A fired for 65 h.

it became more and more obscure with firing time as seen in Fig. 8. It appears that all components, except for the 2223 and 2212 phases, segregated in the grain boundary. Therefore, the excess calcium is supposed to be excluded from the two superconductive phases in film A containing the highest Ca/Sr ratio (Ca/Sr = 1.17), even if the 2223 phase was predominant compared with the 2212 or 2201 phase. The excess copper was also excluded from these phases because the 2Cu/(Ca + Sr) value of the as-deposited film corresponds to 1.8. Assuming that these excess components surround the crystal and disturb the superconductive current, acting as an insulator, the behaviour shown in Fig. 6 can be explained; as the 2223 phase decreased on long-term firing in film A, the excess Ca–Cu–O segregated in proportion to the firing time and acted as an insulator in the grain boundary. For the above reason, the resistance curve showed a tailing to low temperature. Thus it seems that the increasing obscurity of the grain boundary with long-term firing was caused by the segregation of the excess component around the grain as an amorphous state.

4. Conclusion

Bi–Pb–Sr–Ca–Cu–O thin films with various Ca/Sr ratios were prepared by r.f. magnetron sputtering using three targets: $Bi_{0.5}Pb_{0.5}O_x$, $CaCu_{0.75}O_x$ and $SrCu_{0.75}O_x$. The films obtained were fired at 850 °C and evaluated. The following results were obtained.

1. The higher the calcium content of the film, the larger was the amount of 2223 phase produced. In particular, the highest calcium content (Ca/Sr = 1.17) film A produced more than 90% 2223 phase compared with the 2212 phase. In the thin film, the amount of 2223 phase decreased on long-term firing (65 h).

2. The highest calcium content film A showed a reduction in critical temperature on long-term firing. It appears that excess calcium and copper components act to disturb the superconductive current, because they segregate in the grain boundary as an amorphous state.

References

1. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T. ASANO, *Jpn J. Appl. Phys.* **27** (1988) L209.
2. M. TAKANO, J. TAKADA, K. ODA, H. KITAGUCHI, Y. MIURA, Y. IKEDA, Y. TOMII and H. MAZAKI, *ibid.* **27** (1988) L1041.
3. U. ENDO, S. KOYAMA and T. KAWAI, *ibid.* **27** (1988) L1476.
4. H. ADACHI, S. KOHIKI, K. SETSUNE, T. MITSUYU and K. WASA, *ibid.* **27** (1988) L1883.
5. K. KOJIMA, K. KURODA, M. TANIOKU and K. HAMANAKA, *ibid.* **28** (1989) L643.
6. K. KURODA, K. KOZIMA, M. TANIOKU, K. YOKOYAMA and K. HAMANAKA, *ibid. Phys.* **28** (1989) 1586.
7. A. TANAKA, T. MACHI, N. KAMEHARA and K. NIWA, *Appl. Phys. Lett.* **54** (1989) 1362.
8. Y. KOZONO, T. OHNO, M. KASAI, M. HANZONO and Y. SUGITA, *Jpn J. Appl. Phys.* **28** (1989) L646.
9. Y. HAKURAKU, Y. ARIDOME and T. OGUSHI, *ibid.* **27** (1988) L2091.
10. Y. HAKURAKU, Y. ARIDOME, D. MIYAGI, N. G. SURESHA and T. OGUSHI, *ibid.* **28** (1989) L819.
11. H. HAYAKAWA, M. KAISE, K. NAKAMURA and K. OGAWA, *ibid.* **28** (1989) L967.
12. T. YOTUYA, Y. SUZUKI, S. OGAWA, H. IMOKAWA, M. YOSHIKAWA, M. NAITO, R. TAKAHATA and K. OTANI, *ibid.* **28** (1989) L972.

Received 27 February
and accepted 9 March 1990