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Growth and characterization of laser-deposited Ag-doped $YBa_2Cu_3O_{7-x}$ thin films on bare sapphire

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Abstract. Microstructural and superconducting properties of $YBa_2Cu_3O_{7-x}$ thin films grown *in situ* on bare sapphire by pulsed laser deposition using $YBa_2Cu_3O_{7-x}$ targets doped with 7 and 10 wt% Ag have been studied. Ag-doped films grown at 730°C on sapphire have shown very significant improvement over the undoped $YBa_2Cu_3O_{7-x}$ films grown under identical condition. A zero resistance temperature of 90 K and a critical current density of $1{\cdot}2 \times 10^6$ A/cm^2 at 77 K have been achieved on bare sapphire for the first time. Improved connectivity among grains and reduced reaction rate between the substrate and the film caused due to Ag in the film are suggested to be responsible for this greatly improved transport properties.

Keywords. Pulsed laser deposition; Ag-doped $YBa_2Cu_3O_{7-x}$ thin film; high critical current density; sapphire.

1. Introduction

Thin films of high temperature superconductors are highly attractive for micro-electronic and microwave circuits due to their high critical current density and low surface resistance at liquid nitrogen temperature. Excellent films with critical current density higher than 10^6 A/cm^2 and microwave surface resistance lower than 300 μ ohm at 77 K are now routinely prepared on lattice matched substrates such as $SrTiO_3$ and $LaAlO_3$ by pulsed laser deposition (PLD) technique over a wide range of growth conditions. However, the efforts to grow high-T_c thin films on sapphire has not met with desired success. Fabrication of superconducting thin films with high T_c and high critical current density (J_c) on bare sapphire would be ideal for microwave and bolometric device applications because of low microwave loss, good thermal conductivity, high mechanical strength, and low cost of sapphire. But, realization of good quality superconducting films on bare sapphire is hindered by the reaction between the film and the substrate (Naito *et al* 1987) at high temperature which is required for crystalline and oriented growth of the films. Although the T_c reported of $YBa_2Cu_3O_{7-x}$ (YBCO) films on bare sapphire vary from low (70 K) to high (88 K), the J_c of these films at 77 K is always lower by an order of magnitude than the J_c on other commonly used substrates such as $SrTiO_3$ and $LaAlO_3$ (Naito *et al* 1987; Chang *et al* 1990; Char *et al* 1990; Cole *et al* 1992; Merchant *et al* 1992). Therefore, the majority of the efforts still continues to grow the high-T_c superconducting films on sapphire using an efficient buffer layer (Witanachchi *et al* 1989; Schmidt *et al* 1991; Holstein *et al* 1992) which dilutes the large lattice mismatch and prevent the reaction between the film and the substrate at high processing temperatures.

It was in this context that we thought that the doping of Ag, which has shown significant benefit in bulk (Tiefel *et al* 1989; Jung *et al* 1990) as well as in thin films (Singh *et al* 1992; Kumar *et al* 1993; Pinto *et al* 1993) of YBCO materials, may be beneficial in depositing the film at lower temperatures. The deposition temperature is the most crucial parameter which determines the extent of the chemical reaction between the YBCO film and sapphire (Naito *et al* 1987; Char *et al* 1990). In this paper, we report the *c*-axis oriented growth of Ag-doped YBCO films on bare sapphire by pulsed laser deposition (PLD) technique. The novelty of our results lies in the realization of good quality YBCO films at relatively low temperatures with the aid of Ag-doping.

2. Experimental

Undoped and Ag-doped YBCO films were grown *in situ* on $\langle\bar{1}012\rangle$ sapphire substrates by pulsed laser deposition technique. A laser spot of $3{\cdot}5\ \mathrm{mm} \times 1\ \mathrm{mm}$ size was used for ablation. The target-substrate distance was 4·5 cm and the oxygen pressure was 300 mTorr. The films were cooled in ~ 500 Torr oxygen in the growth chamber itself after the termination of film-growth. Other details are the same as reported earlier (Hegde *et al* 1993). In the present study Ag-doped YBCO targets were prepared by adding 7 and 10 wt% of Ag to YBCO powder followed by repelletizing and sintering at 850°C. The films were characterized by four-probe resistance, X-ray diffraction (XRD), energy dispersive X-ray (EDX) analysis and scanning electron microscopy (SEM). The film thickness as measured by surface profilometer was in the range of 1500–2000 Å for 4000 pulses. The film thickness uniformity was found to be within $\pm 5\%$.

3. Results and discussion

3.1 *Transport properties*

The results have shown that substrate temperature was the most critical deposition parameter in growing good quality Ag-doped YBCO films on bare sapphire. If the substrate temperature was too high (≥ 780°C), the films came out clear due to a combined effect of reaction with the substrate and poor sticking coefficient. If the temperature was too low, the crystallinity and orientation were not as good as the films grown at higher temperature, resulting in poor transport properties. It is interesting to note here that the films prepared at lower temperatures were blacker and more shiny as compared to films prepared at higher temperature. However, the T_c of the films deposited at lower temperatures was not as high as that of films deposited at higher temperatures. Figure 1 shows the resistance (R) vs temperature (T) plots of Ag-doped YBCO films grown on sapphire at different temperatures. It is clear from this figure that there is a narrow temperature window in which one can grow films with good metallicity, T_c of 90 K and transition width ≤ 1K. The variation of T_c as a function of substrate temperature is shown in figure 2 which points out that 730°C is the optimum temperature for the growth of Ag-doped films with highest T_c. For comparison, we have also marked in this figure the value of T_c obtained for undoped YBCO film grown on sapphire at

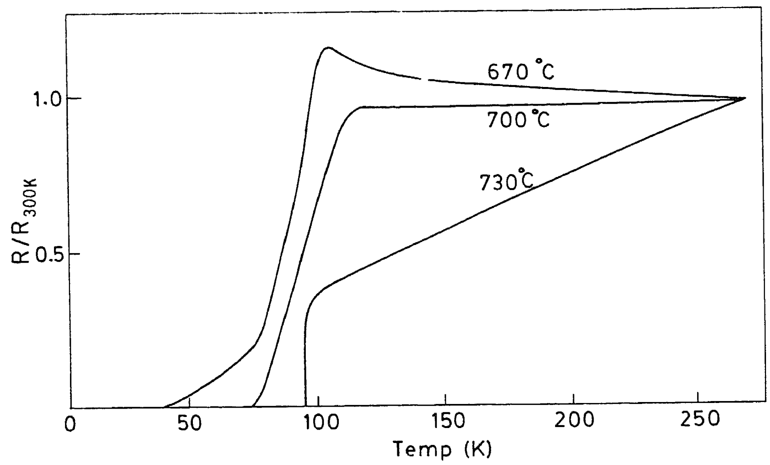


Figure 1. R vs T plots of Ag-doped YBCO films grown on ⟨$\bar{1}012$⟩ sapphire at different temperatures

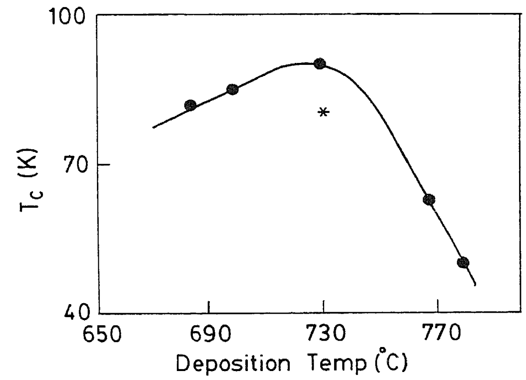


Figure 2. Variation of T_c of Ag-doped YBCO films as a function of deposition temperatures. Shown also in the figure (marked by*) is T_c of undoped YBCO films grown at 730°C for comparison.

730°C with all other deposition parameters being the same as in the case of Ag-doped film grown at 730°C. The value of T_c obtained for the undoped YBCO film in the present study matched well with the T_c value reported in most of the literature (Naito *et al* 1987; Chang *et al* 1988; Cole *et al* 1992; Merchant *et al* 1992). Therefore, we believe that the improvement in the quality of YBCO films with the aid of Ag-doping is definitely due to some roles played by silver.

The critical current density (J_c) of the films deposited at 730°C was measured using 500 μm long and 80 μm wide laser patterned line. The criterion used for J_c measurement was 1 μV/mm. The value of J_c obtained was $1{\cdot}2 \times 10^6$ A cm^{-2} at 77 K in zero field. This value of J_c is comparable to the J_c of YBCO films on commonly used substrates such as ⟨100⟩ $SrTiO_3$ and $LaAlO_3$ and is one of the highest values of transport J_c reported so far for YBCO films on bare sapphire at

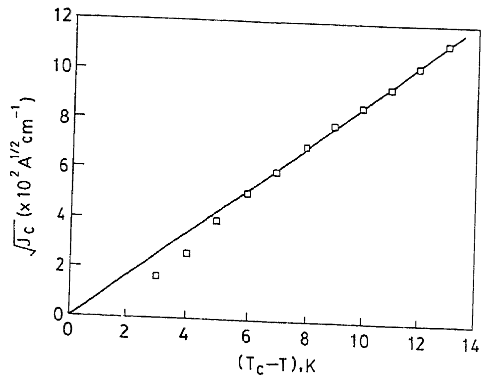


Figure 3. $\sqrt{J_c}$ vs (T_c-T) for Ag-doped film grown at 730°C on ⟨$\bar{1}$012⟩ sapphire.

77 K. Figure 3 shows the plot of $\sqrt{J_c}$ vs (T_c-T) of a Ag-doped YBCO film deposited at 730°C. The linear variation of $\sqrt{J_c}$ with (T_c-T) indicates the presence of superconductor-normal metal-superconductor (S-N-S) type of coupling existing between the superconducting grains as proposed by De Gennes (1964) and Clarke (1969) according to the following expression:

$$J_c \propto (T_c-T)^2 \exp(-d/\xi_n)\,, \tag{1}$$

where d is the thickness of the grain boundary layer and ξ_n the coherence length in the normal metal grain boundary. If we ignore the weak temperature dependence of ξ_n as compared to $(T_c-T)^2$ term, we can write

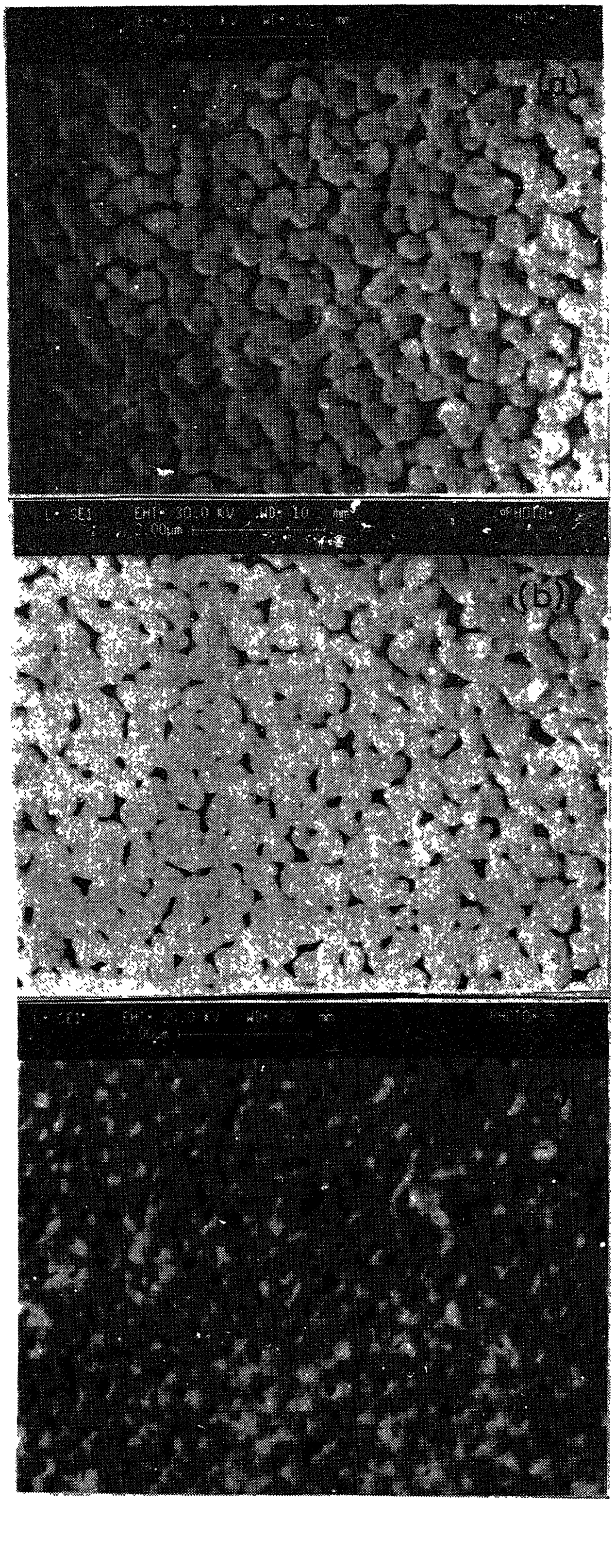
$$\sqrt{J_c} \propto (T_c-T)\exp(-d/2\xi_n)\,, \tag{2}$$

where $\exp(-d/2\xi_n)$ term would determine the slope of $\sqrt{J_c}$ vs (T_c-T) plot. Hence, it is evident that doping of Ag makes the grain boundaries more transparent to the flow of supercurrents.

3.2 *Microstructural studies*

Microstructural studies of undoped and Ag-doped films were carried out using SEM and XRD. Shown in figure 4 are the scanning electron micrographs of undoped and 7 and 10 wt% Ag-doped YBCO films grown on sapphire at 730°C. The thickness of the films was in the range 2000–2200 Å in each case. The undoped film (figure 4a) is not only poorer in surface smoothness but is also constituted of smaller grains (~0·6 μm) as compared to Ag-doped film (figure 4b, 7 wt% Ag-doped). The addition of more Ag to the film results in further smoothening of the film surface (figure 4c, 10 wt% Ag-doped). The smaller grains and rough surface in undoped film is explained on the basis of the film thickness effect (Frost

Figure 4. Scanning electron micrographs of (a) undoped YBCO film, (b) 7 wt% Ag-doped YBCO film and (c) 10 wt% Ag-doped film on ⟨$\bar{1}$012⟩ sapphire grown at 730°C.


(a)
(b)
(c)

1994). According to this effect, the normal grain growth in thin films stagnates when the average grain diameter is two or three times the film thickness. The stagnation of normal grain growth in film is attributed to freezing of atom mobility in the grain boundary region. At the point of stagnation, the grains are columnar and their boundary completely traverses the thickness of the film resulting in the formation of films with relatively large number of voids and poorly connected grains. The grains in Ag-doped film is however, bigger and rather well connected due to secondary grain growth in presence of Ag. The EDX analysis carried out in spot mode on grains and grain boundary regions shows that grains were devoid of Ag and Ag had segregated in intergranular regions. The segregation of Ag in the grain boundary regions results in improved connectivity among YBCO grains and consequently in the realization of high J_c. The SNS type of weak links as established in previous section also suggest this view.

The XRD patterns of Ag-doped YBCO films grown at temperatures ranging from 670–730°C are depicted in figure 5. All the films are *c*-axis oriented. However, the relative intensity of most of the ⟨001⟩ lines of Ag-doped films grown at lower temperatures is not only lesser, the full width at half maximum (FWHM) of these lines are also significantly wider as compared to those of Ag-doped films grown at higher temperatures. This very well explains why the films grown at lower temperatures are having poorer transport properties as discussed in § 3.1.

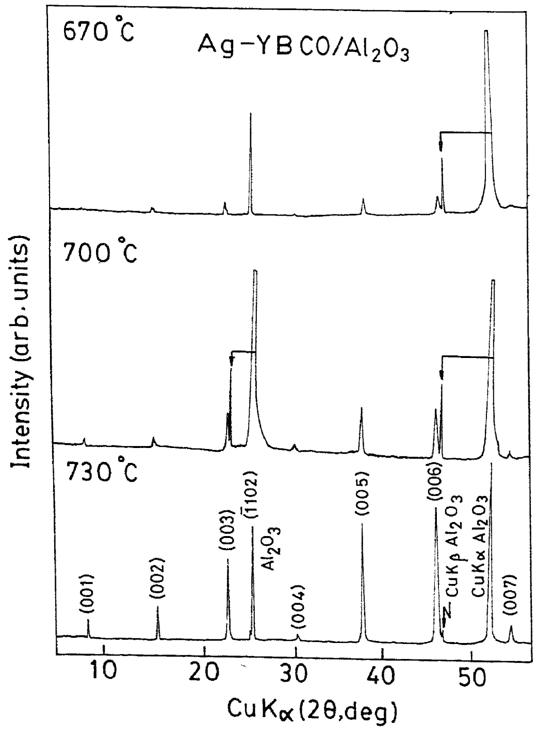


Figure 5. X-ray diffraction patterns of Ag-doped YBCO films grown at different temperatures on ⟨1̄012⟩ sapphire.

The realization of good quality YBCO films doped with Ag is primarily attributed to the significant reduction in the chemical attack of the films by sapphire at relatively low deposition temperatures. The deposition of YBCO films at lower temperatures without suffering from the problems of orientation, crystallinity and phase formation is feasible in presence of silver due to following possible mechanisms. The first mechanism, as suggested earlier (Kumar *et al* 1993), involves the supply of nascent oxygen to the lattice right during its growth. Silver remains in its elemental state in the Ag-doped YBCO targets after sintering. However, it is oxidized in the plume after ablation. These oxidized Ag-species dissociates again when it arrives at the substrate surface and provides nascent oxygen to the growing YBCO lattice. The availability of active oxygen reduces the requirement of higher temperatures for the formation of YBCO lattice. In other words, the supply of active oxygen by Ag atoms to the growing lattice of YBCO enables the formation of orthorhombic phase with right amount of oxygen directly at a substrate temperature of 730°C.

The second mechanism is based on the transfer of momentum of nonreactive Ag-atoms to other species forming the YBCO lattice. This enables the latter to acquire sufficient energy to grow *c*-axis oriented with good crystallinity even at low deposition temperatures. In other words, the presence of highly mobile Ag-atom substitutes kinetic energy for conventional thermal energy and consequently facilitates deposition of YBCO films with good quality at relatively reduced temperature. The third mechanism is based on the catalytic behaviour of Ag atoms, which possibly facilitates material transport by providing a liquid-phase kind of diffusion and hence accelerates the formation of YBCO lattice. The accelerated formation of lattice, as observed in bulk Ag-YBCO composite also (Wu *et al* 1992), significantly reduces the possibility of any reaction that can take place between the film and the substrate.

4. Conclusion

In summary, we have deposited high quality YNCO films on bare sapphire at significantly low temperature by using Ag-doping. The films were having T_c of 90 K and J_c of $1{\cdot}2 \times 10^6$ A cm^{-2} at 77 K. The supply of active oxygen and transfer of kinetic energy to the YBCO lattice by Ag atoms are thought to be the major mechanisms responsible for the realization of good quality YBCO films at relatively reduced temperatures. The ability to grow YBCO films with high T_c and J_c at lower deposition temperatures is very promising for the growth of these films on technologically important substrates such as sapphire. Further work is in progress to explore the practical applications of these films in India in microwave devices such as resonators, filters, delay lines and antennas.

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References

Chang C C *et al* 1988 *Appl. Phys. Lett.* **53** 517
Char K *et al* 1990 *Appl. Phys. Lett.* **56** 785
Clarke J 1969 *Proc. R. Soc. London* **A308** 447
Cole B F *et al* 1992 *Appl. Phys. Lett.* **61** 1727
De Gennes P G 1964 *Rev. Mod. Phys.* **36** 225
Frost H J 1994 *Mater. Charac.* **32** 257
Hegde M S *et al* 1993 *Phys. Rev.* **B48** 6465
Holstein W L *et al* 1992 *Appl. Phys. Lett.* **61** 982
Jung J *et al* 1990 *Phys. Rev.* **B42** 6181
Kumar D *et al* 1993 *Appl. Phys. Lett.* **62** 3522
Merchant P *et al* 1992 *Appl. Phys. Lett.* **60** 763
Naito M *et al* 1987 *J. Mater. Res.* **2** 713
Pinto R *et al* 1993 *J. Appl. Phys.* **73** 5105
Singh R K *et al* 1992 *Appl. Phys. Lett.* **60** 255
Schmidt H *et al* 1991 *Appl. Phys. Lett.* **59** 222
Tiefel T H *et al* 1989 *Mater. Lett.* **7** 363
Witanachchi S *et al* 1989 *Appl. Phys. Lett.* **55** 295
Wu Nae-Lih *et al* 1992 *Appl. Phys. Lett.* **64** 2932