Growth and characterization of laser-deposited Ag-doped YBa$_2$Cu$_3$O$_{7-x}$ thin films on bare sapphire

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Abstract. Microstructural and superconducting properties of YBa$_2$Cu$_3$O$_{7-x}$ thin films grown in situ on bare sapphire by pulsed laser deposition using YBa$_2$Cu$_3$O$_{7-x}$ 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$_2$Cu$_3$O$_{7-x}$ films grown under identical condition. A zero resistance temperature of 90 K and a critical current density of $1.2 \times 10^6$ 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$_2$Cu$_3$O$_{7-x}$ 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 $\mu$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$_2$Cu$_3$O$_{7-x}$ (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 (1012) sapphire substrates by pulsed laser deposition technique. A laser spot of 3.5 mm × 1 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 ±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.
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 $1.2 \times 10^6$ 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
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:

$$J_c \propto (T_c-T)^2 \exp\left(-d/\xi_n\right),$$

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

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

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 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
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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 (1012) 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 $1.2 \times 10^6$ 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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