Oxygen diffusion and defect mechanism in c-axis textured thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by resistivity measurements

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Abstract. Isothermal resistivity measurements have been carried out to study the dynamics of oxygen out- and in-diffusion in thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in the temperature range 648–773 K. The activation energies for the out- and in-diffusion were determined to be 1.36 and 0.7 eV respectively. We have modelled the resistance-time plots for the oxygen in-diffusion using an equation for one dimensional diffusion into a plane. The microstructural defects such as low angle grain boundaries associated with the c-axis oriented grains are believed to provide the required diffusion paths in thin films of YBCO.

Keywords. Oxygen diffusion; high temperature superconductor; resistivity; defects.

1. Introduction

The high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) with an oxygen concentration ranging from $x = 1$ to $x = 0$, can be regarded as an interstitial solid solution of oxygen based on the tetragonal (T) $\text{YBa}_2\text{Cu}_3\text{O}_6$ phase. It is well known that the oxygen content plays a key role in deciding both the normal state and superconducting properties of YBCO (Cava *et al* 1990; Martin *et al* 1990). The oxygen diffusion in orthorhombic YBCO phase mostly occurs in the basal plane and also the diffusivity depends on the crystallographic directions of YBCO (Rothman *et al* 1989, 1991). Consequently, an understanding of the oxygen diffusion is important for processing of both bulk and thin films of YBCO with specific property requirements.

In contrast to bulk (Ottaviani *et al* 1989; Tu *et al* 1989; LaGraff and Payne 1993), study of diffusion in thin films of YBCO is scarce (Yamamoto *et al* 1991) and it assumes importance both for fundamental and technological point of view. *In situ* preparation of superconducting thin films requires a right oxygen partial pressure at a particular substrate temperature to form the tetragonal or orthorhombic phase. We report here the kinetics of oxygen in- and out-diffusion processes in the c-axis textured YBCO films grown on (100) oriented MgO substrates using resistivity measurements.

2. Experimental

The method of YBCO film preparation by glow discharge sputtering and measurements are reported elsewhere (Kuppusami and Raghunathan 1991; Kuppusami *et al* 1993). Four-probe resistivity technique was used to monitor the resistance as a function of time both in the reducing (out-diffusion) and oxidizing (in-diffusion) atmosphere. The latter measurements have been carried out at isothermal temperatures in the range 648–773 K in ambient helium and oxygen atmosphere respectively by monitoring the

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Figure 1. Resistance vs time plots for the films annealed in helium atmosphere.

Figure 2. Time dependence of resistance of the films annealed in oxygen atmosphere.

changes in resistance as a function of time. Resistance and the time data were acquired using a personal computer interfaced with a data acquisition system.

3. Results

Figure 1 shows the resistance versus time plots for out-diffusion of oxygen in the helium atmosphere for the temperature range 648–773 K. As seen from the plots, the change in resistance is very sluggish at temperatures less than 698 K. At temperatures between 698 and 773 K, the change in resistance is almost linear.

The in-diffusion experiments were carried out in the temperature range 648–773 K by introducing oxygen into the sample when the sample resistance was nearly ten times more than that of the sample used for out-diffusion experiments. Figure 2 is the plot showing the resistance as a function of oxygen annealing time. It is noticed that on introduction of oxygen in the oxygen deficient films, there is a rapid decrease in resistance initially and a slow decrease in resistance with time. Since the material in the

Figure 3. TEM microstructures showing (a) mosaic grain boundaries and (b) twin lamellae.

tetragonal form behaves as a semiconductor, the resistance decreases with an increase in temperature. Unlike the out-diffusion rates, the time scale involved to obtain the minimum value of the resistance is rather low.

TEM observation (Raghunathan *et al* 1997) of the films grown on (100) MgO substrates predominantly shows c-axis oriented grains and extensive twin lamellae of about 10 nm (figures 3a and b). As most of the grains have their c-axis parallel to the electron beam, the diffraction pattern from the grains (inset of figure 3b) corresponds to the $[001]$ zone axis.

4. Discussion

The difference in the plots shown in figures 1 and 2 suggests that the diffusion mechanisms are different in out- and in-diffusion processes and the analysis is given below.

Figure 4. Plot of $\ln D$ vs $1/kT$ for oxygen in-diffusion.

The diffusion coefficients for the oxygen in-diffusion can be calculated by a random walk model (Borg and Dienes 1988) using a relation

$$\langle X^2 \rangle = 2Dt,$$

where $\langle X^2 \rangle$ is the root mean square diffusion distance and t the time over which diffusion has occurred. In case of thin films X can be taken as the film thickness and t the time required to reach the minimum resistance from the initial values. From these known values of t and X , the diffusion coefficients for oxygen in-diffusion for the temperature range 648–773 K were calculated. Figure 4 is the $\ln D$ vs $1/kT$ plot that gave an activation energy of about 0.7 eV for oxygen in-diffusion.

The isothermal resistance–time plots reported for oxygen in-diffusion showed a two-step behaviour (figure 2). To characterize the two step processes, the initial and the final slopes of resistance curves of figure 2 were plotted as a function of $1/kT$. These plots yielded activation energies of 0.15 eV and 0.5 eV for the initial and the final step respectively. Therefore, the sum of the activation energies of the initial and final steps (0.65 eV) is equal to the activation energy (0.7 eV) obtained from figure 4. The sharp fall in resistance during oxygen in-diffusion could be attributed to the formation of an oxygen rich skin layer on the surface of the film during the initial stages of diffusion. Formations of such skin layers transform the surface of the film into the orthorhombic structure, thus promoting the twin boundaries and enhancing the oxygen in-diffusion. Since the resistivity technique senses the least resistance path quite quickly, one observes a sudden drop in resistivity in the initial stages of diffusion. Once the oxygen rich skin forms on the surface, further diffusion of oxygen is restricted and is observed as the slowly decreasing resistance as a function of time.

The following equation for one dimensional diffusion into a plane given by Crank (1975) can be used to fit the resistance change (Δ) during oxygen in-diffusion in thin film.

$$\begin{aligned} \Delta &= \frac{R(t) - R(0)}{R(\infty) - R(0)} = \frac{C(t) - C(0)}{C(\infty) - C(0)} \\ &= 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 Dt}{l^2} \right], \end{aligned} \quad (1)$$

Figure 5. Normalized resistance vs time plot for diffusion data obtained at 648 K.

where $C(t)$ is the concentration of the oxygen as a function of time, t and $C(\infty)$ the final concentration after a long duration of oxygen annealing and $R(0)$ the resistance at the beginning of the in-diffusion, $R(t)$ the resistance as a function of time, $R(\infty)$ saturation resistance after a long duration of oxygen annealing and l the film thickness.

Figure 5 illustrates a typical fit of the above equation to the experimental data of the film annealed in the ambient oxygen at the isothermal temperature of 648 K. Also shown is the theoretical fit for $D = 2.5 \times 10^{-16} \text{ m}^2/\text{sec}$ (for $n = 0-5$) which closely matches the experimental data (Tu *et al* 1989).

During out-diffusion the first event to take place is the solid state diffusion, in which oxygen atoms are removed from the lattice and are placed on the surface. Subsequent processes involve surface diffusion, molecule formation and desorption. Tu *et al* (1989) suggested that the activation energies needed for the surface diffusion, formation and desorption of the oxygen molecules could be the surface barrier to the out-diffusion of oxygen. The following equation for surface reaction limited allows one to calculate the activation energy, E for out-diffusion.

$$\frac{\partial \rho}{\partial t} = B_0 \exp(-E/kT), \quad (2)$$

where left hand side of equation is the change in resistivity with time and B_0 is a constant. Figure 6 is the Arrhenius-type plot of the slopes in figure 1 using the above equation. The plot yields an activation energy of 1.36 eV for the temperature range 698–773 K. TEM examination of the YBCO film revealed oriented grains with no

Figure 6. $(\ln dP/dt)^{-1}$ vs $1/kT$ for the film annealed in helium atmosphere.

traces of impurities within the grains or in the grain boundaries. Unlike the misoriented grains with high angle boundaries in the bulk ceramic materials, the mosaic grains with the low angle boundaries carry higher critical current densities. The low angle boundaries associated with the mosaic grains can provide diffusion paths for oxygen diffusion. Though, the lattice diffusion is restricted along the c-axis, several such boundaries can enhance the diffusion rates during the in- and out-diffusion of oxygen.

5. Conclusions

In summary, we have measured the time-dependent electrical resistivity of c-axis textured thin films of YBCO during in- and out-diffusion of oxygen in the temperature range 648–773 K.

The out-diffusion behaviour of the films shows a linear change in resistance as a function of time, while the in-diffusion behaviour exhibits a two-step process: a fast step due to the formation of a skin layer of high oxygen content on the surface of the film and a second slower diffusion step due to the lattice diffusion and structural relaxation and oxygen ordering along the b-direction. Our analysis shows the activation energies for in- and out-diffusion to be 0.7 eV and 1.36 eV respectively.

We have modelled the resistance-time plots for the oxygen in-diffusion using an equation for one dimensional diffusion into a plane. The close theoretical fitting with our experimental data yields the diffusion coefficient of oxygen, $D = 2.5 \times 10^{-16} \text{ m}^2/\text{s}$ at 648 K.

The microstructural features have been found to support the kinetic data provided by the resistivity measurements. Though the oxygen diffusion along the c-axis is restricted, the presence of low angle grain boundaries associated with the mosaic grains is believed to act as the diffusion paths in thin films of YBCO.

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