In situ growth and flux pinning in Ag-doped $YBa_2Cu_3O_{7-y}$ thin films

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We have grown *in situ* Ag-doped $YBa_2Cu_3O_{7-y}$ thin films by high-pressure magnetron sputtering using a stoichiometric target. The sputtering was carried out in a mixture of Ar (70%) and O_2 (30%) at a pressure of 200 mTorr, with the substrate temperature kept at about 700 °C during sputtering. We made a relatively high-pressure oxygen environment by employing an oxygen jet near the substrates. After deposition one atmosphere of O_2 was introduced into the chamber, and the sample was cooled down to room temperature slowly (5 °C/min). This method gives highly reproducible superconducting films with T_c (50%) at 83–88 K and zero resistance at 78–87 K depending on the growth conditions and the substrates used. In magnetic fields there is a narrowing of the resistive transition width for Y-Ba-Cu-O films with Ag impurities. We attribute the narrowing to the enhanced flux pinning due to the Ag impurities.

There have been many reports on the use of various techniques[1–3] to deposit high-T_c superconducting films. Among these techniques the *in situ* sputtering process using a single composite target has been used by many researchers, and it has the main advantage that it is simple to prepare the high-T_c oxide films. However, the disadvantage is that it is not easy to modify the composition of the film. Another problem is that the composition of the film is often different from that of the target (typically the films are Cu poor at high substrate temperature). These deviations are mainly due to the resputtering of the films by negative ions emerging from the cathode. Recent reports[4,5] show that the target composition can be reproduced in the film if a special geometry is adopted which eliminates negative-ion resputtering and a high pressure is used. In this paper we report the studies of *in situ* growth and the flux pinning of the Ag impurities in $YBa_2Cu_3O_{7-y}$ thin films by putting the samples off center and employing high pressure in an rf magnetron sputtering system.

Figure 1 shows a schematic picture of the deposition system used in this study. The target was clamped in the commercial, planar magnetron sputter source. The substrates were placed off center rather than in front of the target. The distance from the target to the substrate is about 2.5 cm. To increase the incorporation of oxygen into the Y-Ba-Cu-O films during the growth of the film, we have made a relatively high-pressure oxygen environment near the substrates by employing an oxygen jet. The sputtering was carried out in a high-vacuum system with a base pressure of about 3×10^{-6} Torr. We have used stoichiometric $YBa_2Cu_{3(1-x)}Ag_{3x}O_{7-y}$ targets with $x=0.05$ and 0.15. The sputtering gas was a flowing mixture of Ar (70%) and O_2 (30%). Typical sputtering conditions are 60 mTorr of O_2, total pressure of 200 mTorr. The substrates were placed off center rather than in front of the target. The substrates were heated to about 700 °C using a temperature controller (Eurotherm model 818) which can stabilize the temperature to within about 1 K. The temperature of the substrates was monitored by a *K*-type thermocouple and Pt thermometer. The thermometers are in thermal contact with the sample holder and close to the sample. The temperature reading from two thermometers is close and within about 5 K. After deposition, normally the pressure of the rf sputtering system was evacuated to 10^{-3} Torr to remove the mixture of Ar and O_2. Then one atmosphere of oxygen was introduced into the chamber. The sample was cooled down from 700 to 600 °C in 10 min, kept at 600 °C for about 1 h, and then slowly cooled down to room temperature at a rate of 5 °C/min. For the oxygen-deficient sample, the superconducting transition temperature was controlled by varying the oxygen pressure during the cooling process. Finally

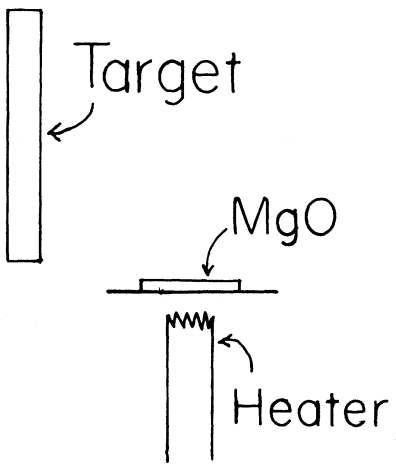

FIG. 1. Schematic picture of the rf sputtering system.

the samples were removed from the chamber. Their appearance was black and shiny. These samples, in general 0.2–1 μm thick, were studied without any post annealing.

In preparing the high-T_c thin films, we used two types of substrates: $SrTiO_3(100)$ and MgO(100). Superconducting films with zero resistance at 78–87 K can easily be reproduced for both types of substrates depending on the growth conditions. Figure 2 shows typically the temperature dependence of resistance of the as-grown films on MgO(100) and $SrTiO_3(100)$. The film on MgO(100) shows an onset superconducting transition temperature at 90 K, T_c (50%)=87.3 K, and a zero resistance at 86 K. The resistance ratio R(300 K)/R(100 K)=2.7 and the resistivity ρ(300 K)=0.5 mΩ cm. The film on $SrTiO_3(100)$ shows an onset superconducting transition temperature at 93 K, T_c (50%)=87.7 K, a zero resistance at 87.2 K, and a resistance ratio R(300 K)/R(100 K)=2.8. We note that the criterion of the zero-resistance temperature we adopt is that the resistance of the film is below 1×10^{-6} Ω and the current to the sample is 3 mA.

Figure 3 shows typically the x-ray-diffraction pattern of the film on $SrTiO_3(100)$ and MgO(100), respectively. The as-grown films show a preferred orientation with the c axis perpendicular to the (100) plane of MgO. We note that the film on $SrTiO_3(100)$ has a phase which shows the

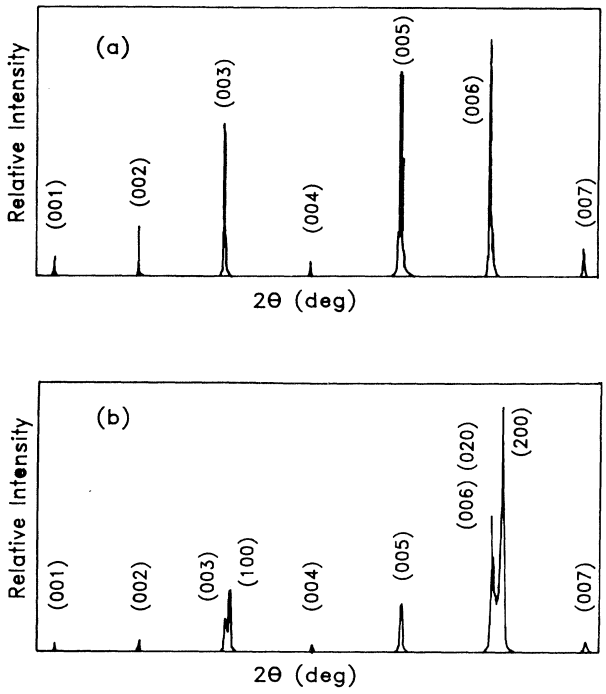

FIG. 3. X-ray-diffraction pattern of the as-grown films on (a) MgO(100) and (b) $SrTiO_3(100)$.

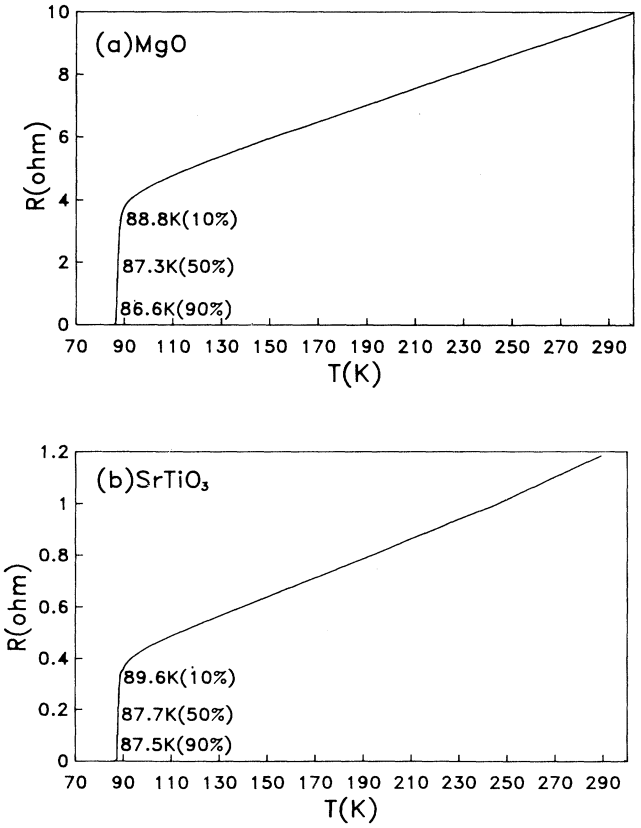

FIG. 2. Temperature dependence of the resistance on (a) MgO(100) and (b) $SrTiO_3(100)$ for films prepared from a $YBa_2Cu_{3(1-x)}Ag_{3x}O_{7-y}$ target with $x=15\%$.

a axis perpendicular to the (100) plane. The films are shining and smooth, as can be seen from the scanning electron micrograph of the films shown in Fig. 4. The distance of the line bar is 1 μm. The inductively coupled plasma atomic-emission data show that the as-grown film has a composition of $YBa_{1.95}Cu_{2.7}$ $Ag_{0.13}O_{7-y}$ for films prepared from $YBa_2Cu_{2.85}Ag_{0.15}O_{7-y}$ targets.

It is necessary to grow and cool superconductors in sufficient oxygen to achieve high-quality films in correct

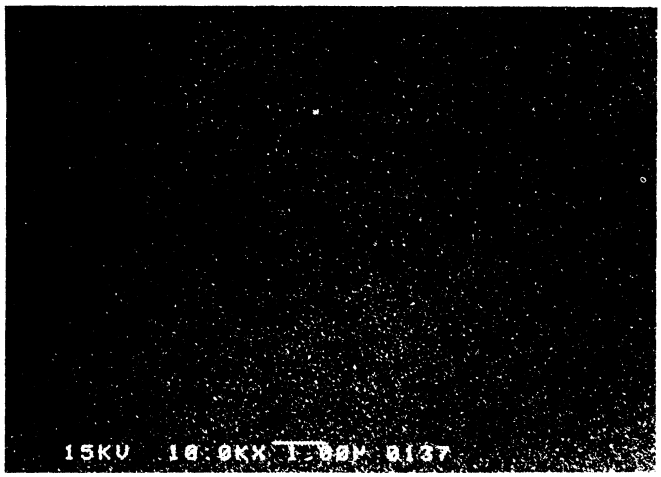

FIG. 4. Scanning electron electron micrograph of the Ag-doped $YBa_2Cu_3O_{7-y}$ film on MgO(100).

structure and without any further heat treatment. Growth with insufficient oxygen leads to a lower critical temperature. Figure 5 shows $R(T)$ as a function of temperature in fields parallel to the c axis and the ab plane for an oxygen-deficient sample grown at 700 °C in a mixture of Ar (70%) and O_2 (30%) but cooled in air at a rate of 5 °C per min. The sample was prepared from target $YBa_2Cu_{2.85}Ag_{0.15}O_{7-y}$. This sample shows T_c (50% resistive) at about 65 K and a zero resistance at about 60 K. The field at 50% resistive transition shows a linear temperature dependence with $dH_{ab}/dT=-2.79$ T/K (the field is parallel to the ab plane), $dH_c/dT=-0.47$ T/K (the field is parallel to the c axis). The anisotropy factor is about 5.9.

One of the most prominent features of the high-T_c thin films is their ability to carry a large transport current in the presence of a magnetic field. In a field the resistivity curve shows a broadening.[6–8] Ag impurities in Y-Ba-Cu-O thin films introduce pinning centers, therefore they improve the flux pinning and current-carrying abilities. The improved pinning due to Ag impurities should show up as a narrowing of the transition width in the resistive curve in a field. Figure 6 shows the normalized resistance, $R(T)/R(T_0)$, as a function of the reduced temperature, $T/T_c(50\%)$, for Y-Ba-Cu-O films with (——) 15% Ag impurities and without (· · · ·) Ag impurities in fields parallel to the ab plane and the c axis, respectively, where T_0 is the onset of the broadening of the resistive transition in a field. A narrowing of the transition width was found in Y-Ba-Cu-O films with Ag impurities compared with that without Ag impurities in both field directions. The reduced transition temperature, $T_c(H)/T_c(50\%$ resistive), as a function of H is shown in Fig. 7. The sample without Ag impurities shows $(dT_c/dH)_c=-1.09$ K/T and $(dT_c/dH)_{ab}=-0.32$ K/T for a field parallel to the c axis and the ab plane, respectively, whereas the sample with Ag impurities shows $(dT_c/dH)_c=-0.84$ K/T and $(dT_c/dH)_{ab}=-0.23$ K/T ($2.5<H<5.5$ T).

It is interesting to compare the pinning of the oxygen-deficient 60-K Y-Ba-Cu-O films with that of the 90-K Y-Ba-Cu-O films. To do this, we replot Fig. 5 as $T(H)/T_c$ (50% resistive) versus H, as shown in Fig. 8. Also shown are data from sample b which was prepared from the same target in sufficient oxygen atmosphere. A broadening of the resistive transition in a field was found in the

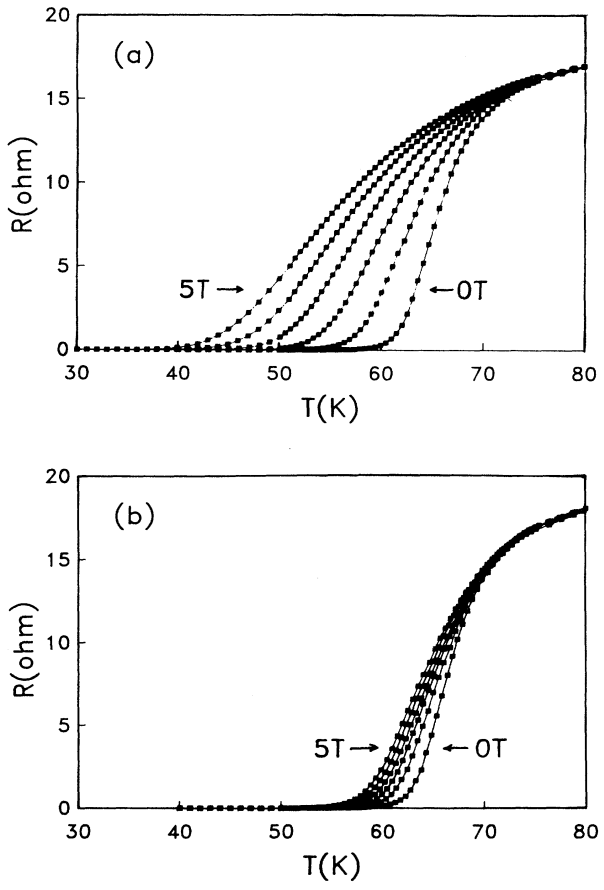

FIG. 5. $R(T)$ as a function of temperature in fields parallel to (a) the c axis and (b) the ab plane. The increment of the field is 1 T in each curve.

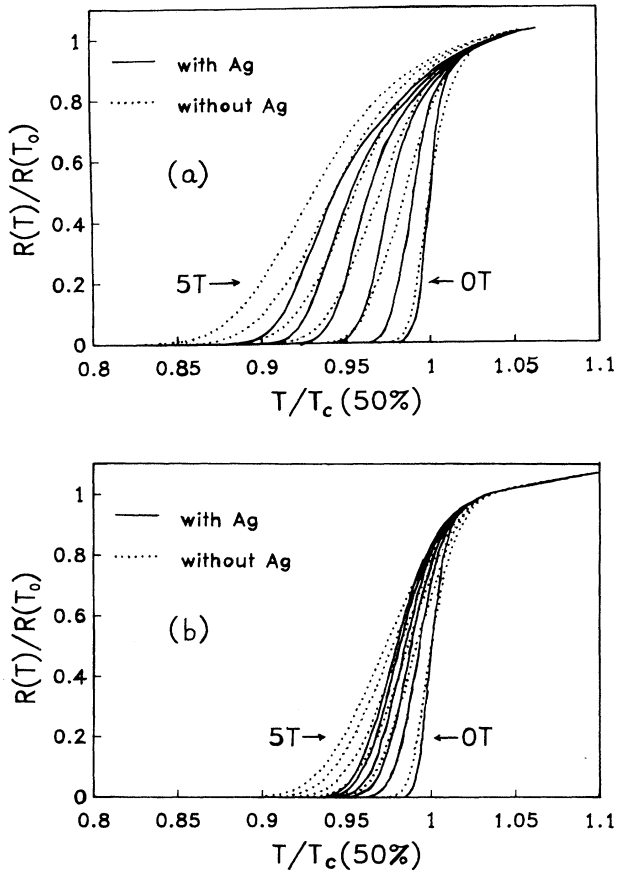

FIG. 6. $R(T)/R(T_0)$ as a function of the reduced temperature, $T/T_c(50\%$ resistive) for Y-Ba-Cu-O films without (· · · ·) and with (——) Ag impurities, $x=15\%$ in magnetic fields parallel to (a) the c axis and (b) the ab plane. The increment of the field is 1 T in each curve.

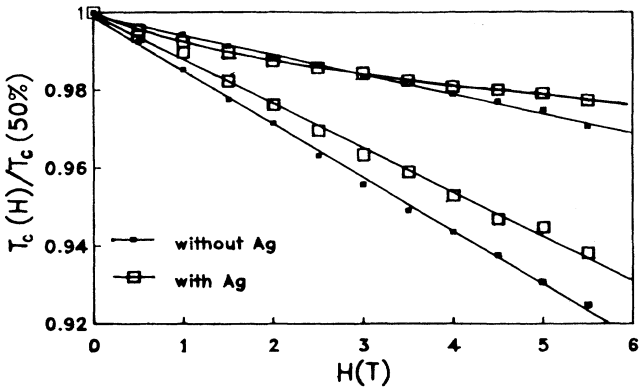

FIG. 7. $T_c(H)/T_c(50\%)$ as a function of the applied field for films without and with Ag impurities. $T_c(50\%)$ is the transition temperature in zero field.

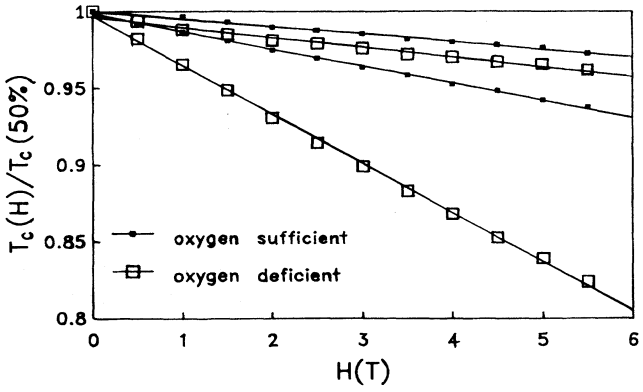

FIG. 8. $T_c(H)/T_c(50\%)$ as a function of the applied field for the oxygen-deficient Y-Ba-Cu-O films with Ag impurities, $x=5\%$. Also shown are data of sample b prepared from the same target in sufficient oxygen.

oxygen-deficient Y-Ba-Cu-O film. The oxygen-deficient 60-K film shows $(dT_c/dH)_c=-2.1$ K/T and $(dT_c/dH)_{ab}=-0.36$ K/T, whereas sample b shows $(dT_c/dH)_c=-0.88$ K/T and $(dT_c/dH)_{ab}=-0.25$ K/T. It is known that there is a depletion of the oxygen chains upon going from the 90- to 60-K phase Y-Ba-Cu-O oxide compounds. The depletion of oxygen chains decreases the electronic coupling between Cu-O layers and affects the physical properties[9,10] of the high-T_c $YBa_2Cu_3O_{7-y}$ superconductor. The data show that the flux pinning is affected by the oxygen stoichiometry in the Y-Ba-Cu-O films and the force of the flux pinning is weaker in the 60-K Y-Ba-Cu-O film compared with that of the 90-K Y-Ba-Cu-O film. Our explanation of this change of the flux pinning is due to the depletion of the oxygen chains, which makes the 60-K phase more anisotropic than the 90-K phase. We believe this anisotropy is related to the flux pinning of the high-T_c films.

In conclusion, we have grown *in situ* Ag-doped Y-Ba-Cu-O thin films by putting substrates off center and employing high pressure in an rf magnetron sputtering system. Superconducting films with zero resistance at 78–87 K can be reproduced. Ag impurities in Y-Ba-Cu-O films were found to improve the pinning ability. A narrowing of the resistive transition in a field was found in Y-Ba-Cu-O films with Ag impurities compared with that without Ag impurities and it is attributed to the enhanced flux pinning due to the Ag impurities in the Y-Ba-Cu-O film.

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