Optical spectroscopic study of the growth dynamics of radio-frequency-sputtered $YBa_2Cu_3O_{7-x}$ thin films

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An optical spectroscopic study of the plasma produced during rf sputtering of an $YBa_2Cu_3O_{7-x}$ target was performed to analyze two basic properties of the deposition process: resputtering effects and oxidation mechanisms. Strong emissions of all the species above a value of the target voltage were found. These observations are associated to a strong secondary electron emission of the target which originates a negative self-bias of the substrate and a subsequent resputtering by argon cations. The addition of different amounts of oxygen to the discharge reveals that preoxidation in the gas phase may decrease the oxygen content in the films: the oxidation of the films is dominated by atomic oxygen.

A great effort has been devoted in recent years to the growth of high-temperature superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) films by sputtering and, although excellent superconducting properties have been reported, there is a lack of understanding of some basic questions related to the growth dynamics. Strong resputtering effects that can cause stoichiometric deviations and etching effects have been explained as due to O^- and O_2^- ions,[1-4] although, to our knowledge, no experimental evidence for the existence of those ions has been presented so far. The growth of superconducting films requires the presence of certain amounts of oxygen in the discharge atmosphere. The way this oxygen incorporates to the film and the dependence of the superconducting properties on the oxygen partial pressure is another point that deserves some attention.

Monitoring the light-emitting species by glow-discharge optical spectroscopy[5-7] (GDOS) constitutes a possible approach in solving the above raised questions. In this letter we present a spectroscopic study of the plasma resulting from rf sputtering a single YBCO target in an effort to gain understanding of the origin of the resputtering phenomena and the oxidation mechanism that yields the *in situ* growth of superconducting films. The nonperturbative, real-time monitored analysis of the plasma will reveal the role played by the secondary electron emission in the bombardment effects, and the negative effect for the superconducting properties of the growth of the film from oxides (YO, CuO, BaO) rather than from atomic species.

The study was carried out in a rf diode sputtering system. The plasma spectra were detected through a quartz window by a computer-controlled monochromator-photomultiplier experimental arrangement which scanned the range of 200–800 nm. The emission lines from neutral and singly ionized species were systematically identified. YO molecular band emissions with strong band heads were also detected. The emission lines result of electronic transitions caused by the deexcitation of species excited by inelastic collisions with energetic electrons.

Since resputtering effects are known to increase at high-power densities, the discharge atmosphere has been optically monitored at increasing target voltages in the range 300–800 V for different AR/O_2 admixtures. The evolution of the intensities of neutral yttrium (Y I) and neutral argon (Ar I) (4674.8 and 6043.2 Å, respectively) as functions of the target applied voltage (V_b) are represented in Figs. 1(a) and 1(b) for different oxygen partial pressures in the discharge. The lines of all the neutral and ionized species present an analogous behavior. In pure argon atmospheres there is a strong increase of the emitted intensities above 400 V of the target voltage. Since no abrupt change was observed in the deposition rate, this fact cannot be related to an increased sputtering rate but to an excitation enhancement. The number and energy of the rf discharge electrons are known to be rather independent on the target voltage, therefore, the observed behavior has to be explained in terms of an increase in the emission of secondary electrons by the target. This effect is less pronounced when oxygen is introduced in the chamber, probably as a result of the partial reconstruction by the oxygen of the bombarded target surface. Further evidence supporting this point can be gained from the "macroscopic" effects of the electrons: heating and negative biasing.

The substrate temperature below target followed qualitatively the same behavior observed in the intensity of the emission lines, reaching values as high as 350 °C for a target voltage of 500 V in 110 mTorr of pure Ar. This value decreased to 150 °C when 10% of O_2 was introduced in the discharge. On the other hand, secondary electrons bombarding insulating or electrically floating substrates will give rise to charge storage effects that will cause a negative bias of the substrates, and as a result they will be subjected to positive ion bombardment.

In order to elucidate the role of the electrons in the bombardment effects, a simple experiment was conducted under different sputtering conditions. Figure 2 shows the radial variation of the growth rates at the substrate holder for (a) pure argon atmosphere and floating substrate, (b) reactive atmosphere and floating substrate, and (c) pure argon atmosphere and metallic grounded substrate. Film erosion under the 1-in. radius target, which represents a first approach to resputtering effects, does not take place in grounded substrates in which charge storage cannot occur. In case (b) we have already seen that the target might not

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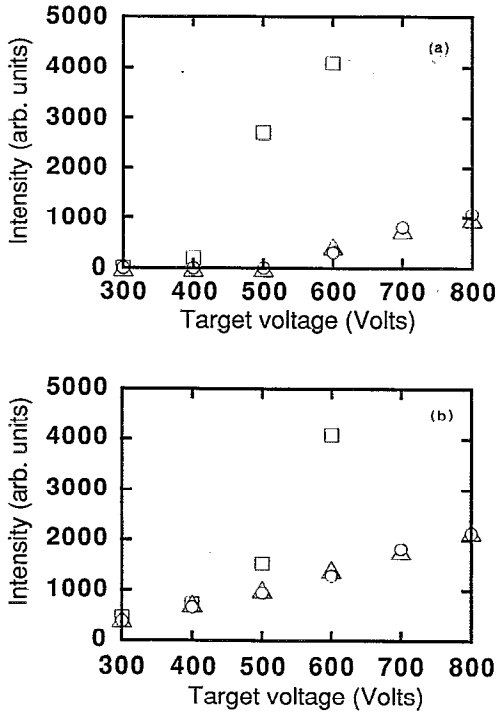

FIG. 1. Target voltage dependence of the emission line (a) $\lambda=4674.8$ Å of neutral yttrium and (b) $\lambda=6043.2$ Å of neutral argon for a total discharge pressure of 110 mTorr and different oxygen contents: (□)0%, (△)10%, (○)25%.

be emitting secondary electrons while in case (c), although a high amount of secondary electrons arrives at the metallic grounded substrate, they cannot accumulate and originate a positive ion bombardment. This strongly suggests that, along with the O^--related resputtering, a bombarding of positive argon ions accelerated towards the negative self-biased substrate is taking place.

The emission spectra also supply information about the oxidation process necessary for the *in situ* growth of superconducting films. In this case we have changed $P(O)_2$, keeping V_b and the growth temperature (T_g) constant (750 V and 680 °C, respectively). The choice of a high V implies the need for growing films at the projection of the target edge (off-axis geometry). A slight bombardment is probably still taking place, but provides a beneficial polishing of the surfaces. The *in situ* superconducting films have smooth surfaces; they are textured and (001) oriented as shown in Fig. 3. The x-ray diffraction patterns show a shift of the (001) peaks to lower angles, i.e., an increase of the c-lattice parameter, when $P(O_2)$ is raised. The variation of c in our *in situ* films can be correlated to first order to differences in oxygen content. Figure 4 shows an increase of the c-lattice parameter along with a decrease of the critical temperature of the films when $P(O_2)$ is raised, and reveals that the higher $P(O_2)$ is, the lower the oxygen content of the films is. A clear decrease of the Y/YO ratio is also detected from GDOS experiments, as shown in Fig. 5. Our results indicate that a high oxygen pressure in the discharge leads to the formation of gas-phase oxides like YO. The resulting films are oxygen poor and present broad superconducting transitions with low critical temperatures (Fig. 4). Transition widths range from 3 K in a 10% oxygen reactive atmosphere to 30 K in a 50% oxygen reactive atmosphere. In these conditions, the resistivity at room temperature rises from 0.5 to 360 mΩ cm, respectively. We conclude that film growth takes place easily from the chemically more reactive atomic phase rather than from metal oxides. This conclusion leads to a better understanding of the empirical observations reported by Yang *et al.*[8] and Hammond *et al.*[9] There is a

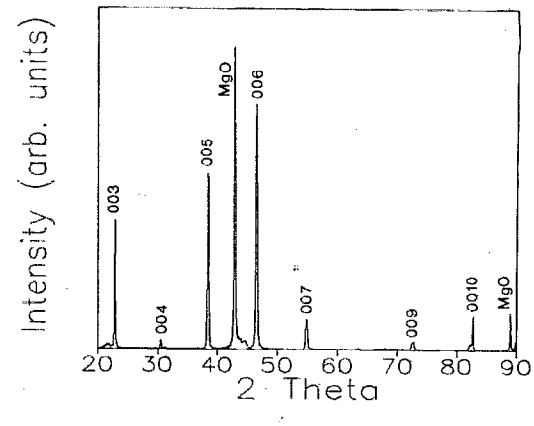

FIG. 3. X-ray diffraction pattern of a typical as-grown film. Only $YBa_2Cu_3O_{7-x}$ (001) and MgO(100) diffraction peaks are present.

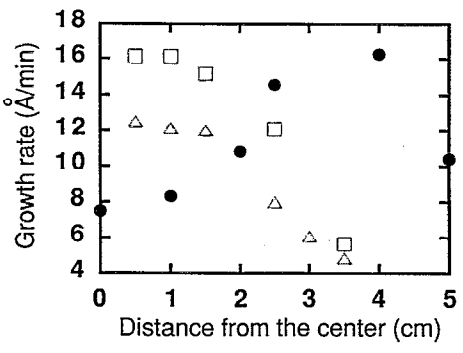

FIG. 2. Growth rate profiles for (●) pure argon atmosphere and floating substrate, (△) reactive atmosphere (50% oxygen) and floating substrate, and (□) pure argon atmosphere and metallic grounded substrate. The target radius is 1 in.

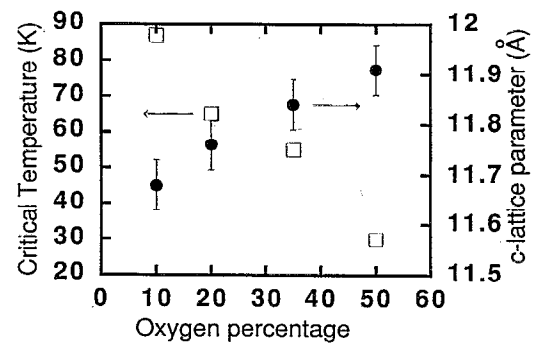

FIG. 4. Dependence of the critical temperature (□) and the c-lattice parameter (●) of the films with the oxygen percentage in the reactive atmosphere ($V_b=750$ V, $T_g=680$ °C, and $P_{total}=110$ mTorr).

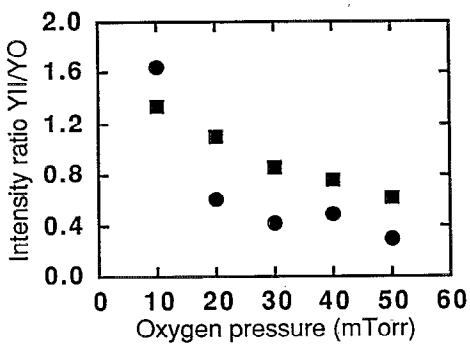

FIG. 5. Ratio of Y II peak heights to the 5972.0-Å YO peak height as a functiom of the oxygen pressure in the discharge: (□) 3496.1 Å Y II emission line, (●) 3093.8 Å Y II emission line. The total pressure was kept constant at 110 mTorr.

value of $P(O_2)$ for a fixed T_g which optimizes the superconducting properties of the films. We propose that the fact that at higher oxygen partial pressures higher growth temperatures are required is related to the presence of the less reactive YO oxides. An external energy (a higher deposition temperature) must be supplied in order to increase reactivity on the substrate.

In summary, an analysis of the emission spectra produced during rf sputtering of an $YBa_2Cu_3O_{7-x}$ target is presented. Monitorizing the emitted intensity under different sputtering conditions points to the self-bias effects caused by secondary electrons as an alternative source for resputtering effects. Characterization of the films as a function of the oxygen partial pressure shows that the growth of the films from atomic rather than from oxidized species requires a lower deposition temperature.

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