Journal of the Less-Common Metals, *164 & 165* (1990) 307-314

ECR-PLASMA ASSISTED LASER ABLATION OF AS-DEPOSITED SUPERCONDUCTING THIN FILMS FOR APPLICATION IN MICROELECTRONICS

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A method for the growth of as-deposited superconducting thin films which combines YAG-laser ablation and oxidation by an ECR-excited oxygen plasma is described. It is demonstrated by depositions on YSZr and on SrTiO3 that this one-step method is fully compatible with the requirements of large surface homogeneity, low substrate temperature and low oxygen partial pressure for application in micro-electronics.

1. INTRODUCTION

The deposition of high T_c superconducting YBaCuO thin films has now advanced to the stage where several techniques (sputtering, ablation, evaporation, MBE, CVD, ...) produce high quality layers. Geerk et al. classify those processes in their review article[1] into two categories :

- the first is a three step procedure depositing the film in the amorphous phase, bringing it to the tetragonal form $Y_1Ba_2Cu_3O_6$ at high temperature (>900 ^oC) and intercalating the oxygen $Y_1Ba_2Cu_3O_7$ at lower temperature (~400 ^oC) and elevated oxygen pressure;
- the second is a two-step procedure (often called "in-situ preparation"), realizing a deposition in the tetragonal phase at temperatures in the region of 650 ^oC-750 ^oC and therefore only requiring an oxygen intercallation step at lower temperatures in an oxygen atmosphere. An equivalent of this step is the slow cooling down in oxygen ambient after deposition by allowing oxygen to fill the deposition chamber.

If the superconducting films are aimed at micro-electronic applications, their production process must satisfy some severe requirements depending on the application :

- large surface homogeneity is needed for use in off-chip interconnections;
- the substrate temperature must be reduced to the range of 550 ^oC-600 ^oC to broaden the range of substrates on which good high T_c material can be grown (e.g. low dielectric insulators, semiconductor substrates for integration with existing GaAs and Si technology);
- the film must be superconducting in the as-deposited state without exposure to a high-pressure post-deposition step, so that multilayer structures can be formed in-situ.

0022-5088/90/$3.50

Up to now no deposition technique is able to fulfill these requirements. From an extrapolation of the data of Kishio[2], it is clear that such a one-step deposition using neutral oxygen would be impossible. A deposition of an $Y_1Ba_2Cu_3O_7$ film at substrate temperatures in the range of 650 ^oC-750 ^oC would necessitate a simultaneous oxygen partial pressure of more than 1000 atm. For low pressure deposition (<1 Torr) of $Y_1Ba_2Cu_3O_7$ the substrate temperature should not exceed 350 ^oC, excluding the formation of a perovskite structure. The more general need for low temperature processing during last years has led to the development of plasma-assisted deposition techniques. Due to the more reactive nature of excited atoms and ions, the plasma enhances the chemical reactions making it possible to synthesize films at lower substrate temperatures. The deposition technique which will be described here is a unique combination of such an ECR-plasma oxidation and a Nd-YAG laser ablation leading to the first one-step production of as-deposited superconducting films at low substrate temperature and low oxygen partial pressure.

2. EXPERIMENTAL SET-UP

The deposition chamber is cylindrical in shape 50 cm in diameter, 70 cm high and made of stainless steel. It has 11 flanges attached to it : one at the top for the heated substrate holder and pressure gauge, one at the bottom for vacuum pumping and 9 in a horizontal plane midway up it . One of these flanges holds the rotating superconducting YBCO pellet 5 mm thick and 20 mm in diameter. On the flange placed at 180^o the introduction chamber and transfer system for the substrate is mounted. Four other flanges have quartz windows, one for the incoming laser, one for Rheed diagnostics in front of the electron gun and another to enable side viewing of the plume and one for the mounting of the substrates. The rotating target pellet is located facing the substrates and parallel to their surface at a distance of 7 cm. The substrates are clamped onto a onto a metal block and are heated by direct radiation. The frequency tripled Nd:YAG laser (Quanta Ray GCR-3) at 355 nm has a pulse energy of 0.2 J with 6 ns pulse duration. The laser beam is not focused and has a diameter of 7 mm and thus produces a fluence of 0.5 J/cm^2 . Irradiation is carried out at 10 Hz and is incident near 15^o to the target surface normal. With each pulse a plume of purple light is visible pointing approximately normal to the pellet surface. Two large flanges (150 mm in diameter) in front of each other and normal to the target-substrate normal contain coils generating a magnetic field distribution inside the chamber. In the center of one of these a coaxial antenna sends microwaves of 2.45 GHz delivered by a continously varable output generator (up to 300 W) via a waveguide structure fitted with 5 mobile circuit termination for impedance matching. The oxygen gas is introduced to the vessel through the coaxial conductor and regulated by means of a microleak. The partial oxygen pressure used in these experiments is measured by turning a Bayert-Alpert gauge to the place where the substrate is located during deposition and is maximally 5 10^{-4} Torr. At this pressure plasma ignition is possible. Plasma conditions are fulfilled at 10 cm from both sides of the substrate where the magnetic field is 875 Gauss. The plasma is transported along the magnetic fieldlines in which the substrate is immersed. The 875 Gauss regions acts as magnetic mirrors and the plasma is confined to a cylindrical region of 50 cm long and 6 cm in diameter which is visible due to its yellow light.

3. PREPARATION OF FILMS

Films were deposited on polycrystalline rough Yttrium stabilized ZrO_2 (YSZr) and on polished (100) $SrTiO_3$ substrates. The deposition temperature was measured by a thermocouple mounted at the backside of the substrate in the environment of the heating filament. Due to the transparancy of the substrates it is impossible to determine the temperature at their surface by the pyrometer. Therefore the quoted substrate temperatures are upper limits and must be reduced by at least 50 ^{o}C, as was verified by observing the melt of a dot of Aluminum placed onto the substrate surface. At the beginning of each deposition the substrate was heated. The background pressure was 2 10^{-6} Torr. Plasma was then started with an oxygen partial pressure of 5 10^{-4} Torr and an injected microwave power of 60 W. Immediately the laser ablation of a superconducting YBaCuO pellet was started. The distance between the substrate and the pellet was 7 cm. Deposition was continued during four hours. After that, the laser was stopped and simultaneously the substrate temperature was quenched by reducing the heater current to zero. The cooling rate (figure 1) is so fast that extra uptake of oxygen is impossible. Moreover, the plasma pressure is not increased during the cooling period. After maximum 15 minutes it is possible to take the film out of the vessel. Without any post treatment films are mounted in a closed cycle refrigerator for 4 probe resistance measurements. Four copper pins at 5 mm distance in a standard square configuration are pressed onto the YBaCuO film without any intermediate contact layer.

4. RESULTS

4.1. Surface homogeneity

The center of the ablated plume was directed to the bottom left of a 2 inch polycrystalline YSZr substrate which was held at 670 ^{o}C at 7 cm distance from the pellet. The further deposition proceeded as described in the previous section. In figure 2.a. is indicated on which spots the film Rutherford Backscattering (RBS) analysis was performed to analyse thickness and composition of the deposited film. A He^{2+} ion beam of 2.270 MeV was used to bombard the film and backscattered particles were detected at an angle of 165^{o}. Most representative examples of the resistance curves measured on the same spots are shown in figure 2.b.

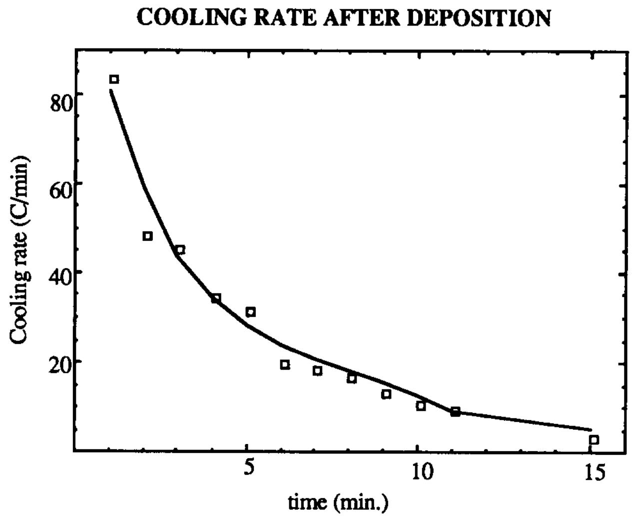
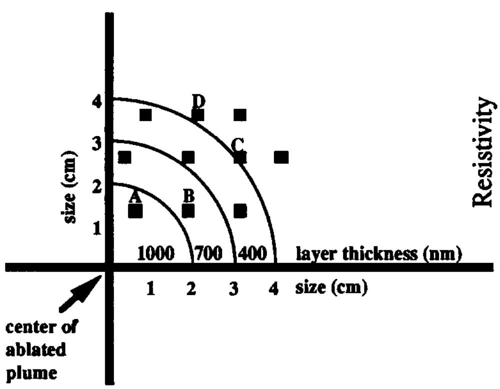


FIGURE 1
Cooling rate of the substrate temperature after deposition of the YBaCuO layer



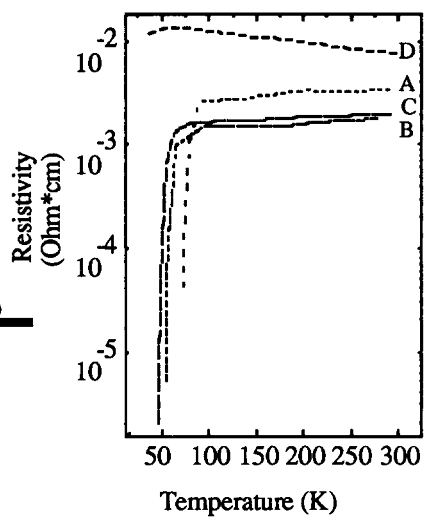


FIGURE 2.a.
A quarter of the ablated laser plume is deposited on an YSZr substrate and analysed by RBS on the indicated spots.

FIGURE 2.b.
Resistivity curves as function of temperature at spots A, B, C and D

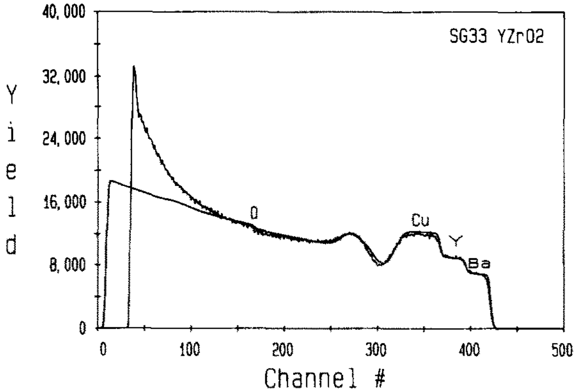


FIGURE 3.a.
Measured and fitted RBS spectrum on spot B

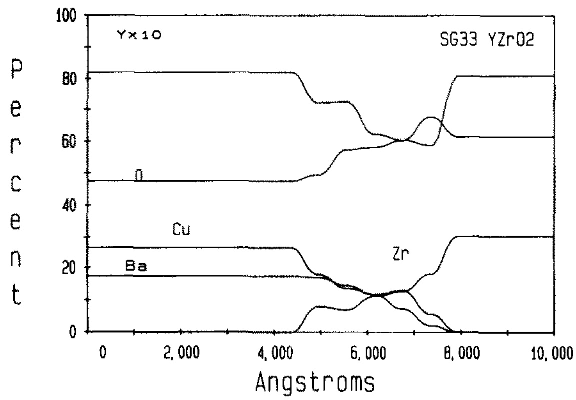


FIGURE 3.b.
A composition diagram as a function of depth

The thickness of the film is 1000 nm and varies less then 10% in a circle with radius of 2 cm. At a radial distance of 3 cm, resp. 4 cm the thickness has decreased with 30%, resp. 60%. The composition of the top layer inside the circle with radius 4 cm (e.g. A,B,C in figure 2.a.) is $Y_1Ba_2Cu_3O_{7-y}$, but is Ba and especially Cu deficient outside this circle (e.g. D). Fitting of the RBS spectrum of point B (figure 3.a.) reveals an interface layer of about 250 nm where the YBaCuO film and the YSZr substrate have reacted : an indiffusion of Y, Ba and Cu together with an outdiffusion of Zr is visible (figure 3.b.). One concludes that the films abroad the 4 cm radius are too thin resulting in a reacted surface layer and therefore not leading to a superconducting behaviour (D). For the other spots (A, B, C) T_c increases with thickness due to the relative thickness increase of the 1-2-3 layer compared to the interface layer. Indeed, as the critical current in these films is very low, the current density decreases with increasing layer thickness, leading to higher T_c values.

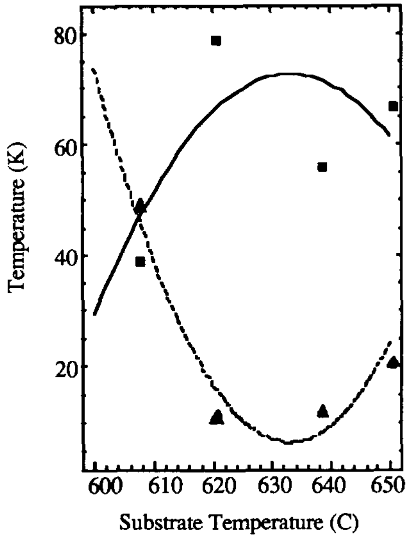
4.2. One-step deposition at reduced substrate temperature and oxygen pressure

The film produced on YSZr for the surface homogeneity study in previous section had very good superconducting properties, taken into account that the underlying substrate has a rough and polycrystalline surface. The resistance curve of the film is drawn in figure 2.b. and shows an onset temperature of 90 ^{o}K and an offset temperature of 75 ^{o}K. Regarding this result of a one-step deposition, it was hoped that deposition on polished monocrystalline $SrTiO_3$ could lead to even better characteristics.

The center of the ablated plume was directed to a 7.5 mm x 7.5 mm (100) $SrTiO_3$ substrate which was heated by direct radiation. At a fixed oxygen partial pressure ($5\ 10^{-4}$ Torr) and injected power (60 W) in the plasma the resistance versus temperature behaviour of the deposited film was studied as a function of the substrate temperature T_S (figure 4.a.). It is clear that not enough oxygen was included at the lowest deposition temperatures below 610 ^{o}C (this means around 560 ^{o}C substrate temperature). At deposition temperatures above 650 ^{o}C (above 600 ^{o}C substrate temperature) the oxygen pressure of $5\ 10^{-4}$ Torr is too low to prevent outdiffusion. The resistance curve of these films shows an onset at 90 ^{o}C, but a long tail is caused by an oxygen deficient phase in the film. This became clear as the film with the same growth parameters but with a supplementary step consisting of a post -treatment in oxygen atmosphere at 450 ^{o}C during 30 minutes before cooling down to room temperature, exhibits a higher T_c around 90 K. In the intermediate deposition temperature region (between 560 ^{o}C and 600 ^{o}C substrate temperature) it is possible to produce an as-deposited superconducting film. To be sure that the use of the ECR-oxygen plasma in which the substrate is immersed is the key of the succesful one-step growth, a film was prepared under exactly the same conditions but using neutral oxygen at nominally the same flowrate. This film had a semiconductor behaviour from 300 K to 5 K. The same study was performed at a higher microwave power of 300 W, leading to films with lower T_c values as displayed in figure 4.b.

Up to now the best characteristics of an YBaCuO film deposited on $SrTiO_3$ are an onset temperature of 90 ^{o}K and an offset temperature of 80 ^{o}K. It seems that the parameters of the oxygen plasma, -although not fully understood at the moment-, play an important role in determining the quality of the deposited layer. Therefore future study will concentrate on plasma diagnostics to try to understand its influence. Different polarisation effects on $SrTiO_3$ and YSZr are a possible explanation for the fact that it was more easy to optimize the film growth on YSZr than on $SrTiO_3$.

In figure 5.a. the resistance curve of the film grown at a deposition temperature of 620 ^{o}C (570 ^{0}C substrate temperature) and in an oxygen plasma of $5\ 10^{-4}$ Torr is shown as a function of the current. Although critical current densities were not measured yet, it is clear that the values are still very low. It was not possible to channel through this layer and the fit of the random RBS spectrum revealed an important interface layer of 180 nm as is clear in the composition diagram of figure 5.b. In the future special attention will



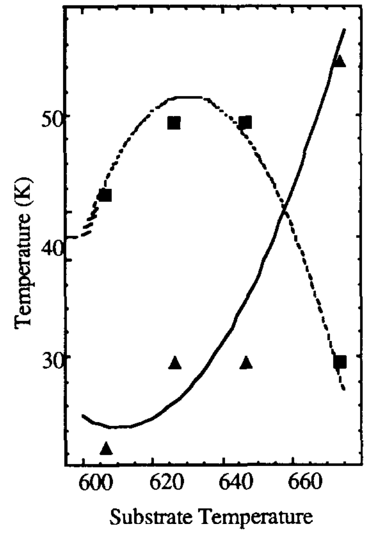


FIGURE 4.a. FIGURE 4.b.
Offset temperatures (squares) and transition width (onset - offset temperature) (triangles) of films deposited at different substrate temperatures and with an injected microwave power of 60 W (4.a) or 300 W (4.b)

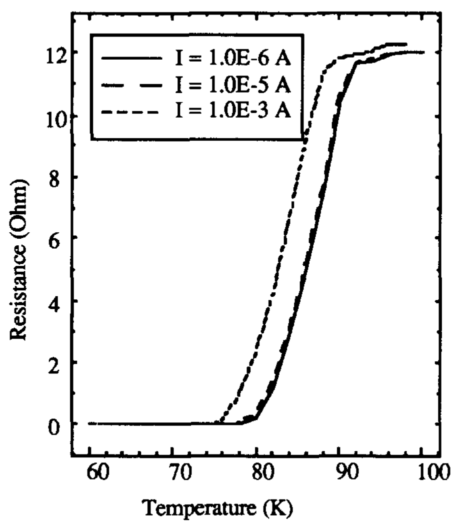


FIGURE 5.a.
Resistance curve as a function of temperature and current

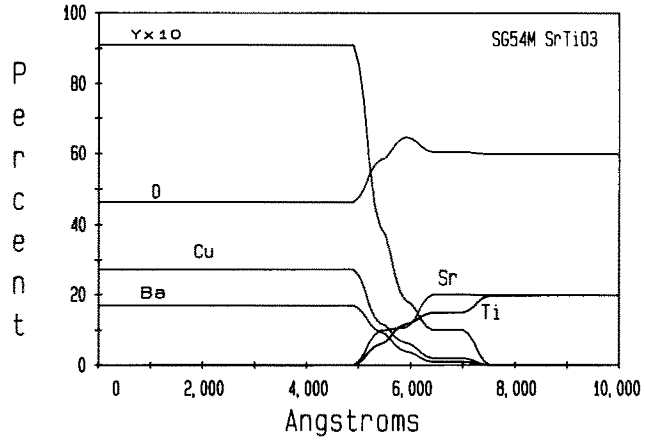


FIGURE 5.b.
Composition diagram as a function of depth

be paid to substrate cleaning and background pressure to promote epitaxial film growth. Moreover a higher laser fluence will be used to decrease the growing time (4 hours) during which the substrate and the film are heated and the plasma influence will be studied in detail.

5. CONCLUSION

It has been demonstrated that superconducting YBaCuO films can be deposited in one step at low substrate temperature in an oxygen ECR-plasma at low partial pressure. This opens new possibilities towards the in-situ production of multilayers as well as towards the integration of superconducting films with classical micro-electronics (GaAs, Si). As the YAG laser ablation and plasma oxidation provide large superconducting surfaces, off-chip interconnections become a possible application. Future material research will therefore be directed to the reduction of the interface layer, the growth of single crystalline films and the deposition on semiconductor substrates.

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