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IN SITU GROWTH OF HIGH TEMPERATURE SUPERCONDUCTOR THIN FILMS WITH EVAPORATION TECHNIQUES USING OZONE AS AN OXYGEN SOURCE.

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High quality $YBa_2Cu_3O_7$ thin films have been grown in situ on various substrates using MBE techniques and an ozone jet. The best films so far were grown on $SrTiO_3$ and had a $T_{c,onset}$ of 88 K and a T_{c0} of 80 K. One 200 nm thick film grown on bare silicon had a $T_{c,onset}$ of 88 K and a T_{c0} of 60 K. This film showed no or negligible superconductor substrate interactions according to RBS measurements.

1. INTRODUCTION

High temperature superconductor thin films with very high critical current densities can be made by several fabrication methods, like sputtering, laser ablation and evaporation techniques. The first films that were produced by these methods were made by depositing the required amount of the constituent elements on a substrate and a post-annealing treatment to form the required crystal structure. Because this crystal structure is formed after the deposition of the film a higher annealing temperature is required compared to forming the superconductor during the the growth of the film. Not only might this in-situ growth result in thin films with better transport properties due to less reactions at the superconductor-substrate interface, but it will certainly yield less reactions with artificial barriers when these are exposed to the high temperatures. Several succesfull attempts to fabricate in-situ superconducting thin films at considerably lower growth temperatures have been reported by other groups using various techniques (1,2,3).

The biggest problem of using MBE techniques for in-situ growth is the incorporation of oxygen in the film. Though other fabrication techniques like sputtering and laser-ablation can use high enough oxygen partial pressures during growth to form and stabilize $YBa_2Cu_3O_7$ (4), MBE techniques limit the total pressure to 10^{-4} mbar, which is far from enough. By using ozone instead of oxygen this pressure problem can be circumvented (5).

2. FABRICATION EQUIPMENT

The films are fabricated in an UHV system which contains two electron guns and one effusion cell. The system is pumped by a turbo molcular pump and a Ti sublimation pump. Base pressure of the system is about 10^{-8} mbar. Yttrium and copper are evaporated from the e-guns and the barium is evaporated from the effusion cell. The evaporation flux from all the sources is controlled by a feedback system which uses one multiplexing mass spectrometer for flux measurement. The flux from the e-guns is controlled by adjusting the emission of the gun. This high quality feedback system has been described elsewhere (6).

The flux from the effusion cell is also controlled by a feedback loop because the flux from this particular type of effusion cell turned out to be sensitive to high partial ozone pressures when evaporating barium. The total pressure in the system is measured with a ionization vacuum gauge which is located near the turbo molecular pump. The fluxes from the various sources are calibrated with a single quartz crystal monitor which is located next to the substrate holder.

The ozone is fabricated in a silent discharge. This ozone generator consists of a stainless steel rod in a glass tube through which ambient oxygen flows. The stainless steel rod is driven by a high voltage source. The whole discharge chamber is cooled by liquid nitrogen. The ozone/oxygen mixture that is fabricated is lead into a glass chamber through a small orifice. This chamber is held at 77 Kelvin by liquid nitrogen cooling. When enough mixture has been condensed this chamber is pumped down. Because ozone/oxygen mixtures with a higher ozone content have a lower vapour pressure at the same temperature this pumping removes the oxygen from the mixture. Pumping is stopped when the pressure drops below 10^{-1} mbar. After purification the ozone can be lead into the vacuum system through a glass/PTFE valve and a stainless steel tube. The pressure in the deposition chamber, which is proportional to the vapour pressure in the liquid ozone vessel, can be adjusted by heating the glass chamber relative to the liquid nitrogen bath.

3. FABRICATION PROCEDURES

First of all the the fluxes from the various sources are set to give the desired composition with the ozone flux turned off. A typical total evaporation flux that we used was about 0.2 nm/s. Then the substrate holder is heated up to about 700 °C and the ozon flow is turned on by heating the still until the total amount of mass flux on the quartz crystal monitor deviates 50% from the initial value. This is the maximum ozone pressure that can be used during the

evaporation, because above this pressure the mass spectrometer signal starts to deviate too much due to decreasing sensitivity of the instrument at high pressures. This decrease of sensitivity results in a clear increase of the total mass flux on the quartz crystal monitor because the mass spectrometer signals are held constant by the feedback loops. This happens at a pressure of 10^{-5} mbar measured by the ionization vacuum pressure gauge. This corresponds to a estimated pressure of about 10^{-4} mbar at the substrate position which is deduced from the increase in total presure when the evaporation sources are turned off at the end of the evaportion session. After adjustment of the ozone flow the substrate shutter is opened until a film with a estimated thickness of about 100 nm is grown. Subsequently the sample shutter is closed and the evaporation sources are cooled down as fast as possible, while the substrate holder is maintained at high temperature until the flux from all the sources has vanished, because the substrate shutter also blocks the ozone jet on the substrates. Then the sample shutter is reopened and the substrate holder is allowed to cool down in about half an hour to room temperature. During and after deposition the total ozone flux into the system is held constant.

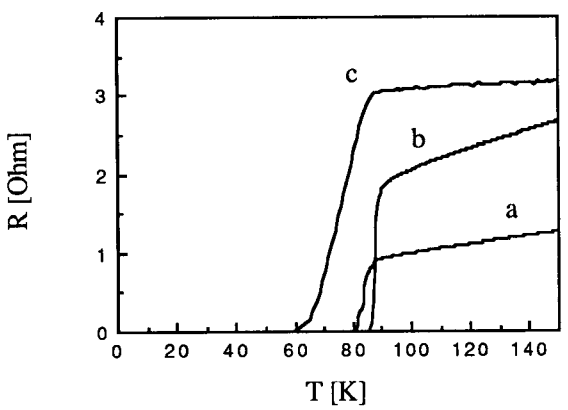

FIGURE 1
Resistance R versus temperature T for a) an in situ grown film on SrTiO3, b) a post annealed film on SrTiO3 from the same batch and c) an in situ grown film on bare silicon. The resistance scale for the sample on silicon has been compressed by a factor of ten.

4. RESULTS

This evaporation procedure resulted in films that exhibited superconductivity without any post-annealing procedure. The best film grown so far is fabricated on a (100) SrTiO3 substrate and exhibits a superconductive transition with a onset at 88 K and a T_{c0} of 80 K (figure 1, curve a). The temperature of the substrate holder of the in-situ grown film was during deposition 700 °C. A film that was grown during the same evaporation run but at room temperature and that was post annealed at 850 °C in an ambient oxygen atmopshere showed the same onset but a T_{c0} of 85 K (figure 1, curve b). The resistive tail may be explained by a not full oxydation of the in situ grown film.

Several films that were evaporated on sapphire (012) substrates showed a resistive transition with a T_{c0} of 80 K, which is higher than previously reported on films grown on sapphire using a post-anneal step. One film that was deposited on (001) Si had a resistive transition with $T_{c,onset}$ of 88 K and T_{c0} of 60 K (figure 1, curve c). This film was however grown in a deposition run during which the ozone flux had been increased too high which resulted in a average growth rate of 2 nm/s, which might be an explanation for the superconductive transition found in this film. The RBS spectrum of this film is shown in figure 2. This spectrum shows no or negligible interaction of the $YBa_2Cu_3O_7$ with the substrate.

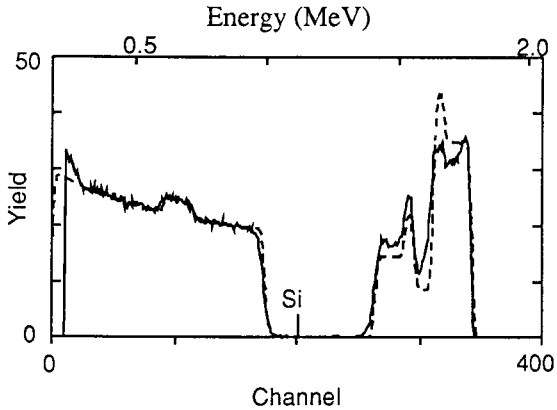

FIGURE 2
Rutherford backscattering spectrum for an in situ grown film on bare silicon. The dashed line represents the calculated spectrum of a 200 nm $YBa_2Cu_3O_7$ film on silicon.

5. CONCLUSIONS

Using ozone as an oxygen source it is possible to grow $YBa_2Cu_3O_7$ films under non equilibrium conditions in an MBE system on $SrTiO_3$ substrates which become fully superconducting at 80 K. The reduction of the substrate temperature generally results in better quality films on substrates that gave poor results with any post anneal process: on sapphire substrates a T_{c0} of 80 K can be accomplished and on bare silicon superconducting thin films can be grown with a $T_{c,onset}$ of 88 K and a T_{c0} of 60 K.

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