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

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Abstract

High quality $YBa_2Cu_3O_7$ thin films are grown in situ on various substrates ($SrTiO_3$, Al_2O_3, Si) using MBE techniques and an ozone jet. The yttrium and copper are evaporated from electron gun sources and the barium is evaporated from a Knudsen cell. All sources are controlled by a single mass spectrometer feedback system to obtain the correct fluxes at high partial ozone pressures. During deposition the partial ozone pressure at the substrate position is estimated to be 10^{-3}-10^{-2} mbar. The substrate holder temperature is 700 °C. The real substrate temperature is estimated to be lower than 650 °C. The films are analyzed with R(T) , X-ray diffraction and RBS measurements. SEM photographs are taken of the surface. The best film so far is grown on $SrTiO_3$ and has a $T_{c,onset}$ of 88 K and a T_{c0} of 80 K. One 200 nm thick film grown on bare silicon has a $T_{c,onset}$ of 88 K and a T_{c0} of 60 K. This film shows negligible superconductor-substrate interactions according to the RBS measurements.

Introduction

High temperature superconductor thin films with very high critical current densities can be made by several fabrication methods, such as sputtering, laser ablation and evaporation techniques. When the superconductor is crystallized during the deposition lower temperatures can be used compared to post annealing. This lower temperature will result in fewer reactions at the superconductor-substrate interface and in less reactions with artificial barriers. Several succesful attempts to fabricate in-situ superconducting thin films at considerably lower growth temperatures have been reported by other groups using various techniques [1,2,3,4].

The most severe 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 $YBa_2Cu_3O_7$ [5], MBE techniques limit the total pressure at the sources to 10^{-4} mbar, which is not enough. A solution to this problem is using some form of activated oxygen, like ozone, as has been demonstrated by D.D.Berkley et al.[4], or by making a large pressure gradient near the substrates [6,7].

Fabrication equipment

The films are fabricated in a Balzers UHV system (UTS 500) which contains two electron guns (Balzers ESQ 300U) and one effusion cell (Luxel, Radak II). The system is pumped by a turbo molcular pump and a Ti sublimation pump. Base pressure of the system is 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 total pressure in the system is measured with a ionization vacuum gauge which is located near the turbo molecular pump. The flux signals from the mass spectrometer are calibrated with a single quartz crystal monitor which is located next to the substrate holder.

The flux from the e-guns is controlled by adjusting the emission of the gun. To improve the stability of the e-guns the electron beam is swept over the melt by high voltage deflection plates at high frequencies (500 Hz in the x-direction and 4 kHz in the y-direction). This reduces the partial pressure over the melt and results in a very stable beam profile. The electron gun feedback system and its performance have been described elsewhere [8]. The flux from the effusion cell is also controlled by a feedback loop because the barium flux from this particular type of effusion cell turned out to be sensitive to high partial ozone pressures when operated at a constant temperature.

The ozone is fabricated in a "silent" discharge [9]. This ozone generator consists of a stainless steel rod in a glass tube through which oxygen ambient flows. The stainless steel rod is driven by a high voltage source at 500 Hz. Introducing a cooling of the discharge chamber results in an order of magnitude higher ozone yield [10]. The ozone/oxygen mixture that is fabricated is leaked into a glass chamber through a small orifice. This chamber is cooled to 77 Kelvin by liquid nitrogen. When enough mixture is 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 leaked into the growth chamber 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. The estimated pure ozone production is 0.01 mole per hour.

During deposition the substrates are clamped to a stainless steel plate which is radiatively heated from the back. The heater assembly consists of a long tantulum wire which is wrapped around two aluminium oxide rods. The temperature of the substrate holder is measured by a thermocouple inserted in the stainless steel plate.

Fabrication procedure

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 is 0.2 nm/s. Then the substrate holder is heated up to 700 °C and the ozone flow is turned on by heating the still. The maximum ozone pressure that can be used during the evaporation is limited to a value above which the mass spectrometer sensitivity starts to decrease. The 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. The ozone pressure is increased until the total mass flux on the quartz crystal monitor deviates 50% from the initial value. This happens at a pressure of 10^{-5} mbar as measured by the ionization vacuum pressure gauge, which corresponds to an estimated pressure of about 10^{-4} mbar in the upper part of the chamber. Because the ozone inlet tube ends at 4 cm from the substrate position we estimate the partial ozone pressure at the substrate position to be 10^{-3}-10^{-2} mbar. After adjustment of the ozone flow the sample shutter is opened until a film with an estimated thickness of 100 nm is grown. The sample shutter is closed and the evaporation sources are cooled down as fast as possible, while the sample holder is maintained at high temperature until the flux from all the sources has vanished, because the sample shutter also blocks the ozone jet on the substrate. The sample shutter is reopened and the sample holder is allowed to cool down in about half an hour to room temperature. During and after deposition the temperature of the ozone still is held constant, which implies that the ozone flux into the growth chamber is also constant.

Results

This evaporation procedure results in films that are superconducting without any post-annealing procedure. The best film grown so far was deposited on a (001) $SrTiO_3$ substrate and has a superconductive transition with an onset at 88 K and a T_{c0} of 80 K (fig.1). The temperature of the substrate holder of the in-situ grown

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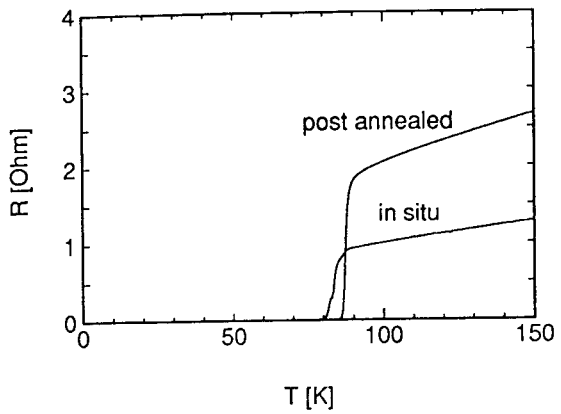

Figure 1. Resistance versus temperature for the in situ sample grown on $SrTiO_3$ and for a post annealed sample on $SrTiO_3$ that was deposited during the same run at room temperature. $T_{c,onset}$ of the in situ grown sample was 88 K and it had a T_{c0} of 80 K.

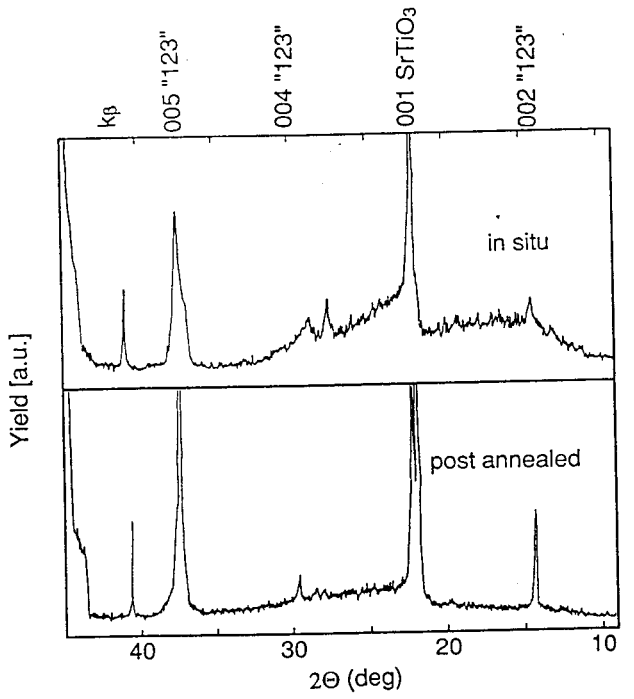

Figure 2. X-ray diffraction scan of the in situ grown sample and the post annealed sample of fig.1. The post annealed sample has much higher and sharper c-axis peaks, indicative of a better developed crystal structure.

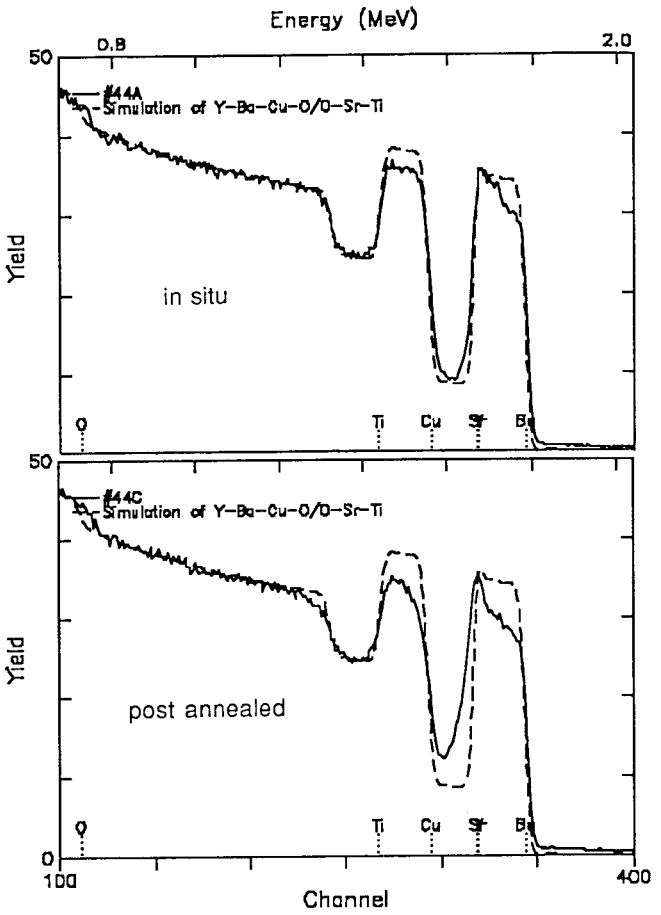

Figure 3. RBS spectra of the in situ grown sample and the post annealed sample of figure 1. Both samples were grown on $SrTiO_3$. The figure also shows a simulation of an ideal 123 layer of the same thickness (dashed curve). The surface energies of the constituent elements are indicated on the lower axis. According to these spectra there is no interdiffusion between the film and the substrate for the in situ grown film.

film during deposition was 700 °C. Measurements with a pyrometer after the production of these films indicated however that the temperature of the substrate itself may be 20-200 °C lower due to the poor thermal contact between the substrate and the sample holder. A film that was grown during the same evaporation run, but at room temperature and which was post annealed at 850 °C in an ambient oxygen atmopshere showed the same onset but a T_{c0} of 85 K (fig.1). From films that are grown in a different evaporation system under similar growth conditions, but in which the actual substrate temperature is known (within 10 °C), it is estimated that the substrate temperature of the in situ sample must have been below 650 °C. Figure 2 shows the X-ray diffraction spectra of the in situ and the post annealed film. Clearly the "123" c-axis peaks are better pronounced in the post annealed film. It is therefore not clear whether the resistive tail is caused by oxygen deficiency in the in situ grown film or a less well developed crystal structure. The c-axis of the in post annealed film is 11.64±0.03 Å, which is about the same as the bulk value of 11.68 Å. The c-axis of the in situ film is however expanded to 11.77±0.03 Å, which is in accordance with data of Matijasevic et al.[7]. Figure 3 shows the RBS spectra of both films. According to these spectra there is no interdiffusion between the film and the substrate for the in situ grown film. The substrate edge of the post anealed film may indicate that this sample has some interdiffusion, but this may also be an indication of a less smooth film. These spectra also show that the compositions of the films deviate from the exact 1-2-3 ratio. We think this is caused by a calibration error due to the difference in the positions of the quartz crystal and the sample holder.

The best film that was deposited on sapphire (012) substrates shows a resistive transition with a $T_{c,onset}$ of 85 K and a T_{c0} of 70 K (fig 4). Post annealed films that grown on sapphire in the same vacuum system without ozone usually show a long resistive tail in the R(T) curve [11]. This film has an extended c-axis of 11.80±0.03 Å. One film deposited on (001) Si has a resistive transition with $T_{c,onset}$ of 88 K and T_{c0} of 60 K (fig 4). The critical current density of this sample as measured by transport measurements is 10^2 A/cm^2 at 4.2 K. This film was deposited in a deposition run during which the pressure had been increased too much which resulted in a average growth rate of 2 nm/s. The X-ray diffraction spectrum of this film, which shows well pronounced "123" c-axis peaks is shown in figure 5. The c-axis of this film is also extended: 11.81±0.05 Å. The RBS spectrum of this film is shown in figure 6.

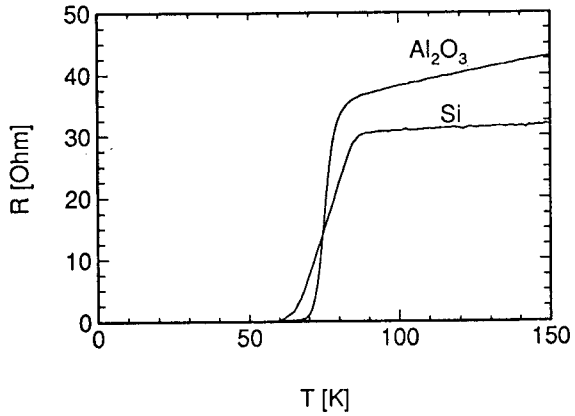

Figure 4. Resistance versus temperature for the in situ samples grown on sapphire and on silicon.

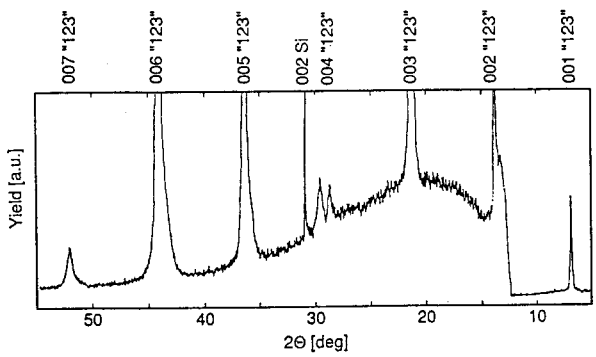

Figure 5. X-ray diffraction scan of the sample grown on silicon of figure 4. This scan shows well developed c-axis peaks.

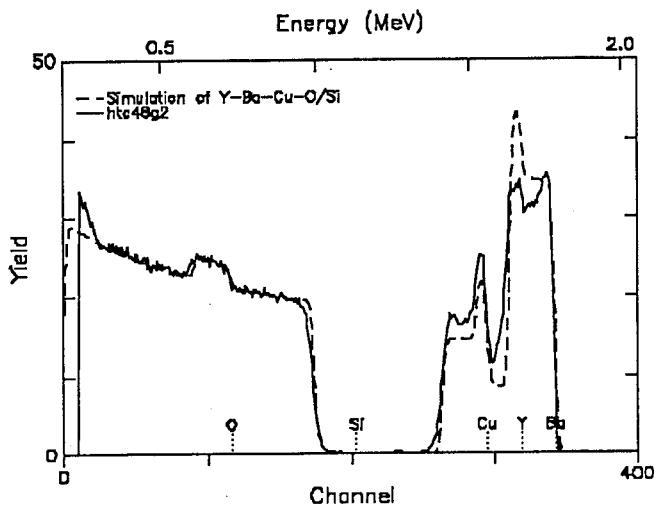

Figure 6. RBS spectrum of the sample grown on silicon of figure 4. The figure also shows a simulation of an ideal 123 layer of the same thickness (dashed curve). The surface energies of the constituent elements are indicated on the lower axis. According to this spectrum hardly any interdiffusion between the silicon substrate and the film can be observed.

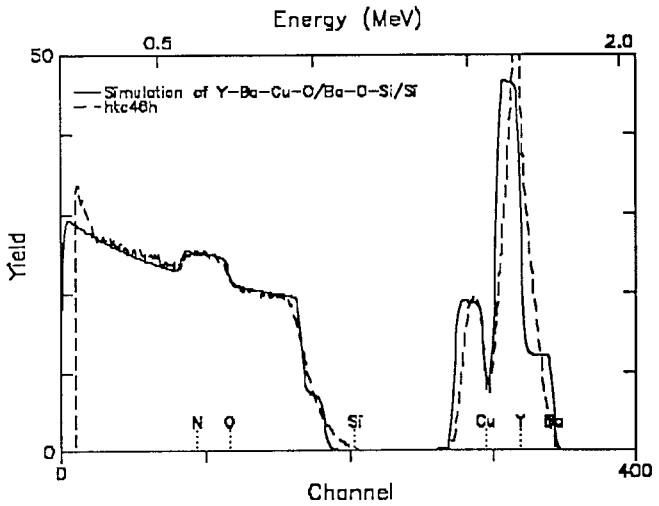

Figure 7. RBS spectrum of a film grown on silicon at a too high temperature (dashed curve). The silicon has diffused through the film all the way up to the surface and barium has diffused into the substrate. The figure also shows a simulation of an ideal 123 layer and a BaSiO layer on a silicon substrate (solid curve). The surface energies of the constituent elements are indicated on the lower axis.

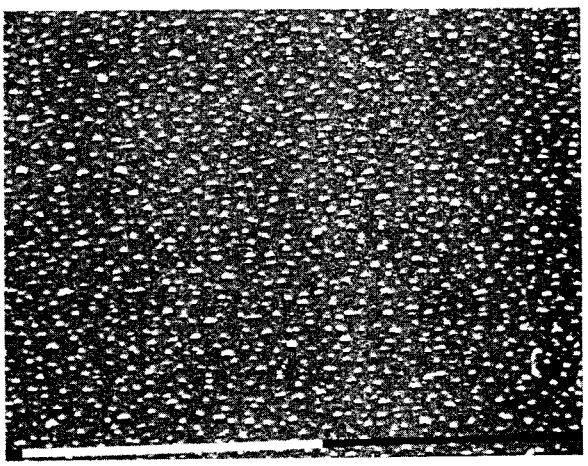

Figure 8. SEM photgraph of the surface of the in situ grown film of figure 4. The white bar is 10 μm long. So far all our in situ grown films show a regular pattern of submicron droplets on the surface, which might be caused by the deviation of stoichiometry of these films.

This spectrum shows no or negligible interdiffusion of the $YBa_2Cu_3O_7$ with the silicon substrate. Films that were deposited on silicon at higher temperatures show silicon interdiffusion up to the surface of the film (fig.7).

Some films on sapphire, $SrTiO_3$ and silicon which were apparently grown at a too low substrate temperature showed traces of a-axis oriented $YBa_2Cu_3O_7$ in the X-ray diffraction spectra. Most of these films show however semiconducting behaviour. Films that were grown at too high temperatures have peaks in the X-ray diffraction indicative of (110) oriented $YBa_4Cu_3O_9$. XPS spectra of these films indicate that the copper in these films was fully oxydized.

A typical SEM photograph of the surface of an in situ grown film (in this case on SrTiO3) is shown in figure 8. This photograph shows that the surface is covered by many submicron size droplets. These may be the result of the small deviations in the stoichiometry of these films.

Summary

Using ozone as an oxygen source it is possible to grow 100 nm thick $YBa_2Cu_3O_7$ 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 give poor results with the post anneal process: on sapphire substrates a T_{c0} of 70 K can be accomplished in 100 nm thick films and on bare silicon superconducting 200 nm thick films can be grown with a $T_{c,onset}$ of 88 K and a T_{c0} of 60 K. According to the RBS measurements the silicon sample has negligible interdiffusion with the substrate. All superconducting samples with a composition close to 123 show an extended c-axis.

Acknowledgements

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References and notes

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