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

H.M.Appelboom, J.P.Adriaanse, H.I.de Groot, G.Rietveld, D.van der Marel and J.E.Mooij.

Faculty of Applied Physics, Delft University of Technology, P.O. Box 5046, 2600 GA Delft, The Netherlands.

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 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.

1. 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 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].

2. 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 preformance have been described elsewhere[6]. 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[7]. 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[8]. 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.

3. 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
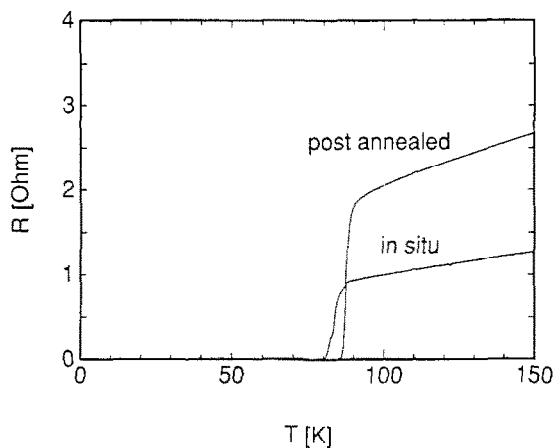
FIGURE 1

Resistance versus temperature for the in situ sample grown on SrTiO3 and for a post annealed sample on SrTiO3 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.
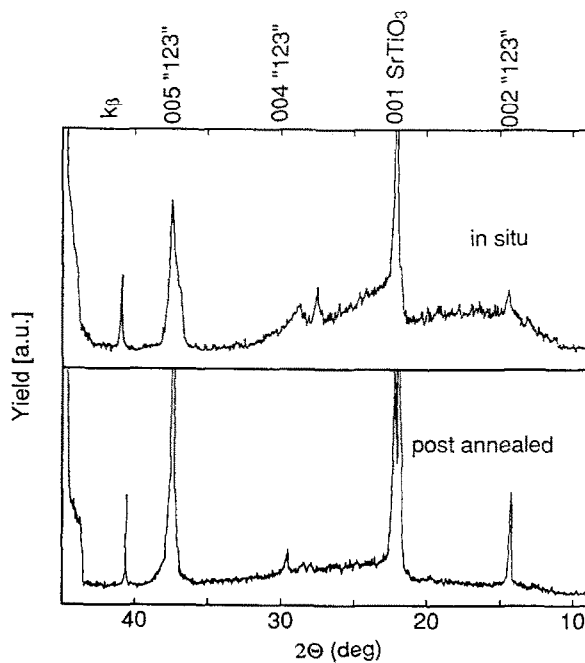

FIGURE 2

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.

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.

4. 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) SrTiO3 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 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 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). Figure 2 shows the X-ray diffraction spectra of both films. 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. 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 aneeled
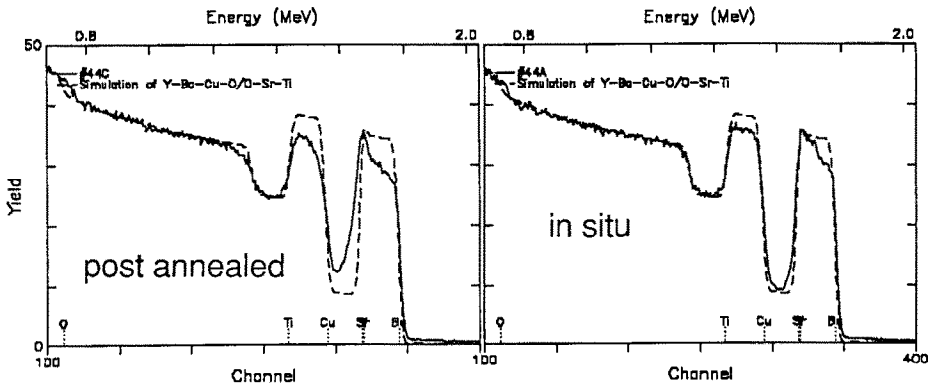

FIGURE 3
RBS spectra of the in situ grown sample and the post annealed sample of figure 1. Both samples were grown on SrTiO3. The figure also shows a simulation of an ideal 123 layer of the same thickness (dashed curve). The surface energies of the constituent elements are indicated on the lower axis. According to these spectra there is no interdiffusion between the film and the substrate for the in situ grown film.

film 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[9]. One film
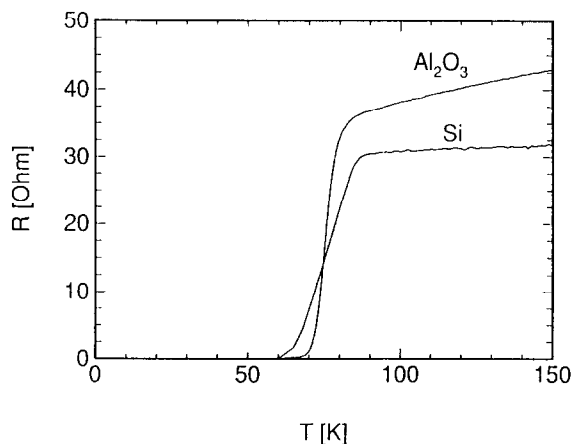

FIGURE 4
Resistance versus temperature for the in situ samples grown on sapphire and on silicon.
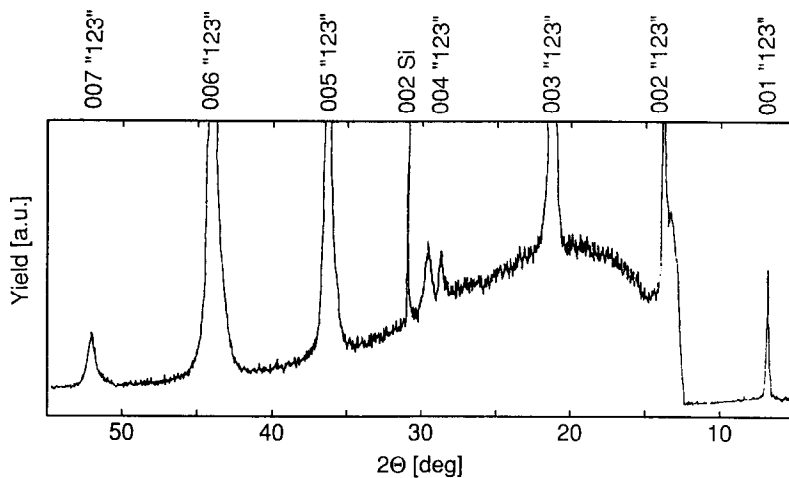

FIGURE 5
X-ray diffraction scan of the sample grown on silicon of figure 4. This scan shows well developed c-axis peaks.

deposited on (001) Si has a resistive transition with $T_{c,onset}$ of 88 K and T_{c0} of 60 K (fig 4). 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 RBS spectrum of this film is shown in figure 6. 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 showed silicon interdiffusion up to the surface of the film.
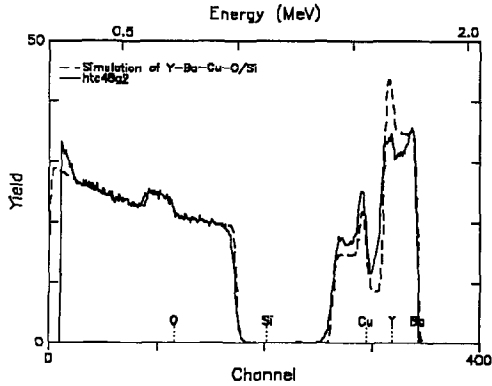

FIGURE 6

RBS spectra 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

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.

A typical SEM photograph of the surface of an in situ grown film (in this case on SrTiO3) is shown in figure 7. 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.

5. CONCLUSIONS

Using ozone as an oxygen source it is possible to grow 100 nm thick YBa$_2$Cu$_3$O$_7$ films under non equilibrium conditions in an MBE system on SrTiO3 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.

REFERENCES AND NOTES

1) R.M.Silver, A.B.Berezin, M.Wendman, and A.L.de Lozanne, Appl.Phys.Lett 52, 2174 (1989).

2) C.B.Eom, J.Z.Sun, K.Yamamoto, A.F.Marshall, K.E.Luther, T.H.Geballe, and S.S.Laderman, Appl. Phys. Lett. 55, 595 (1989).

3) T. Venkatesan, X.D.Wu, B.Dutta, A.Inam, M.S.Hegde, D.M.Hwang, C.C.Chang, L.Nazar, and, B.Wilkens, Appl. Phys. Lett. 54, 581 (1989).

4) D.D.Berkley, B.R.Johnson, N.Anand, K.M.Beauchamp, L.E.Conroy, A.M.Goldman, J.Maps, K.Mauersberger, M.L.Mecartney, J.Morton, M.Tuominen, and Y-J.Zhang, Appl. Phys. Lett. 53, 1973 (1988).

5) R.Bormann and J.Nölting, Appl. Phys. Lett. 54, 2148 (1989).

6) R.H.M.van de Leur, A.J.G.Schellingerhout, J.E.Mooij, and F.Tuinstra, Appl. Phys. Lett. 52, 1005 (1988).

7) M.Horváth, L.Bilitzky, and L.Hüttner, Ozone (Elsevier Science Publishers, Amsterdam , 1985).

8) This increase was observed with the mass spectrometer in the vacuum chamber. Though absolute measurements of the purity of the ozone can not be performed by a mass spectrometer in the growth chamber because of the recombination of the ozone on the chamber walls, a relative increase can readily be observed. The maximum 48 peak we have observed so far was 10% relative to the 32 peak.

9) A.J.G.Schellingerhout, R.H.M.van de Leur, D.Schalkoord, D.van der Marel, and J.E.Mooij, Z.Phys.B 71, 1 (1988).