PHYSICAL PROPERTIES AND INTERFACE STUDIES OF $\text{YBa}_2\text{Cu}_3\text{O}_7$ THIN FILMS DEPOSITED BY LASER ABLATION ON Si (111) WITH BUFFER LAYER

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The physical properties of laser-deposited YBaCuO on Si using a single buffer layer of ZrO_2 and a double layer of NiSi_2 and ZrO_2 have been studied. The influence of the deposition temperature has been investigated. Interface studies were performed by RBS and SAM. SEM pictures, resistivity and critical current measurements complete this study. The granularity of the films is very important for the diffusion of the Si.

1. INTRODUCTION

Laser ablation is a simple technique for the deposition of high quality high T_c superconducting films. Especially, on substrates which are known to be sensitive to diffusion, the laser-induced evaporation leads to promising results. In this respect it is of interest to study the possibilities to deposit high quality YBaCuO on silicon with this technique¹. For that purpose we have used two different types of substrates; Si(111) with a single buffer layer of ZrO_2 and Si + ZrO_2 with an extra diffusion barrier of NiSi_2 .

In this paper, we present the influence of the deposition process parameters on the film properties. Special attention is paid to the interdiffusion between the different (buffer) layers. We deposited 250 nm YBaCuO layers with T_{zero} up to 86 K, with a critical current density of $2 \times 10^4 \text{ A/cm}^2$ at 77 K. The interdiffusion has been investigated by means of Rutherford Backscattering Spectroscopy (RBS) and Scanning Auger Measurements (SAM). The grain size of the deposited layers are obtained by Scanning Electron Microscopy.

2. EXPERIMENTAL DETAILS

2.1. Equipment

The films were deposited with an excimer laser (XeCl , 308 nm, 2 Hz, 80 mJ). The substrates could be heated up to 850 °C by a thermo coax. The spot size of the laser beam was $1.5 \times 3 \text{ mm}^2$, with an energy density of 2 J/cm^2 . The oxygen pressure was 30 Pa and the target-to-substrate distance was about 30 mm. The films with typical dimensions of $10 \times 10 \text{ mm}^2$ were, after deposition, cooled

down to room temperature at 1 bar of oxygen in 1.5 hr.

Resistivity measurements with a current density of 1 A/cm^2 were carried out on a bridge of $10 \times 100 \text{ } \mu\text{m}^2$. The bridges were structured by the excimer laser using a contact mask. In some cases wet chemical etching with standard photo resist and diluted H_3PO_4 (1:150) was used.

The RBS spectra were analyzed using RUMP computer code. The Auger spectra were taken with the Perkin-Elmer PHI-600 Multiprobe. Detailed analysis was done by line profiles at the crater edge², see fig. 1. X-ray diffraction patterns have been obtained by a Debye-Scherrer diffractometer with a $\text{Cu K}\alpha$ source. SEM pictures were taken with a Philips PSEM 500.

FIGURE 1

Schematic drawing of the crater edge profiling. At the edge, the interfaces are stretched and can be studied in detail. The angle between the normal of the sample surface and the crater edge is 0.04 degree.

2.2. Substrates

The substrates were prepared using the following route:

$\text{Si}(111) + \text{ZrO}_2$

By means of dc sputtering a layer of 200 nm was deposited on $\text{Si}(111)$ from a polycrystalline ZrO_2 target. Before the deposition of YBaCuO , the substrate was heated up to 600°C in a pressure of 30 Pa oxygen, during 30 min. The ZrO_2 buffer layer is polycrystalline.

Si(111)+NiSi₂+ZrO₂

The layer was prepared by oxidizing a 53 nm thick amorphous layer of Ni and Zr in a ratio of 23:77. The layer was deposited on Si(111) by electron gun evaporation and annealed for 2 hours at 500 °C in 1×10^{-2} Pa oxygen. The oxygen reacts with the zirconium and forms a 120 nm thick polycrystalline ZrO₂ layer. The nickel reacts with the silicon, forming an 40 nm epitaxial layer of NiSi₂. More details about this fabrication technique can be found in the paper of de Reus et al.³

3. RESULTS

3.1 Resistivity and X-ray diffraction measurements

The properties of the YBaCuO layer are very dependent on the substrate temperature during deposition. In fig. 2 the onset temperature T_{ons} and the T_{zero} are given for a number of films. The films were prepared under same process conditions, only the substrate temperature was changed. The YBaCuO layer has a typical thickness of 250 nm. From the figure three regimes can be distinguished: the low temperature side $T_{\text{sub}} \leq 700$ °C, the intermediate region 700 °C $\leq T_{\text{sub}} \leq 730$ °C, and the high temperature side $T_{\text{sub}} \geq 730$ °C.

FIGURE 2

T_{onset} and T_{zero} as a function of the substrate temperature during deposition for two different substrates: Si(ZrO₂) [box] and Si(NiSi₂)ZrO₂ [triangles]

The best results were obtained in the intermediate regime. T_{ons} is about 91 K and T_{zero} varies from 80-86 K. The T_{zero} of the films deposited on $Si(NiSi_2)ZrO_2$ is 1-2 degrees higher than the corresponding $Si(ZrO_2)$ values and there is no difference in T_{ons} . The optimum deposition temperature is in the case of $Si(NiSi_2)ZrO_2$ about 10 degrees higher, but still low compared to the $YBaCuO$ films deposited on monocrystals⁴. The X-ray diffraction patterns of all the films prepared in this regime show only c-axis orientations. No other reflections have been observed. The oxygen stoichiometry in the films as calculated from the 2θ -values is between 6.9 and 7.

At low deposition temperatures the superconducting properties become worse. The T_{zero} decreases rapidly with decreasing T_{sub} . X-ray diffraction analysis still shows c-axis orientations, although the peaks become somewhat broader and other reflections like (110/103) occur. The intensities of the (001) reflections are a factor 100 lower than the values obtained from films that were prepared in the intermediate regime. This reduction can not be explained by the broadening or other reflections, so the film becomes amorphous. The calculated oxygen content decreases from 6.9 to 6.7, which explains the reduction of T_{ons} . These effects seem to be substrate independent.

At high deposition temperatures there is a large influence of the substrate temperature on T_{zero} . X-ray diffraction patterns show only c-axis orientations and the intensities are of the same order of magnitude as the values observed for the films deposited in the intermediate regime. The calculated oxygen stoichiometry is almost 7. Although these results do suggest good quality films, the superconducting properties deteriorate. To explain this behaviour we performed surface and interface studies on the films. The differences between the used substrate types look in first instance negligible, but large differences have been found in the resistivity and critical currents of the deposited layers. The films deposited on $Si(NiSi_2)ZrO_2$ have critical current values, that are 10 times larger than the values for the films on $Si(ZrO_2)$. The best values obtained are at 77 K for $Si(NiSi_2)ZrO_2$ $J_c \approx 2 \times 10^4$ A/cm² and for $Si(ZrO_2)$ $J_c \approx 3 \times 10^3$ A/cm². The lowest residual resistivity values at $T = 0$ K, obtained by extrapolation, are 40 $\mu\Omega$ cm for $Si(NiSi_2)ZrO_2$ and 120 $\mu\Omega$ cm in the case of $Si(ZrO_2)$. At high deposition temperature these values increase to 2000 $\mu\Omega$ cm or even more.

3.2 Interdiffusion studies

The Auger sputter profiles of an $YBaCuO$ layer on $Si(ZrO_2)$ and $Si(NiSi_2)ZrO_2$ are given in fig. 3 and, respectively, fig. 4. The spectra were taken after a 100 nm thick layer of $YBaCuO$ was sputtered away. All the interfaces ($YBaCuO/ZrO_2 - ZrO_2/Si$) and ($YBaCuO/ZrO_2 - ZrO_2/NiSi_2 - NiSi_2/Si$) are sharp

and almost no reactions could be observed. Within the detection limit of the apparatus we have not seen Si diffusion through the ZrO_2 bufferlayer, indicating that this layer is sufficient to prevent the YBaCuO layer against diffusion of silicon.

FIGURE 3

Auger sputter profile of an YBaCuO film deposited on Si with a 250 nm ZrO_2 buffer layer deposited at a substrate temperature of 710°C .

FIGURE 4

Auger sputter profile of an YBaCuO film deposited on Si with a 120 nm ZrO_2 buffer layer and a 40 nm epitaxial NiSi_2 layer in between. Substrate temperature was 720°C . Before this spectrum was taken, a 100 nm thick layer had been sputtered away.

FIGURE 5

RBS spectrum of the YBaCuO layer on Si(NiSi₂)ZrO₂. Substrate temperature is 720 °C. Scattering angle is 170 degree. Sample tilt is 7 deg. The surface channels are indicated with the arrows. The dash curve represent the simulated RBS values.

In fig.5 the RBS spectrum is given of an YBaCuO layer on Si(NiSi₂)ZrO₂. From these data again the clear separation of the different layers can be observed. The broadening of the Zr peak near channel 250 and the trailing edge of the Ba peak near channel 275 indicate that some BaZrO₃ has formed. The Ni peak at channel 200 is slightly asymmetric indicating some Ni diffusion into the Si substrate. Also some Si diffusion has taken place into the epitaxial NiSi₂ layer. Although we could not observe any Si diffusion through the ZrO₂ layer into the YBaCuO, we clearly see effects of the deposition temperatures on the superconducting properties. These effects are also substrate dependent. For that reason we looked to the granularity of the films. SEM pictures showed that the YBaCuO layers consist of grains. These grains are imposed by the polycrystalline ZrO₂ layer, as proved by observations of cleaved surfaces. In the case of Si(ZrO₂) the ZrO₂ grains are typically 0.1 μm and for Si(NiSi₂)ZrO₂ these grains are in the order of 1 μm. Along these grain boundaries elements like Si can diffuse into the YBaCuO layer, suppressing the

superconducting properties. This diffusion increases with increasing temperature. The diffusion along grain boundaries can not be observed by RBS or SAM, because the grain boundary volume is very small compared to the total detected volume.

To investigate the diffusion in more detail crater edge line profiling has been performed. In fig. 6 a line profile is given for an YBaCuO layer on Si(NiSi₂)ZrO₂. The data were obtained by scanning along the curve 1 (see fig.1). From calculations we found that the angle between the normals of the sample surface and the crater edge is about 0.04 degree. With this method we were able to investigate the interfaces and grain boundaries in more detail. From the data of fig.6 we see a Cu deficiency near the ZrO₂ layer and a Cu-

FIGURE 6

Crater edge lineprofile of the YBaCuO layer on Si(NiSi₂)ZrO₂. Substrate temperature is 720 °C and deposition time is 35 min. Notice the Cu diffusion through the ZrO₂ layer.

rich region between the ZrO₂ and the NiSi₂ layers. The Cu transport only occurs at high deposition temperature and with deposition times longer than 10 min. For YBaCuO films deposited with a laser pulse frequency of 5 Hz, within 7 min. no Cu diffusion occurs at all. The data of fig.6 are not decisive about the diffusion of the Si along the grain boundaries. Assuming that the Cu deficiency can only be explained by diffusion along the grains one should expect that the same happens with the Si. This Si diffusion is consistent with the deteriorated superconducting properties obtained at high deposition temperatures.

4. CONCLUSIONS

With the laser ablation technique it is possible to deposit high quality thin YBaCuO films on silicon substrates with a buffer layer. Zero temperatures up to 86 K have been achieved, with critical current densities up to 4×10^4 A/cm² at 77 K. Interdiffusion studies like Auger sputter profiles and RBS show that monocrystalline ZrO₂ is sufficient to prevent the diffusion of Si. At high deposition temperatures the films are c-axis oriented with high oxygen content, but the films consist of grains. The Si diffusion takes place along the grain boundaries. This explains the high T_{0ns} and broad transition of these films. The films deposited on Si(NiSi₂)ZrO₂ show better results than the films deposited on Si(ZrO₂) substrates. The deposition temperature is less critical, the zero temperature of the YBaCuO films is slightly higher (in general 1-2 degrees), the resistivity at room temperature is smaller, and the critical current is higher by a factor of ten. The results can be explained by the grain size of the ZrO₂ layer, which is in the case of Si(NiSi₂)ZrO₂ ten times larger than the grains of the ZrO₂ of the Si(ZrO₂) substrate. The improvement yet to be made is the preparation of monocrystalline ZrO₂ buffer layer on the epitaxial NiSi₂.

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