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Micro-PIXE and channeling PIXE analysis of Ag-doped $YBa_2Cu_3O_{7-\delta}$ thin films

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Abstract

Nuclear Microscopy, utilizing a 2 MeV He^+ beam for channeling Rutherford Backscattering (RBS) and PIXE analysis, was used to characterise Ag-doped $YBa_2Cu_3O_{7-\delta}$ thin films and measure the lateral distribution of the Ag. The samples were prepared by in situ two-beam pulsed laser deposition in order to investigate the effects of such dopings on critical current densities [1,2]. Films deposited at temperatures above 650°C form needle-like surface structures with a length of up to 100 μm; these tend to align with in-plane *a–b* axis. Results for a sample prepared at a substrate temperature of 730°C and a maximum Ag concentration of 5 at.% are discussed. The needle-like structures were found to be rich in Ag and Cu, and the $YBa_2Cu_3O_{7-\delta}$ film contained 0.02 at.% Ag. Broad beam PIXE-channeling results indicate that 19% of the Ag is substitutional.

1. Introduction

$YBa_2Cu_3O_{7-\delta}$ (YBCO) is an important material in the development of high-temperature superconducting thin film devices. The reduction of weak links and the improvement of long-term chemical stability are still challenging issues, and advanced deposition techniques and the introduction of doping materials such as Ag have been shown to improve these film properties. A new approach that allows full control over a wide range of parameters is the Dual Beam Pulsed Laser Deposition (DBPLD) [1,2]. The process is briefly described, all samples discussed here were deposited by this technique.

Ion beam analysis of YBCO samples has mostly focussed on Rutherford Backscattering (RBS) and RBS channeling studies in recent years [3–5], only a few groups have used a combination of PIXE and RBS [6,7]. Li et al. [5] have used RBS channeling to investigate the lattice position of Ag in laterally homogenous Ag-doped YBCO samples deposited by laser ablation of a premixed target. These workers found that two thirds of the retained Ag occupied substitutional sites. Here we report first results from our use of micro-PIXE and PIXE channeling to investigate lateral

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structures and crystalinity of Ag-doped YBCO thin films.

2. Sample preparation

The YBCO sample discussed here was produced by Dual Beam Pulsed Laser Deposition (DBPLD), a technique that allows the in situ doping of Ag in the YBCO film on $SrTiO_3$ (100) substrates ($5\times10\times0.1$ mm^3) with a wide range of well-controlled process parameters. The system used has been described in detail elsewhere [1,2] and only a brief description is given here. A KrF laser ($\lambda = 248$ nm) is operated at 5 Hz with 300 mJ/pulse during the deposition. A splitting lens is used to divide the laser beam in two branches. One of them is focussed onto a rotating YBCO target, while the other is focussed on a small Ag target mounted at the center of the YBCO target, so that a small separation (2 mm) of the beam spots is achieved. Both beams had energies of 150 mJ/pulse, and the laser fluences on the YBCO and the Ag were 2.0 and 1.5 mJ/cm^2, respectively. The substrate was mounted on a heater 5 cm away from the target, which maintained the substrate temperature at 730°C. The samples were grown for 25 min under an oxygen pressure of 0.20 mbar. The superconducting transition temperature T_C and the critical current density J_C were derived from inductive measurements and found to be 88 K and 2×10^6 A/cm^2. Fig. 1 shows a secondary electron microscope (SEM) image of the sample. Bar-like structures of 1–2 μm width and up to 150 μm length are observed, mostly oriented along the in-plane *a*/*b* axes of the YBCO film, with a height of around 100 nm. A second set of much shorter bars is also seen, at 45° to the large bars and assumed to be associated with grain boundaries of twined crystals.

3. Experimental

The measurements were carried out using the nuclear microscope facility at the National University of Singapore [8]. For the broad beam channeling measurements an He^+ beam of typically 2 nA was used. RBS spectra were recorded with a 50 mm^2 PIPS detector of 14 keV resolution at 160° scattering angle. PIXE spectra were recorded with a 62 mm^2 Si(Li) detector at a distance of 20 mm from the target. The targets were mounted on a eucentric goniometer that has a 14 mm translational range for both the *x* and the *y* direction and allows rotations up to 20° around both the *x* and the *y* axis with a resolution of 0.1 mrad. The beam spot size was typically 300 μm. The micro-PIXE data were taken in the same geometry, but the focussing of the beam to a spot size close to 1 μ necessitated a reduction in beam current to typically 100 pA. The use of a proton beam for PIXE was initially considered, but test measurements showed that the background produced by the intense Sr-L X-rays from the substrate, as well as Secondary Electron Bremsstrahlung (SEB), effectively masked the relatively weak Ag-L peaks in the spectra.

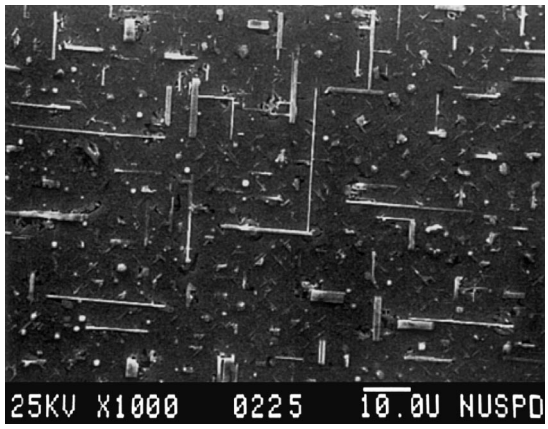

Fig. 1. SEM image of an Ag-doped YBCO sample.

4. Results and discussion

4.1. Channeling measurements

Fig. 2 shows the RBS spectrum of an undoped YBCO specimen on $SrTiO_3$, together with a RUMP simulation from which the indicated thickness and composition were taken. The contributions from the individual elements are also

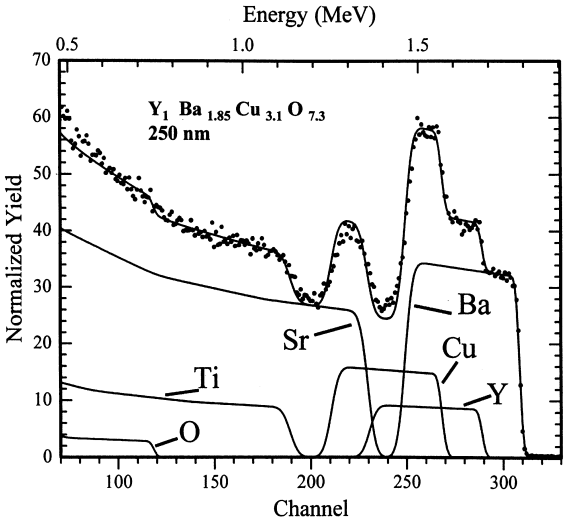

Fig. 2. RBS spectrum of an undoped YBCO/$SrTiO_3$ sample, the contributions from the individual elements are indicated.

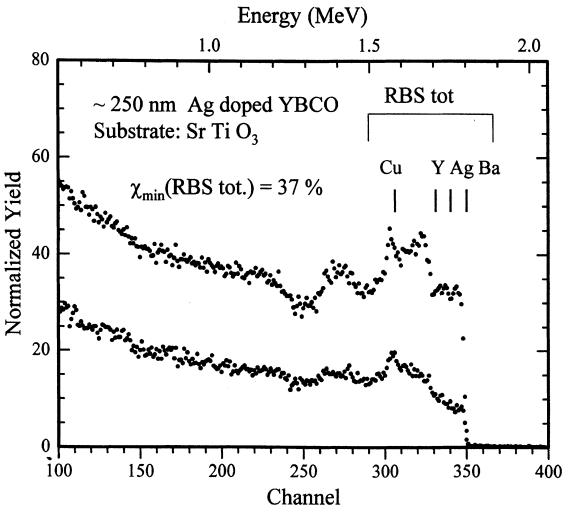

Fig. 3. Random and channeled RBS spectra from an Ag-doped YBCO sample. The surface energies of the metals in the film are indicated.

plotted. In the analysis the stopping power data from Ziegler et al. [9] with the corrections given by Børgesen et al. [3] and Quan et al. [4] were used. Both the stoichiometry and the thickness are close to the values expected from the composition of the (commercial) YBCO target and Atomic Force Microscopy (AFM) thickness measurements. It has been reported [7], and was confirmed by our measurements, that good quality YBCO/$SrTiO_3$ samples display typical backscattering χ_{min} values of 5% for a 2MeV alpha beam along the (100) direction, with similar PIXE χ_{min} values for Y, Ba and Cu as long as the target is thin and the poor depth resolution of PIXE does not affect the PIXE channeling results.

Fig. 3 shows the random and the RBS channeled spectra of the Ag-doped sampled. No attempt was made to fit the random RBS spectrum, because from Fig. 1 it is clear that no laterally homogenous layer structure exists. However from the indicated region a 'total' RBS χ_{min} value was derived. Fig. 4 shows the PIXE spectra taken simultaneously with the data from Fig. 3. It is clearly visible that all X-ray lines from the thin film are reduced except for the Ag-L lines. Table 1 gives the χ_{min} values for the Y, Ba, Cu and Ag X-ray lines as well as the 'total' RBS χ_{min} as indicated in Fig. 3, and the statistical uncertainties. The χ_{min} values for Y, Ba, Cu and the 'total' RBS χ_{min} are quite consistent (37–47%), but the Ag value is clearly higher (81%). Even though the lateral nonuniformity of the sample does not allow to determine the crystal quality in the film regions free of the bar-like structures, the results suggests that 19% of the Ag occupies substitutional sites. It

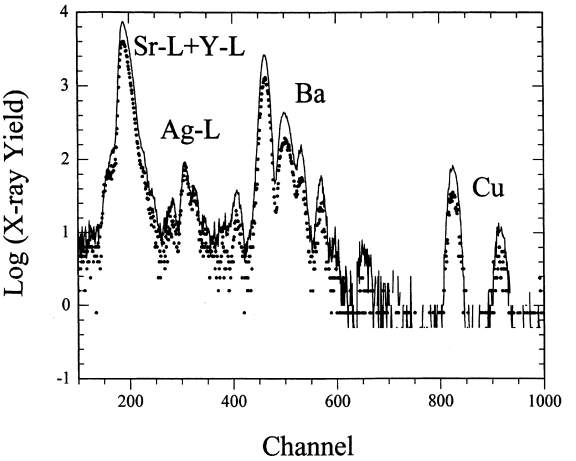

Fig. 4. PIXE spectra taken simultaneously with the RBS data from Fig. 3. The fully drawn line indicates the random spectrum, and the dotted line shows the aligned spectrum.

Table 1
χ_{min} values for the PIXE channeling data in Fig. 4 and the 'RBS total' region indicated in Fig. 3

Signal	χ_{min} (%)
Y Kα	38.8±9.2
Ba Lα	46.6±0.3
Cu Kα	42.0±1.7
RBS (tot)	36.7±0.3
Ag Lα	80.5±2.3

should be noted that PIXE channeling results in well-resolved signals for the different elements present, as opposed to the RBS data where severe elemental signal overlap is present.

5. Microbeam measurements

Fig. 5 shows elemental maps for Ag and Cu measured on the Ag-doped sample. The Ag distribution shows vertical bar-like structures, and in the top right region there is an even more diffuse horizontal bar barely discernible. This fuzziness is attributed to a slight target movement during the 4 h run that was necessary to generate reasonable statistics.

The Cu maps show that the bar-like structures are also rich in Cu. The length and width of the structures are consistent with the SEM data (see Fig. 1). The list-mode data acquisition allows to generate PIXE spectra from selected regions of an elemental map. From such an analysis of 'bar-covered' and 'bar-free' regions it was found that Ag X-ray intensity stemming from the 'bar-covered' regions is 5.8 times higher than from the YBCO film. If matrix effects are neglected (passing through a 250 nm YBCO thin film, a 2 MeV alpha beam looses about 5% of its energy, and the absorption of an Ag Lα X-ray is about 13%) one can estimate that in the 'bar-free' regions about 0.02 at.% Ag are retained, where the Ag-L X-ray production cross section from [10] was used. A similar low Ag content was reported for Ag-doped YBCO thin films deposited by laser ablation of premixed Ag-doped YBCO targets [5]. Focussed beam channeling measurements on samples with a lower number of bar-structures are currently under way to investigate the lattice position of the Ag retained in the YBCO film.

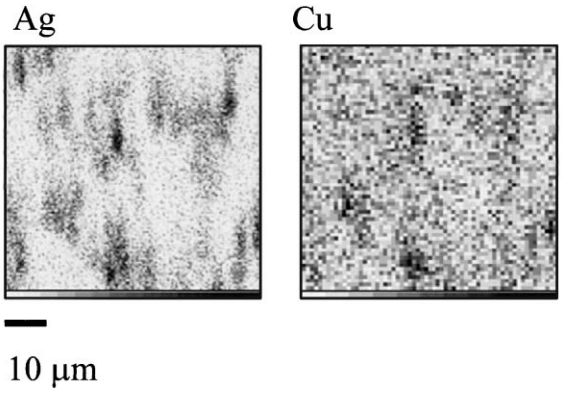

Fig. 5. PIXE elemental maps for Ag and Cu taken from an Ag-doped YBCO sample.

6. Conclusion

RBS Channeling and PIXE analysis combined with micro-PIXE, utilizing a 2 MeV He^+beam were used to characterise YBCO thin films and measure the lateral distribution of the Ag. Results for a sample prepared at substrate temperatures of 730°C and a maximum Ag concentration of 5 at.% are reported. Needle-like structures seen in SEM images were found to be rich in Ag, whilst the YBCO film retained 0.02 at.% Ag. Broad-beam PIXE-channeling results indicate that 19% of the Ag is substitutional. The combination of the techniques used is shown to be a powerful tool for the analysis of the structure of doped YBCO samples.

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