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SIMS study of low energy $^{2}H^{+}$ ion-implanted $YBa_2Cu_3O_{7-\delta}$ thin films

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Abstract

Thin films of $YBa_2Cu_3O_{7-\delta}$ (YBCO) deposited by sputtering on $LaAlO_3$ and $SrTiO_3$ substrates have been implanted with 50 keV $^{2}H^{+}$ (deuterium) ions at doses of 1×10^{12} cm^{-2} and 1×10^{16} cm^{-2}. Depth profiles of the high dose implants obtained by secondary ion mass spectrometry (SIMS) were compared with Monte Carlo simulations (TRIM90) and showed evidence of channelling in the substrates. The superconducting transition temperature, T_c, measured by a.c. susceptibility (ACS) disappeared for the high dose implanted samples and X-ray diffractometry (XRD) showed that the YBCO c-axis length had increased, indicating a loss in oxygen content. After annealing the implanted samples with a rapid thermal annealer in O_2 and N_2 atmospheres, SIMS profiles indicated the fast diffusion of deuterium out of the films.

1. Introduction

Ion implantation can enhance the critical current, J_c, of thin films of high temperature superconductors (HTS) [1, 2] and therefore holds considerable technological and scientific interest . The enhancement arises from the introduction of damage which forms flux-pinning centres. However, excessive damage from a high implantation dose causes the superconducting properties of the implanted samples to deteriorate. This may be due to the formation of weak links in the sample or, in the case of YBCO, the reduction of the oxygen content [3].

The $^{2}H^{+}$ ion is attractive as an implantation species because its low mass allows implantation deep into a thin film, or even through the film, with minimal sputtering of the film surface, when using modest energies of up to 200 keV. Furthermore, deuterium can be detected readily by SIMS as a tracer when carrying out depth profile studies to determine the implantation range.

Rapid thermal annealing (RTA) is used extensively in the semiconductor industry to anneal out the damage caused by ion implantation and to activate the implanted dopant. The fast changes in temperature achieved by RTA may help to minimise or prevent interdiffusion between the YBCO films and the substrates [4, 5]. This becomes especially important if Si substrates are used with the eventual aim of producing HTS-semiconductor hybrid devices [5, 6]. However, we were primarily interested in whether the short annealing times with RTA would be sufficient to restore the T_c of samples implanted with a high dose of $^{2}H^{+}$ ions. It was also of interest to study the SIMS depth profile of the deuterium implant following the anneal and to determine whether annealing in O_2 and N_2 atmospheres would produce significant differences.

2. Experimental Procedure

YBCO films with thicknesses in the range of 100 ~ 400 nm, which had been deposited on $SrTiO_3$ (CAM4) and $LaAlO_3$ (NPL1b, NPL2b) by sputtering, were initially characterised by a.c. susceptibility (ACS), X-ray diffractometry (XRD), and vibrating sample magnetometry (VSM), respectively for values of T_c, c-axis length, and J_c. The ACS apparatus, which was operated at about 1 MHz, is described elsewhere [7]. The XRD data were obtained with a Cu K_α beam on a Philips PW1730, and the VSM measurements were carried out with an Oxford Instruments 3001.

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The films were sub-divided and implanted with $^2H^+$ ions using a Wickham 200 keV Ion Implanter. Implantation doses of 1×10^{12} cm^{-2} (low dose) and 1×10^{16} cm^{-2} (high dose) at 50 keV were used at normal incidence to the samples. The implanted films were then characterised again using the above techniques.

In order to check the ion implantation range, pieces cleaved from the samples with the higher dose implants were profiled with an Atomika 6500 SIMS, using a 40 nA, 10 keV Cs^+ beam scanning over an area of about 300 μm x 300 μm. A 1 ~ 2 keV electron beam was simultaneously scanned over the same region to provide charge compensation, since the substrates are insulators. The analyses recorded the intensities of negative ions sputtered from the samples. The depth of each crater was measured after a SIMS session with a Talystep stylus profile-meter.

The remaining pieces of the implanted films were sub-divided again and annealed in an RTA in O_2 and N_2 atmospheres at 800 °C for 20 s with a pressure of 1 atmosphere. The samples were characterised for a third time by ACS, XRD, and VSM, and finally SIMS was used to study the deuterium depth profile of the annealed samples.

3. Results

The VSM results showed that the ion implantation caused the length scales of the screening currents to decrease in all cases. This indicated the production of weak links and the probable degradation of transport current characteristics, despite the apparent enhancement of J_c as calculated from the magnetisation data. The J_c results and VSM measurements are reported and discussed in greater detail elsewhere [8].

Films with initially low T_c values of about 80 K, such as NPL1b and CAM4, showed increases in T_c of about 1 ~ 3 K, following the low dose $^2H^+$ implant. However, for NPL2b, which had an initial T_c of 92 K, there was no change in T_c after the low dose implantation. T_c could not be detected for pieces of NPL1b and CAM4 after high dose implants, but NPL2b retained a T_c value of about 70 K, although the inductive transition width had broadened to about 20 K from an initial value of about 0.5 K.

The superconductive transition disappeared for all the films annealed in N_2. On the other hand, after the O_2 anneal a T_c value of 39 K was detected for the high dose implanted piece of NPL1b, signalling the return of superconductivity, though for the low dose implanted piece the T_c dropped to 79 K from 86 K. For both the high and low dose implanted samples of CAM4, T_c could not be detected after the O_2 anneal.

Table 1 shows that the c-axis length of the NPL1b YBCO film, as determined from room temperature XRD data, increased following the high dose $^2H^+$ implant from 11.69 Å to 11.84 Å, which corresponds to the oxygen content of $YBa_2Cu_3O_{7-\delta}$ decreasing from about 6.8 to 6.0 [9]. After the O_2 anneal the oxygen content recovered partially to about 6.47. For the sample annealed in N_2, the c-axis, not surprisingly, did not change significantly from the as-implanted sample.

The c-axis length of the NPL2b film likewise showed an increase following the high dose implant. However, for the low dose implant the c-axis length appeared to decrease slightly.

Table 1. c-axis length of implanted YBCO films

Sample	State	c-axis (Å)	7-δ	T_c (K)
NPL1b	unimplanted	11.69	6.8	83
(YBCO on $LaAlO_3$)	$^2H^+$ implant: 50 keV, 1×10^{16}cm^{-2}	11.85	6.0	-
.....	$^2H^+$ implant: 50 keV, 1×10^{16}cm^{-2} RTA: 800°C, 20s, O_2	11.74	6.47	39
.....	$^2H^+$ implant: 50 keV, 1×10^{16}cm^{-2} RTA: 800°C, 20s, N_2	11.84	6.0	-
NPL2b	unimplanted	11.68	6.9	92
(YBCO on $LaAlO_3$)	$^2H^+$ implant: 50 keV, 1×10^{16}cm^{-2}	11.706	6.7	70
.....	$^2H^+$ implant: 50 keV, 1×10^{12}cm^{-2}	11.66	7.0	92

The SIMS depth profiles (fig. 1 ~ 4) of the high dose implanted samples clearly show the presence of the deuterium implant. Compared to the TRIM90 [10] simulation for a 50 keV $^2H^+$ implant, the actual implants appear to have gone deeper into the samples. The TRIM90 profile is plotted in arbitrary units normalised to the deuterium signal in the SIMS data which have not been corrected for sputter rates differences between the films and substrates. The SIMS analyses on the low dose implanted samples did not detect the deuterium implant, but this was as expected because the signal would have been about four magnitudes smaller than the level detected for the high dose implants.

In the depth profile of the as-implanted sample of NPL1b (fig. 1), the YBCO film is represented by the

$^{63}Cu^-$ signal and the $LaAlO_3$ substrate is shown by the $^{27}Al^-$ signal. The steady levels of the $^{16}O^-$ and $^{27}Al^-$ signals after the sputter crater broke through the film into the substrate indicate that good charge compensation conditions were being maintained. The film thickness varied from about 350 nm to about 400 nm across the sample as determined by cross-sectional transmission electron microscopy (TEM). The twinned nature of the substrate made it difficult to obtain accurate measurements with the Talystep.

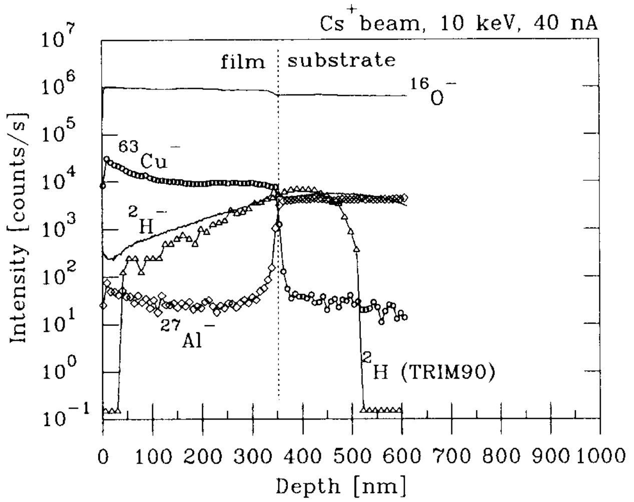

Figure 1. SIMS depth profile of NPL1b sample implanted with a 1 x $10^{16}cm^{-2}$ dose of 50 keV $^{2}H^+$ ions.

The depth profile of the as-implanted sample of CAM4 (fig. 2) shows that the deuterium implant is deeper than that for NPL1b. The YBCO film on CAM4 was about 130 nm thick according to Talystep measurements.

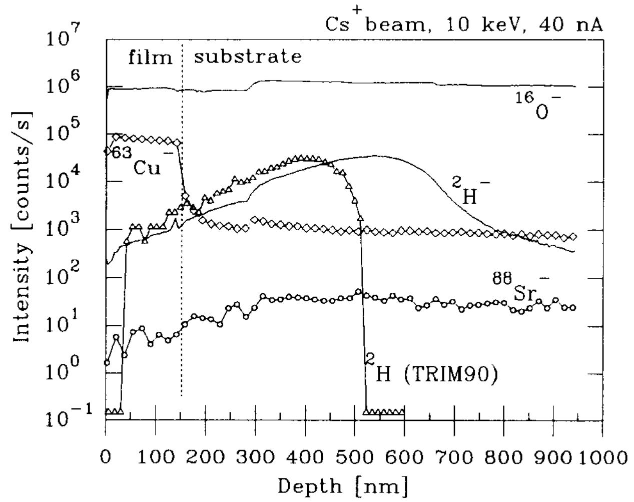

Figure 2. SIMS depth profile of CAM4 sample implanted with a 1 x $10^{16}cm^{-2}$ dose of 50 keV $^{2}H^+$ ions.

The SIMS depth profiles for the high dose implanted NPL1b films annealed by RTA (fig. 3 ~ 4) show the remnants of the deuterium implant profile in the $LaAlO_3$ substrates, but the deuterium signal has levelled out in the O_2 annealed film and virtually disappeared in the N_2 annealed film.

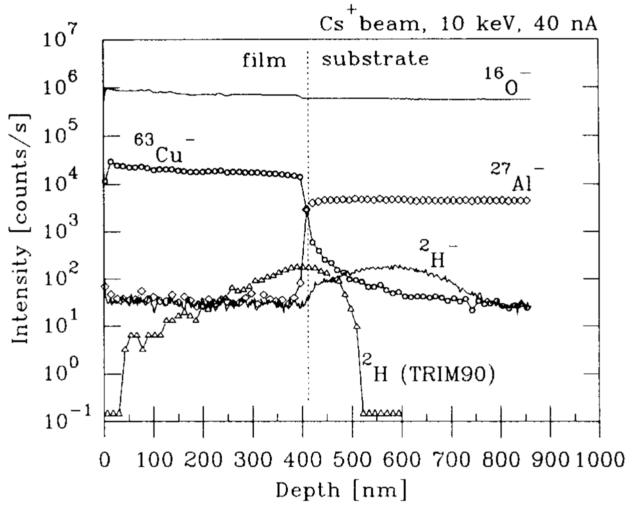

Figure 3. SIMS depth profile of NPL1b sample implanted with a 1 x $10^{16}cm^{-2}$ dose of 50 keV $^{2}H^+$ ions and annealed at 800°C for 20 s in O_2.

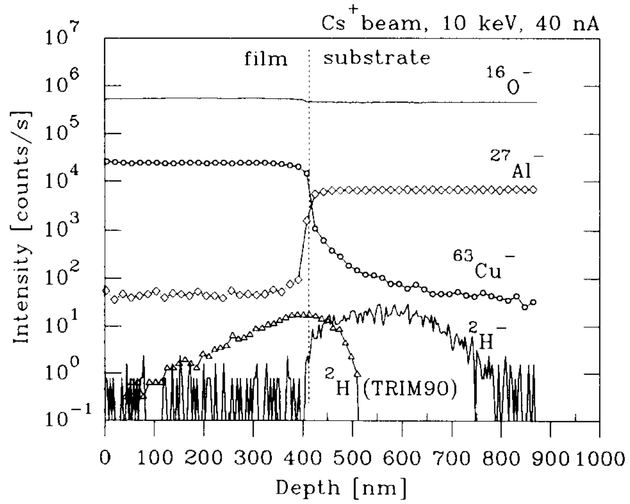

Figure 4. SIMS depth profile of NPL1b sample implanted with a 1 x $10^{16}cm^{-2}$ dose of 50 keV $^{2}H^+$ ions and annealed at 800°C for 20 s in N_2.

4. Discussions

A number of groups have reported T_c enhancement in proton-implanted YBCO thin films [1, 11] and bulk material [12]. A possible explanation has been considered from the J_c results and is reported elsewhere [8].

The T_c values of the samples as related to their oxygen content from the c-axis lengths [9] agree well with Cava et al. [13]. The c-axis change indicates that the structural change from ion implantation is most probably due to the loss of oxygen. This is supported by TRIM90 calculations which show that 50 keV $^2H^+$ ions have a maximum range of about 500 nm in YBCO and predominantly produce oxygen vacancies. Furthermore, annealing in O_2 caused the c-axis length of the high dose implanted NPL1b sample to decrease, indicating an increase in oxygen content, and superconductivity was recovered, albeit with a T_c of only 39 K.

The prospect of the fast annealing and oxygenation of YBCO films was demonstrated with RTA in O_2 , but the annealing conditions need to be optimised if the initial T_c values shown by the virgin samples are to be regained. Annealing in N_2 caused the loss of superconductivity by reducing the oxygen content of the YBCO films. Work is in progress to study the effects of different RTA temperatures with an O_2 atmosphere on YBCO films.

SIMS showed that deuterium was implanted deeper than expected from TRIM90 calculations. This was most probably due to the implantation being carried out at normal incidence to the sample surface resulting in ion channelling in the films and substrates.

The VSM data [8] suggested that the damage introduced by the low dose implants exceeded the optimum level for J_c enhancement. This could be due to too many ions being stopped within the film. The SIMS results together with TRIM90 calculations indicated the presence of deuterium in concentrations of up to 1×10^{16} cm^{-3} in the NPL1b films when scaled to the 1×10^{12} cm^{-2} low dose implant. We plan to increase the implantation energy in order to reduce the level of deuterium left in the films and to study the effect on J_c values.

The SIMS profiles showed that the $^2H^-$ signal in the O_2 annealed sample was about 10 times greater than that in the N_2 annealed sample. Although the samples were analysed consecutively, background levels in the SIMS may have changed and work is planned to clarify the matter. However, the main feature of the two profiles was the very rapid diffusion of deuterium through the YBCO film. This may be partly due to the presence of grain boundaries and voids in the films, as observed with a scanning electron microscope (SEM), but, in any case, the small size of the deuterium atom would suggest high mobility through complex crystal structures. The work with different RTA temperatures will provide more data on this matter.

5.Conclusions

SIMS depth profiles of YBCO films implanted with 50 keV $^2H^+$ ions at a dose of 1×10^{16}cm^{-2} have shown, in conjunction with TRIM90 calculations, that at a dose of 1×10^{12}cm^{-2} a significant level of deuterium would be stopped in the YBCO thin film. It seems that this caused greater damage than the optimum level for J_c enhancement [8], indicating the need for higher implantation energies. The T_c enhancement suggests further study is required on the chemical role of deuterium in YBCO. Finally, the RTA provided a fast method of annealing and oxygenation, but operating conditions need to be optimised.

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