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1997 J. Phys.: Condens. Matter 9 L61

(http://iopscience.iop.org/0953-8984/9/6/003)

J. Phys.: Condens. Matter **9** (1997) L61–L66. Printed in the UK PII: S0953-8984(97)77864-0

LETTER TO THE EDITOR

The relationship between open volume defects and deposition conditions of superconducting thin-film $YBa_2Cu_3O_{7-x}$

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Received 17 September 1996, in final form 30 October 1996

Abstract. The relationship between the open volume defects and the deposition conditions of superconducting thin-film $YBa_2Cu_3O_{7-x}$ was studied by the position lifetime technique. Using a low-energy pulsed positron system, positron lifetime as a function of implantation energy was measured on epitaxial superconducting thin-film $YBa_2Cu_3O_{7-x}$ deposited on yttrium stabilized cubic zirconia substrates (YSZ) with pulsed laser deposition in a partial pressure of air under different conditions. The results show that the type of open volume defect is independent of deposition conditions such as the substrate temperature, T_s, and the air pressure, p_a. The defect concentration increases with decreasing T_s and increasing p_a.

Growth-related defects are known to play an important role in achieving high critical current density. Recently much attention has been focused on defect studies of epitaxial $YBa_2Cu_3O_{7-x}$ film. Using scanning tunnelling microscopy it was found that there is a high density of spiral growth structures, each of which contains a screw dislocation [1]. In addition, inclusions, twin boundaries, *c*-stacking faults and a number of nanometre holes were also observed using transmission electron microscopy in the films [2]. As yet, not much information has been obtained about the metal-ion vacancies in epitaxial $YBa_2Cu_3O_{7-x}$ film. Positron annihilation spectroscopy is the only method to detect open volume defects, from single-atom vacancies to voids [3]. With a conventional positron experiment using positrons from a natural radiation source with a broad energy distribution up to 0.5 MeV only bulk materials can be investigated. Variable-energy positron beams have a selectable energy with a narrow energy distribution, allowing a depth-resolved measurement, and hence they can be applied to defect studies of thin films. In comparison with measurements of Doppler broadening of annihilation radiation, the positron lifetime spectrum can be resolved into several components and provide much more information about open volume

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0953-8984/97/060061+06$19.50

defects. With the pulsed low-energy positron system Zhou *et al* measured epitaxial thin-film $GdBa_2Cu_3O_{7-x}$ deposited by magneto-sputtering [4] and epitaxial thin-film $YBa_2Cu_3O_{7-x}$ deposited by co-evaporation [5]. They found two types of open volume defect in the thin-film $GdBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$: (i) deep positron trapping centres, such as metal-ion vacancies; (ii) shallow positron trapping centres, such as dislocations and twin boundaries.

In this letter we report the positron lifetime studies of epitaxial superconducting thin-film $YBa_2Cu_3O_{7-x}$ deposited on an yttrium-stabilized cubic zirconia (YSZ) substrate using pulsed laser deposition in a partial pressure of air. A plateau in the relationship between positron mean lifetime and implantation energy was observed. The lifetime spectra can be analysed with a sum of two exponential components. From the variation of the positron lifetime parameters with the deposition conditions, such as the substrate temperature, T_s, and the air pressure, p_a, the properties of the open volume defects in the film are discussed.

The samples of epitaxial thin-film $YBa_2Cu_3O_{7-x}$ were deposited by pulsed laser deposition on a single-crystal YSZ substrate using a partial pressure of air. An excimer KrF laser was focused onto a stoichiometric $YBa_2Cu_3O_{7-x}$ target to produce a fluence of about 1.5 cm^{-2}. (100)-oriented YSZ single-crystal substrates were used in this study. The substrate temperature T_s was monitored using a thermocouple embedded in a hole in the heater block. The chamber pressure p_a was controlled by a throttle valve. The detailed preparation process has been published previously [6]. X-ray diffraction (θ–2θ scan, ϕ scan and rocking curve) investigations showed that films at optimal conditions had their c-axes perpendicular to the substrate surface. The misalignment along the c-axis was less than 0.3° and twin boundaries in the a–b-plane were less than 3°. The superconducting critical temperatures of the films were measured using a four-point probe. The thicknesses of the films were estimated to be 400 nm.

Positron lifetime measurements were performed using the pulsed low-energy positron system [7]. As in a continuous slow-positron beam, positrons from a 500 Mbq (13 mCi) ^{22}Na source were moderated in a single-crystal tungsten foil and accelerated in vacuum onto the sample under investigation. To allow lifetime measurements to be performed a time structure was superimposed on the beam. This was achieved by passing the continuous beam through a sequence of radio frequency buncher and chopper, resulting in a pulsed width at the target of 150 ps with a repetition frequency of 50 MHz. The annihilation quanta were detected with a BaF_2 scintillator, which, in coincidence with the pulsed signal, forms the basis of conventional positron lifetime spectrometer with a resolution of 210 ps. In this work more than 10^6 counts were accumulated for each spectrum. The spectra were analysed using a modified version of Positronfit with unconstrained fitting. All the lifetime spectra were measured at room temperature.

Positron lifetime measurements were performed on epitaxial superconducting thin-film $YBa_2Cu_3O_{7-x}$ deposited on YSZ substrates in air using a pulsed laser deposition method under different conditions. The positron mean lifetime as a function of implantation energy displays a plateau between $E = 3$ keV and $E = 8$ keV for several samples: a typical result is shown in figure 1.

The variation of positron mean lifetime with implantation energy can be well understood qualitatively [8]. Because of the existence of positron surface states and trapping at defects at the surface, the positron mean lifetime at surface is larger than that within the films and the single-crystal substrates. The epitaxial thin film contains many crystalline imperfections, some of which can trap positrons, thus the positron mean lifetime in the film should be longer than that in the substrate. As the implantation energy rises, the mean implantation depth increases and hence the fraction of positrons annihilating near or at the surface decreases.

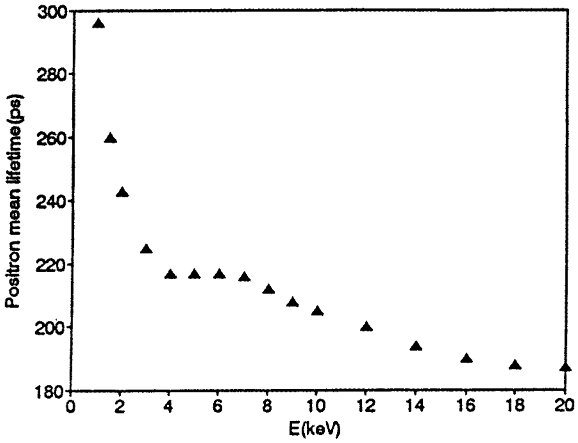

Figure 1. The positron lifetime as a function of implantation energy at room temperature for epitaxial superconducting thin-film $YBa_2Cu_3O_{7-x}$ prepared by pulsed laser deposition. $T_s = 750\,^\circ C$, $p_a = 440$ mtorr, $T_c = 89$ K and $\Delta T_c = 0.5$ K.

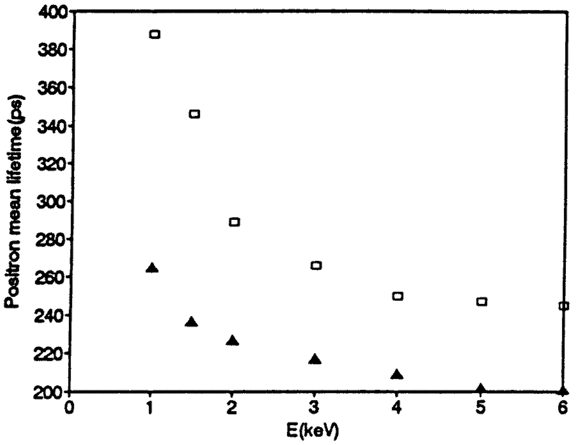

Figure 2. The positron lifetime as a function of implantation energy for two $YBa_2Cu_3O_{7-x}$ epitaxial superconducting thin films prepared by pulsed laser deposition under the same air pressure $p_a = 420$ mtorr. ▲, $T_s = 760\,^\circ C$; □, $T_s = 730\,^\circ C$.

This results in the decrease of positron mean lifetime at the low-energy end ($E \leqslant 3$ keV). At higher energies ($E \geqslant 8$ keV) a fraction of the positrons begins to penetrate into the substrate gradually from the implantation profile. This is the reason why the positron mean lifetime decreases slowly down to annihilation characteristics in the substrate. At intermediate energies the defects in the film can trap positrons effectively and information about the open volume defects in the film can be ascertained.

The positron lifetime spectra were resolved in terms of a sum of two exponential components with a variance better than 1.2. This model is only strictly valid for homogeneous systems [9]. We can reasonably use it to analyse the spectra corresponding to the plateau region in figure 1 for example $E = 5$ keV, where the positron back-diffusion

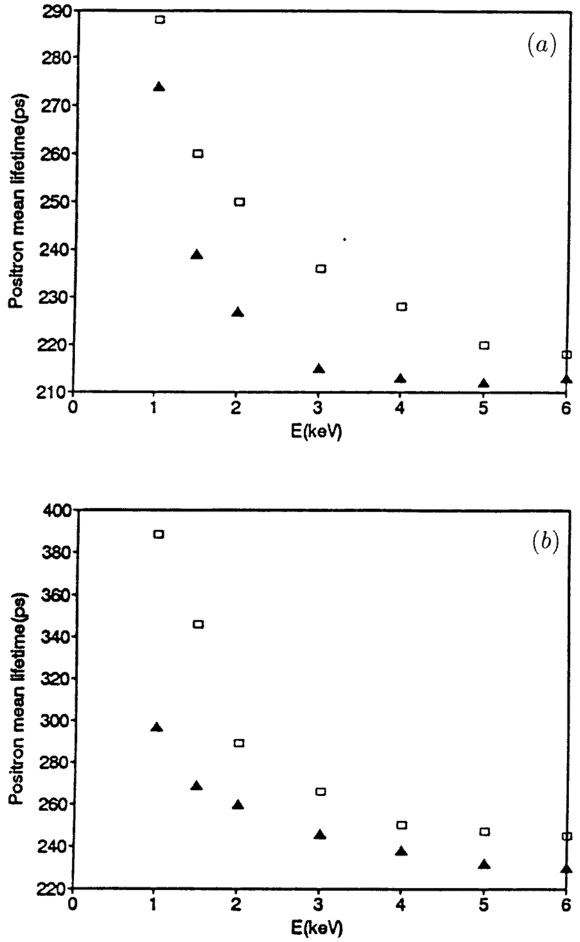

Figure 3. The positron lifetime as a function of implantation energy for $YBa_2Cu_3O_{7-x}$ epitaxial superconducting thin films prepared by pulsed laser deposition under the same substrate temperature: (a) $T_s = 740\,^\circ C$; ▲, $p_a = 530$ mtorr; □, $p_a = 580$ mtorr; (b) $T_s = 730\,^\circ C$, ▲, $p_a = 250$ mtorr; □, $p_a = 420$ mtorr.

is suppressed and only a small fraction of the positrons penetrates into the substrate. In the following we concentrate on discussion of the variation of positron lifetime parameters at $E = 5$ keV with different deposition conditions.

Figure 2 shows the positron mean lifetime as a function of implantation energy with different substrate temperatures, T_s, under the same pressure of air, p_a. It can be seen that the positron mean lifetime increases with decreasing T_s. From figure 3 we can see that, for a constant T_s, the positron mean lifetime rises with increasing air pressure.

In general, the increase of positron mean lifetime in these samples can be caused by two effects: (i) the changes of defect types, (ii) the increase of the defect concentration. The relations of the lifetime parameters to deposition conditions are listed in table 1. The characteristic lifetime value (τ_2) of positrons annihilating in the defects of the pulsed laser deposition epitaxial film $YBa_2Cu_3O_{7-x}$ appears to be 326 ps and independent of deposition conditions. The trapping state lifetime τ_2 is a measure of the electron density (related to the

Table 1. Positron lifetime parameters (see the text), τ_2 and I_2, at 5 keV with the deposition conditions, the substrate temperature T_s and the air pressure p_a, superconducting critical temperature T_c, and the relative defect concentration $C_v/C_v(0)$.

T_s (°C)	p_a (mtorr)	τ_2 (ps)	I_2 (%)	$C_v/C_v(0)$	T_c (K)
760	420	326	16.9	0.89	84
730	420	327	46.9	3.86	88
730	250	325	36.6	2.53	< 77
740	580	325	26.5	1.58	90.8
740	530	326	18.6	1	91

size) of the defects. Therefore the defect type concerning τ_2 is not affected by the substrate temperature T_s and the air pressure p_a during deposition. The variation of the positron mean lifetime is from I_2 (the relative intensity of τ_2), or the defect concentrations. Neglecting the shallow trapping effect in the films at room temperature, which has been confirmed to be unimportant at elevated temperatures [5], and using the two-state trapping model [3], the relative defect concentration for each sample can be obtained and these are listed in table 1. Under the same air pressure a lower substrate temperature results in a higher defect concentration. This occurs because the surface mobility of the deposited particles is reduced with a lower substrate temperature and thus the deposited particles cannot obtain enough dynamic energy to fill vacancies before the depositing particles arrive. Thus there are more vacancies left in the film with lower substrate temperature. At $T_s = 730\,^\circ\mathrm{C}$ and $T_s = 740\,^\circ\mathrm{C}$ the defect concentration increases with air pressure. At higher pressure, the mean free path of the depositing particles is small, and they lose energy by colliding with air particles. Effectively, the laser plume containing ablated materials is smaller, and one has to put the substrate closer to the target. With a smaller plume, more dense material will arrive at a small spot on the substrate, which leads to a higher possibility of creating defects. Furthermore, with higher pressure, the substrate traps more air particles on its surface. When the depositing particles arrive at the substrate, some of their energy will be spent on kicking off the trapped particles. Therefore, some of the depositing particles have less chance to fill vacancies which left defects in the depositing surface. Since the defect type (i.e. τ_2) remains unchanged no significant fraction of impure atoms fills vacancies. The air molecules may be in interstitial positions and near or at the surfaces of the films. From table 1 we can also see that the superconducting critical temperature is not obviously related to the open volume defects.

In conclusion, using the low-energy pulsed positron system in Munich, the relationship between the open volume defects and the deposition conditions was studied for epitaxial superconducting thin-film $\mathrm{YBa_2Cu_3O_{7-x}}$ prepared by pulsed laser deposition in a partial pressure of air. The results show the defect type is independent of deposition conditions. The defect concentration increases with decreasing substrate temperature and increasing air pressure. It seems that the open volume defects have no direct correlation to superconducting critical temperature. It is worth pointing out that the open volume defects only include the defects which have strong trapping ability for positrons because the measurements were carried out at room temperature in the present work.

The authors would like to acknowledge P Sperr and M Falter-Zech for their help in this work. Two of them (XYZ and XKL) would like to thank the Alexander von Humboldt Foundation for a fellowship and the Universität der Bundeswehr München for kind hospitality. JAD would like to thank the Royal Society for financial support in the form of a research fellowship.

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