Applied Surface Science 149 (1999) 125–129

applied surface science

Characterisation of Al^+-implanted LiF by a monoenergetic positron beam

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Abstract

We have studied the radiation damage created by the implantation of 100 keV Al^+ ions into LiF crystals using a monoenergetic positron beam whose energy can be varied. The fluence range investigated was 10^{13} to 10^{16} ions cm^{-2}. Pronounced effects of radiation damage are seen in the line shape of the positron spectrum. The measured *S*-parameter is used to characterise the radiation damage as a function of depth. A four-layer model is used to fit the data using the computer program VEPFIT. The Positron Annihilation Spectroscopy (PAS) results are correlated with optical absorption measurements on the crystals. The use of positrons to profile the radiation damage as a function of depth below the ion implantation surface is shown to be feasible for lithium fluoride crystals.

Keywords: Positron beam; Al^+; LiF

1. Introduction

Ion implantation in an alkali halide creates a high concentration of defects in a thin layer near the surface of the crystal. The thickness of this layer is determined by the range of penetration of the ions. These defects are produced on the anion sublattice by excitonic mechanism, and are primarily *F*- and *H*-centres which, under appropriate conditions, can aggregate to form complexes (see Hobbs [1], Townsend [2] and Comins et al. [3]). Because the defects are located near the surface at a high concentration, they are well-suited to be studied by optical methods and slow positron beam technique. Colour centres in LiF produced by ions in the energy range 100 KeV–2 MeV have been reported by Davenas et al. [4], Afonso et al. [5], Abu Hussan and Townsend [6] and Davidson et al. [7,8]. These optical studies show that coloration is due to *F* and *F* aggregate centres formed in the implanted region. At high fluences, extra coloration may occur due to small metallic particles usually referred to as colloids.

Positron annihilation spectroscopy (PAS) is now a well-established technique for the study of defects in solids [9,10]. Conventional lifetime studies have been done on some alkali halides. Williams and Ache [11] measured positron lifetimes in proton and gamma irradiated NaCl. Dupasquier [12] measured positron

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PII: S0169-4332(99)00186-5

lifetimes in additively and electrolytically coloured KCl crystals. These workers identified F-centres as the positron traps in NaCl.

Angular correlation studies on KCl crystals have shown that the angular momentum distributions of additively coloured KCl are narrower than those for 'pure' KCl. This narrowing can be understood in terms of the annihilation of trapped F-centre electrons having comparatively small momenta [13,14]. The recent development of slow positron beams [15], which have both depth selectivity and defect sensitivity, makes the study of defects at and near crystal surface possible.

Variable energy positron beam spectroscopy has been widely used as a non-destructive, depth-profiling probe of vacancy-related defects in condensed matter [15]. Upon implantation into the solid, the positrons lose most of their kinetic energy (thermalize) within a few picoseconds and then diffuse until annihilating with electrons. The positron implantation or 'stopping' profile, $P(E,z)$, is defined as the depth distribution of the positrons after they have thermalized and is given by the Makhov function [16].

$$P(E,z) = -\frac{\mathrm{d}}{\mathrm{d}z}\exp-\left[(z/z_0)^m\right] \tag{1}$$

where z is the depth and m is the shape parameter that is usually taken to be 2. The depth parameter, z_0, has a simple relation to the mean implantation depth, $\bar{z}$, of the form $\bar{z} = z_0\pi^{1/2}/2$, and $\bar{z}$ is given by:

$$\bar{z} = AE^n/\rho, \tag{2}$$

where A and n are constants (taken to be 40 nm g cm^{-3} $(keV)^{-n}$ and 1.6, respectively), ρ is the density (g cm^{-3}), and E is the energy (in keV) [17].

The Doppler broadening of the annihilation line shape, characterised by the S-parameter, which is defined as the area under the central part of the annihilation photopeak divided by the total area [15], is a measure of the electron momentum distribution at the annihilation site. The measured S-parameter is actually a linear, superposition of contributing S-parameters from the surface and the bulk for the case of a single layer system and can be expressed as:

$$S(E) = S_{surf} f_{surf}(E) + S_{bulk}(1 - f_{surf}(E)) \tag{3}$$

where $f_{surf}(E)$ is the fraction of positrons annihilating at the surface, or more generally for a multilayer system as:

$$S(E) = S_{surf} f_{surf}(E) + \sum_i S_i f_i(E) \tag{4}$$

where i denotes the ith layer.

The object of the present work is to study the radiation damage in LiF following the implantation of 100 KeV Al^+ ions in the fluence range 10^{13}–10^{16} cm^{-2} and to characterise the damage by slow positron beam technique. The results of the PAS measurements are correlated with the results of optical measurements.

2. Experiment

Pure LiF plates of thickness 1 mm were obtained from BDH (Merck) in the United Kingdom. Square samples of side 8 mm were cut from the plates using a diamond saw. Ion implantations with 100 keV Al^+ ions were performed at the Schonland Research Centre for Nuclear Sciences at the University of the Witwatersrand. Implantations were done in the fluence range 10^{13}–10^{16} ions cm^{-2}. The penetration depth of 100 keV Al^+ ions in LiF is estimated by TRIM calculations to be 0.15 μm.

Optical absorption spectra were measured at wavelengths between 200 nm and 600 nm using a CARY 400 spectrophotometer in order to optically characterise the defects in the ion-implanted LiF.

Positron beam measurements were performed with a variable energy slow positron beam at Research Centre Rossendorf (Germany). The beam has a diameter of ~ 3 mm and a maximum implantation energy of 50 keV. Positrons from ^{22}Na source (30 mCi) were moderated by a tungsten foil of about 6 mm diameter and a thickness of 5 μm in order to produce a monoenergetic beam. After moderation the positrons are pulled off by a 30 V beam formation section and then transported and focused by magnetic field and accelerated to achieve the required positron implantation energies [18]. The implanted positrons rapidly thermalize ($< 10^{-11}$ s) and then diffuse (in the absence of an electric field) until they annihilate with electrons, producing pairs of gamma ray (511 keV) photons that are detected by a high-purity germanium (HPGe) detector. The detector resolution was 1.26 keV (FWHM) at 511 keV. The positron annihilation spectra (5×10^5) counts were accumulated at positron beam energies ranging from 0.03 keV to 25 keV, which corresponds to maximum mean implantation depth of ~ 2.61 μm. The annihilation spectrum was characterised by the *S*-parameter. The absence of ion cores at vacancy-type defects means that these sites act as trapping sites for positrons. Annihilation with low energy valence electrons at these defects results in a narrowing of the photopeak corresponding to an increase in the *S*-parameter.

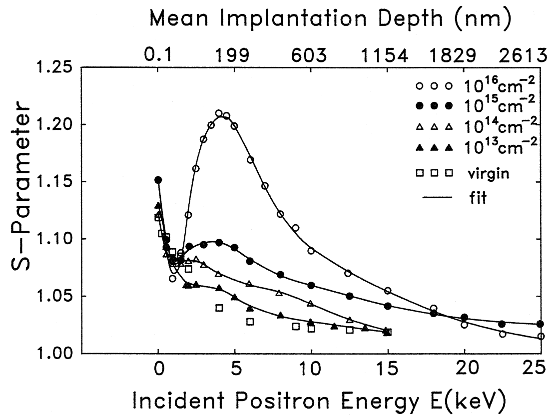

Fig. 2. *S*-parameter vs. positron implantation energy. Data are normalised to the bulk *S*-parameter. The solid lines indicate the best fit to experimental data.

3. Results and discussion

Optical absorption spectra of LiF following implantation with Al^+ ions are shown in Fig. 1. At the lowest fluence of 4×10^{15} cm^{-2}, F(245 nm, 5.06 eV) and F_2(444 nm, 2.79 eV) bands are present together with bands near 211 nm and 414 nm. The band near 211 nm is attributed to an aluminium colloid formed from the implanted ions. Absorption at 414 nm may be due to F_{2A}-centres [19]. With increasing fluence above 1×10^{16} cm^{-2}, the colloid band grows rapidly and dominates the absorption spectrum at a fluence of 6×10^{16} cm^{-2}. The colloid band is located near 203 nm (6.11 eV) at this fluence level.

F band absorption is characteristic of ion-implanted alkali halides and comprises an anion vacancy which has trapped an electron. Colloid bands form readily in LiF following ion implantation at room temperature [20], and arises when plasmon resonance of electrons occurs in small metallic particles contained in a dielectric host. In LiF, absorption by *F*-centres and by Al colloids occur in a similar part of the spectrum.

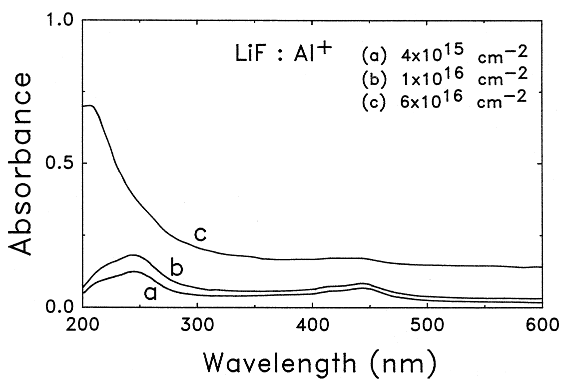

Fig. 1. Absorbance vs. photon wavelength between 200 nm and 600 nm for LiF crystal after implantation with Al^+ ions.

For the analysis of the positron annihilation data, the computer program VEPFIT [21] was used to fit the experimental data by analysing the energy dependence of the *S*-parameter. In Fig. 2, we show the *S*-parameter (normalised to the bulk value) vs. incident positron energy at various fluences. Since the highest beam energy used was 25 keV, corresponding to a maximum mean implantation depth of $\sim$ 2.61 μm, all of the positrons can be considered to be annihilating in the samples.

For the virgin sample, the *S*-parameter value is $S_{surf} = 0.5309 \pm 0.0007$ at the surface and decreases rapidly before levelling off at the bulk value $S_{bulk} = 0.4890 \pm 0007$. The effective positron diffusion length in this sample is $L_+ = 79 \pm 2$ nm. The *S*-parameter of the implanted samples has a large surface value which is similar in magnitude to that of the virgin sample. However, our analysis shows that the surface layer in ion-implanted samples is characterized by a shorter positron diffusion length than the 79 nm value mentioned above. The *S*-parameter decreases rapidly to a minimum value at positron energy ~ 1 keV corresponding to a mean implantation depth of 12 nm. The *S*-parameter curves exhibit a broad maximum around positron beam energy of 2.5 keV for fluences 10^{13} cm^{-2} and 10^{14} cm^{-2}, and 4.5 keV for fluences 10^{15} cm^{-2} and 10^{16} cm^{-2}. Further as the implantation fluence is increased, the peaking in *S*-parameter progressively increases. The *S*-parameter gradually decreases beyond positron beam energy corresponding to its peak value and reaches the bulk value beyond 12 keV for the low dose samples and beyond 25 keV for the high dose samples. This indicates that spatial extent of defect distribution is larger in high dose samples as compared to that for low dose samples and also that at high fluences the region of damage extends beyond the penetration depth of the implanted ions as calculated by TRIM.

The VEPFIT analysis of the data identifies four layers in the irradiated samples, where the undamaged part is included as one layer. These are shown in Fig. 3a, b, c and d and the normalised *S*-parameters for each dose are given in Table 1. In general, there is a surface layer about 30 nm thick through which all implanted ions passed with shorter positron diffusion length than that of the bulk. The shorter positron diffusion length compared to that of the bulk implies positron traps (i.e., defects) were created near the surface due to the ion implantation. The

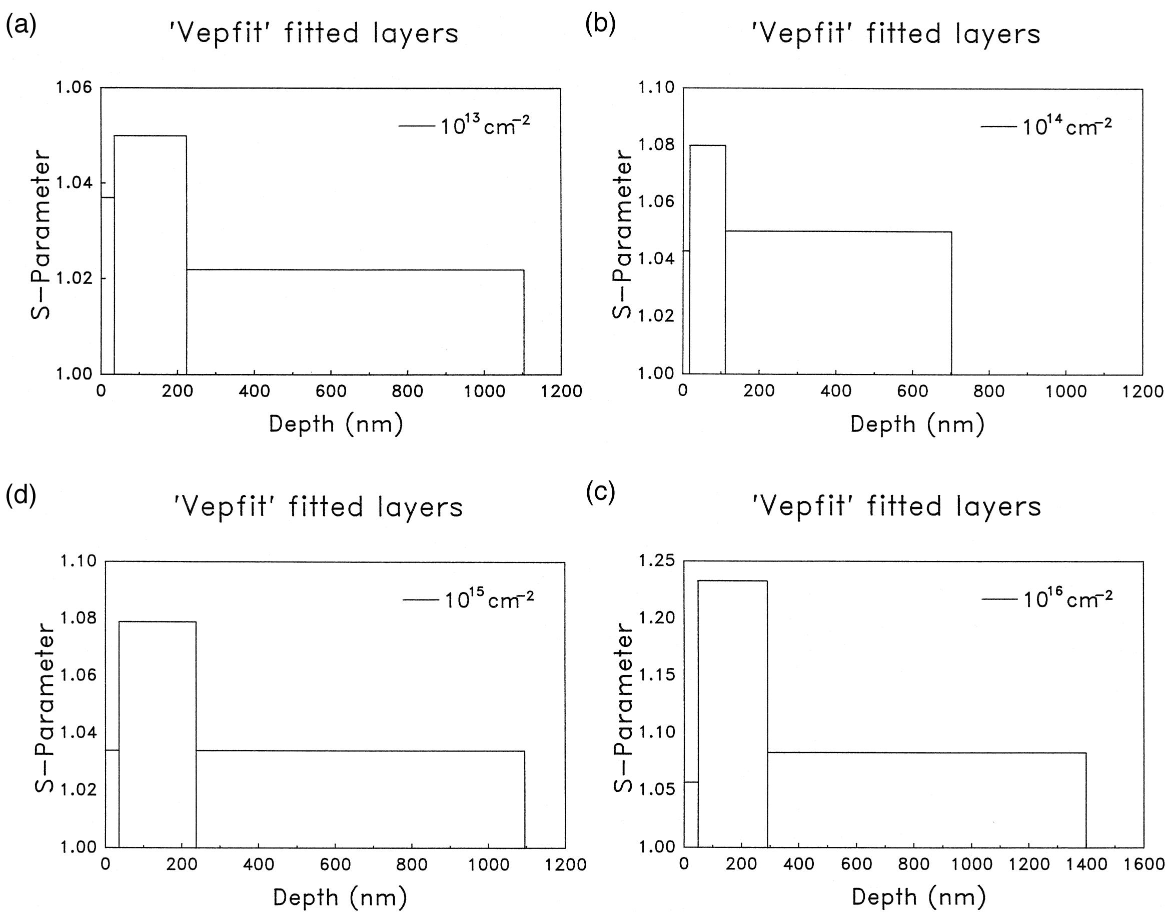

Fig. 3. (a) Normalised *S*-parameter vs. depth diagram for LiF implanted with 10^{13} Al^+ ions cm^{-2}. (b) Normalised *S*-parameter vs. depth diagram for LiF implanted with 10^{14} Al^+ ions cm^{-2}. (c) Normalised *S*-parameter vs. depth diagram for LiF implanted with 10^{15} Al^+ ions cm^{-2}. (d) Normalised *S*-parameter vs. depth diagram for LiF implanted with 10^{16} Al^+ ions cm^{-2}.

Table 1
Normalised S-parameter for the fitted layers

Ion fluence	10^{13} cm^{-2}	10^{14} cm^{-2}	10^{15} cm^{-2}	10^{16} cm^{-2}
S_1/S_{bulk}	1.037	1.043	1.034	1.057
S_2/S_{bulk}	1.050	1.080	1.089	1.233
S_3/S_{bulk}	1.022	1.052	1.032	1.083

surface layer is followed by a layer with a very high S-parameter and a short diffusion length. The high S-parameter may be the result of positrons annihilating with electrons with very low momentum associated with F-centres. We have observed the existence of these centres in our optical absorption measurements shown in Fig. 1. The high S-parameter layer is followed by a small S-parameter layer which indicates the existence of small density of defects in that layer. The damage is deeper than the ion-implanted region in this layer. The undamaged bulk follows the small S-parameter layer.

The damage depth of the sample implanted with a fluence of 10^{14} cm^{-2} is shorter compared to the other samples. The S-parameter is consistently larger for the 10^{14} cm^{-2} sample than the 10^{13} cm^{-2} sample over the whole energy range. It seems that the peak of the S-parameter moves away from the surface with increasing fluence. There are signs of a double peak on the 10^{14} cm^{-2} sample (Fig. 2).

The normalised S-parameter of the implantation range (S_2/S_{bulk} in Table 1) makes a sudden jump from 1.08 in fluence range 10^{13}–10^{15} cm^{-2} to 1.23 at 10^{16} cm^{-2}. This coincides with the appearance of a colloid band at similar fluence in optical absorption spectra.

4. Conclusion

Positron annihilation measurements have been performed on LiF samples implanted with 100 keV Al^+ ions at fluences in the range 10^{13}–10^{16} cm^{-2}. The positron annihilation radiation is shown to be sensitive to radiation damage in the implanted region. By varying the energy of the incident positrons we have identified different layers of damage below the implanted surface. Optical absorption measurements suggest that positrons annihilate with F-centre electrons in low dose samples. A sudden jump in the S-parameter in high dose samples (between 10^{15} and 10^{16} cm^{-2}) coincides with the onset of colloid absorption in optical absorption spectra. Results indicate that radiation damage is detected beyond the ion implantation depth as determined by TRIM. Such an effect is known in certain oxide materials [22], and is now observed also in LiF.

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