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Surface annealing of gallium arsenide studied with low-energy positrons

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Abstract. The sub-surface region of semi-insulating gallium arsenide, after annealing at a range of temperatures, has been investigated with a positron beam. A positron diffusion model analysis of the Doppler lineshape parameter as a function of positron energy shows significant variations in the surface region due to annealing. A comparison with infrared spectroscopy measurements suggests that the observed changes are due to positron trapping at Ga vacancies associated with the formation of Ga_{As} antisite defects. After annealing at 900 K, a layer of positively charged As vacancies induces an electric field which in turn prevents positrons from diffusing to the surface.

1. Introduction

Ion implantation into gallium arsenide is an important technique in the fabrication of devices. However, the method also causes damage to the lattice which must subsequently be repaired by annealing the crystal to temperatures of the order of 1000 K.

One of the obstacles that hinders development of ion-implantation technology in GaAs is that, as temperatures approach 850 K, the surfaces of GaAs crystals dissociate rapidly with arsenic evaporating at a far greater rate than the gallium (Foxon *et al* 1972). In practice a number of techniques have been developed to preserve the GaAs surface during annealing; they include passivation using a dielectric encapsulating film, heating in an arsenic overpressure, and transient heating with a laser or scanned electron beam (Morgan and Eisen 1985).

The aim of this work is to identify the nature of the defects generated by annealing near the surface of an unimplanted sample. One of the most convincing methods of identification of point defects in GaAs is by studying the localized vibrational modes (LVMs) which are detected by infrared spectroscopy. We shall compare our positron beam measurements with those obtained by infrared spectroscopy bearing in mind that the surface conditions probed by the positron beam are simulated in bulk samples used in infrared transmission by irradiating them with fast particles, such as neutrons or electrons, which will penetrate the materials, causing damage, to a depth of approximately 1 mm.

It is well established that positron annihilation spectroscopy is a powerful tool for studying defects in metals (Hautojarvi 1979) and there is a growing body of work that suggests that the same is true for studies of defects in semiconductors

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including GaAs (Dannefaer 1988, Dannefaer *et al* 1984, Corbel *et al* 1988). Until recently many positron annihilation studies on semiconductors have employed bulk techniques which are not sensitive to changes at the surface of a sample. However, the development of monochromatic low-energy positron beams has enabled surface and near-surface (< 1 μm) effects to be studied using positrons (Schultz and Lynn 1988). Experiments with positron beams on semiconductors have determined depth profiles of defects in ion-implanted Si and GaAs (Keinonen *et al* 1988, Saarinen *et al* 1991), the positron mobility in Si (Makinen *et al* 1990), the interface depth, chemistry and electric field distribution for SiO_2 overlayers on Si (Nielsen *et al* 1989, Baker and Coleman 1989, Smith *et al* 1991) and provided evidence for shallow positron trapping in GaAs (Saarinen *et al* 1989).

2. Experimental procedure

Experiments were performed on the Xenophon low-energy positron beam at Royal Holloway and Bedford New College (Britton *et al* 1985). Essentially energetic positrons from a radioactive source are first slowed down to a few electron volts using a tungsten mesh moderator and are then transported as a monochromatic beam to a target. By applying a negative bias to the target holder it is possible to control the impact energy and hence the penetration depth of the positrons. The stopping depth distribution of the positrons is given by the Makhovian profile

$$P(z, E) = (\mathrm{d}/\mathrm{d}z)\exp(-z^2/z_0^2) \tag{1}$$

where z is the depth in Å and z_0 is an energy-dependent parameter given by

$$z_0 = \alpha E^n/\rho \tag{2}$$

(ρ is the material density in g cm^{-3}, $\alpha = 4.5$ μg cm^{-2} and $n = 1.6$ (Vehanen *et al* 1985)). Photons arising from annihilations in the sample are recorded using an intrinsic Ge detector, mounted directly behind the target, connected to an amplifier and a multichannel analyser.

The samples under study were cut from an etched, Czochralski-grown semi-insulating GaAs wafer approximately 400 μm thick which had received no other treatment. Prior to mounting in the positron beam, samples were annealed in a vacuum of 10^{-7} Torr for 15 minutes at a pre-determined temperature within the temperature range 550–900 K. The annealed specimen was then transferred to the target holder of the beam. Annihilation spectra for positron energies from 0 to 10 keV were recorded for a range of annealing temperatures.

3. Results and analysis

Figure 1 shows the Doppler lineshape parameter S plotted as a function of incident positron energy for unannealed GaAs and for the material after annealing at 575, 640, 670, 740, 770, 800 and 900 K.

In each case the results were analysed using the positron diffusion model (see Schutz and Lynn 1988). After reaching thermal energies, the implanted positrons

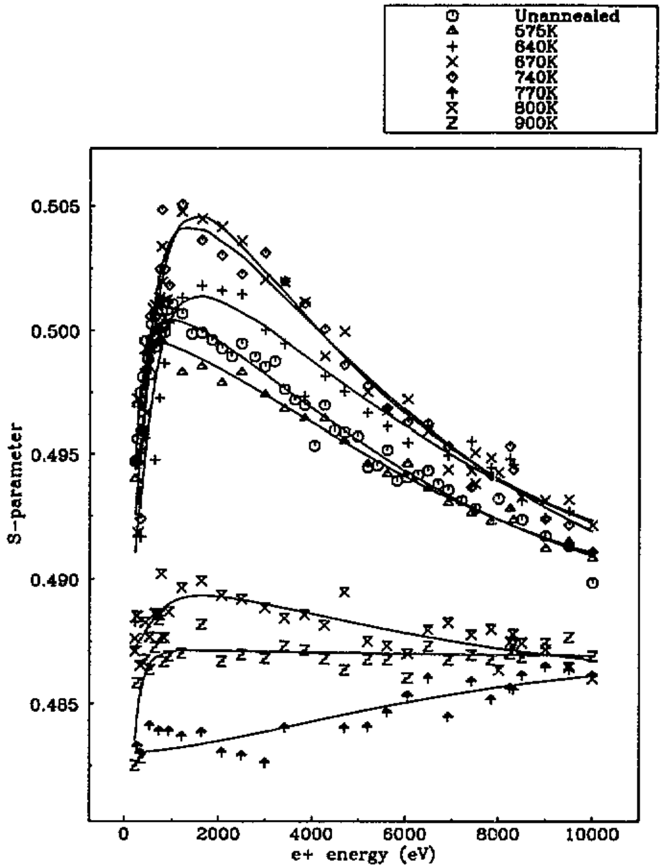

Figure 1. The lineshape parameter S plotted as a function of incident positron energy for etched gallium arsenide. This graph shows the results obtained for the unannealed sample and the material annealed at 575, 640, 670, 740, 770, 800 and 900 K.

may either annihilate in the bulk of the material or diffuse back to the surface. The lineshape parameter at a given energy is

$$S(E) = J_s S_s + (1 - J_s) S_b \tag{3}$$

where S_s and S_b are the lineshape parameters corresponding to 100% annihilations in the surface and bulk. J_s is the fraction of positrons diffusing back to the surface and is defined as

$$J_s = \int_0^\infty P(z, E) \exp(-z/L^+)\, \mathrm{d}z \tag{4}$$

where L^+ is the positron diffusion length. At low incident energies (< 1.5 keV) there is a sharp rise in the S-parameter in all but one of the data sets (770 K). This may be due to epithermal effects and may be accounted for by including an extra term in the expression for $S(E)$ such that

$$S(E) = J_{ep} S_{ep} + (1 - J_{ep}) \left[J_s S_s + (1 - J_s) S_b \right] \tag{5}$$

where S_{ep} is a characteristic lineshape parameter for epithermal effects and J_{ep} is defined in a similar manner to J_s using an inelastic scattering length L_{ep} (Britton *et al* 1988).

The lines drawn through the data points shown in figure 1 are the least-squares fits of this model to the results. The parameters L^+ and L_{ep} were found to be 1800±140 Å and 21±6 Å, respectively. The surface and bulk parameters S_s and S_b are shown plotted as a function of annealing temperature in figure 2.

4. Discussion and conclusion

Figure 2 clearly shows that significant changes take place at the surface of semi-insulating gallium arsenide due to annealing at different temperatures. Between 300 and 600 K, S_s appears to change very little, but rises between 600 and 670 K suggesting an increase in positron trapping. Beyond 740 K, S_s drops sharply, reaching a value approximately equal to S_b at 770 K. As there is little variation in S_b with annealing temperature, the observed changes in the sample must be occurring at, or very close to, the sample surface.

It is assumed that no appreciable outgassing of As occurs at the crystal surface below an annealing temperature of 850 K. We attribute the changes in the S-parameter to isolated defects released from defect complexes near the surface. Of the six types of intrinsic point defects that occur in GaAs, we need not consider the two types of interstitial since they anneal out at lower temperatures (<500 K) and of the anti-sites and vacancies we need only consider $\mathrm{Ga}_{\mathrm{As}}^{-}$ and $\mathrm{V}_{\mathrm{Ga}}^{-}$ which might trap positrons because of their negative charge.

We may compare our positron beam measurements with those made by Maguire *et al* (1986) using infrared spectroscopy. The infrared measurements were, however, made on bulk GaAs samples that had been subjected to fast particle irradiations, so any comparison is justified only if the surface imperfections studied here are similar to the defects studied by Maguire *et al*. We believe justification is provided by previous infrared studies (Collins *et al* 1986) which showed that defects created in bulk samples by fast-particle irradiations exhibit annealing behaviour that is similar to that of surface damage produced by ion-implantation.

The spectra of Maguire *et al*, which were recorded with a good signal-to-noise ratio, show spectral lines that are unambiguously ascribed to defect centres. The interpretation of the annealing behaviour is clear. Initially Si and B impurity atoms in the damaged samples are situated predominantly on the Ga sites. When the samples are annealed, a temperature is reached at which the impurity atoms start to switch to As lattice sites, as indicated by a drop in the strength of the LVM arising from the impurity located on the Ga site as well as an increase in the LVM arising from the impurity located on the As site. At higher annealing temperatures the situation is reversed. The precise temperature at which these changes take place (shown in table 1) differs for the two impurities as would be expected since the equilibrium of the process will depend on the defect atom. (No such changes were observed when unirradiated samples were annealed.)

The process taking place is that of first a release of V_{As} from the damage centres created by the irradiation, followed by a release of V_{Ga} at a higher anneal temperature. Maguire *et al* argue that the migration of the vacancies occurs by nearest-neighbour movement rather than by next-nearest-neighbour movement, so

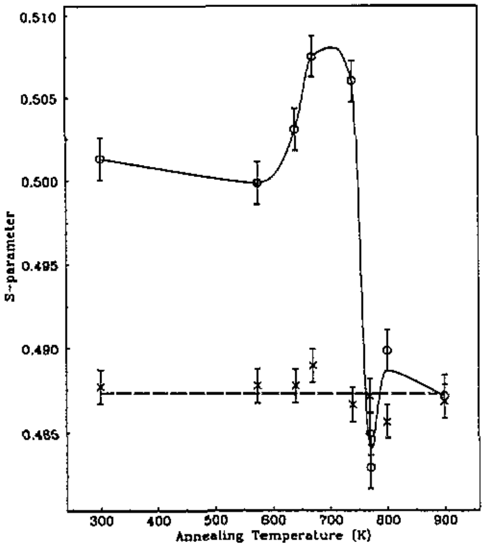

Figure 2. The parameters S_s (circles) and S_b (crosses), obtained from diffusion model analysis of the S-parameter curves (figure 1), plotted as a function of annealing temperature. The rise in S_s at 600 K is interpreted as being due to trapping at Ga vacancies associated with the formation of Ga_{As} antisite defects. Beyond 740 K, S_s drops sharply as Ga vacancies anneal out. The changes observed in S_b are believed to be statistical.

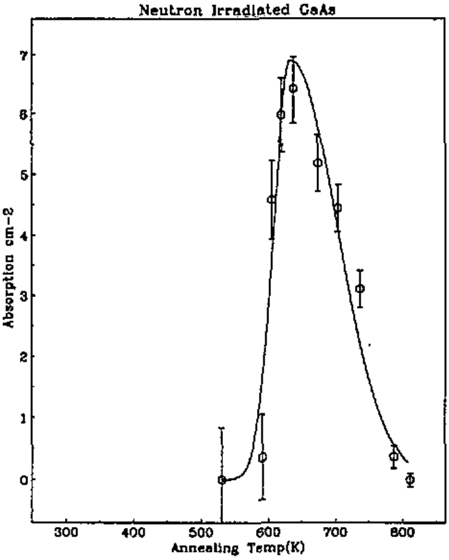

Figure 3. Absorption strength at the 119 cm^{-1} feature observed in the infrared absorption spectrum for n^0-irradiated gallium arsenide (Collins *et al*). The defect responsible for the feature at this wavenumber is believed to be the Ga_{As} antisite.

Table 1. Comparison of the annealing behaviour of defect centres in GaAs situated on the As lattice site, observed by infrared spectroscopy, with the parameter S_s obtained from positron annihilation data.

Defect centre and frequency of the LVM line (entries 1–3)	Anneal temperature at which the LVM from the defect is first detected	Anneal temperature at which it has maximum strength	Anneal temperature at which it can no longer be detected
$^{11}B_{As}$, 601 cm^{-1}	490	720	870
$^{28}Si_{As}$, 399 cm^{-1}	570	770	970
$^{69+71}Ga_{As}$, 119 cm^{-1}	570	670	830
S_s-parameter for PA	570	700	770

the release of V_{As} into the crystal would be followed by a reaction

$$V_{As} + Ga_{Ga} \rightarrow Ga_{As} + V_{Ga}.$$

It would be even more convincing if it were possible to observe the intrinsic defects directly. Although LVMs due to intrinsic defects are neither predicted theoretically nor observed experimentally, Collins *et al* (1986) have observed a resonant (or quasi-localized) mode in the far infrared spectral region (119 cm^{-1}). This mode was observed in a series of samples damaged by neutron irradiation including one that was undoped, showing that the mode arose from an intrinsic defect. The annealing behaviour of this defect (figure 3 and table 1) is so similar to that of the impurity atoms on the As lattice site seen in other samples that it was attributed to the gallium atom on the As lattice site, i.e. the gallium antisite defect, Ga_{As}.

A comparison of the annealing behaviour of this antisite defect with the positron annealing graph (figure 2), which is summarized in table 1, shows several common features. Although in principle the Ga_{As}^- defect may trap positrons in a Rydberg state, we are not aware of any cases where changes in the Doppler parameter S have been associated with such trapping. Rather we think it more likely that the S-parameter variations are a result of site switching yielding a V_{Ga}^- which may or may not migrate to form a defect complex. That is, the changes in S_s at different annealing temperatures are due to variations in the concentrations of gallium vacancies. Thus the rise in S_s above 600 K corresponds to the creation of Ga vacancies in the site switching, and the drop beyond 740 K will be due to the removal of these vacancies.

There is a connection between our conclusions and the hypothesis Dannefaer *et al* (1984) used to account for their bulk lifetime measurements in GaAs. They suggested the creation of Ga_{As} defects at higher temperatures (>770 K) accompanied by the formation of V_{Ga}, but believed that the latter defects were sufficiently mobile to disappear, leaving Ga_{As} defects which were responsible for the trapping. Of course, we must emphasize that we are looking essentially at surface effects, and not bulk phenomena.

It is interesting to note that the results for the 900 K annealed sample show that the lineshape parameter for the surface has the same value as the bulk parameter. This suggests that all the positrons entering the sample and thermalizing are annihilating in the bulk of the material. This would only be possible if positrons were somehow prevented from reaching the surface. Annealing above 850 K is known to produce an excess of As vacancies near the surface of GaAs due to the evaporation of As. These As vacancies have been shown to be donors, i.e. positively charged (Chiang and Pearson 1975), and hence a thin surface layer of these vacancies would induce an electric field in the GaAs. This field may be strong enough to repel any positrons diffusing to the surface, and hence all annihilations would take place in the bulk of the material. A similar effect has been observed at the SiO_2/Si interface, where an electric field in the semiconductor induced by trapped charges reduces the fraction of positrons diffusing towards the interface from the substrate (Nielsen *et al* 1989, Smith *et al* 1991).

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