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Investigations of positron lifetimes in InP with a pulsed positron beam

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Abstract. Indium Phosphide layers grown by gas source Molecular Beam Epitaxy, (MBE) have been studied by positron lifetime spectroscopy using the recently modified pulsed positron beam in Munich. The as-grown samples are known to be phosphorous rich and contain a high concentration of vacancy-type defects. On annealing, phosphorous precipitates are formed and the concentration of free volume defects increases. Positron lifetime spectroscopy has identified the grown in defects to be indium vacancies at a concentration around 10^{18}cm^{-3}. The dominant defects after annealing exhibit a positron lifetime characteristic of divacancies and are present at concentrations in excess of $5 \times 10^{19}\text{cm}^{-3}$.

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Defects have a profound influence on the electrical and optical properties of semiconductors, limiting their technological application. In principle, III–V semiconductors GaAs and InP, with their large direct band gap of around 1.4 eV, promise considerable advantages over silicon, particularly for optoelectronics applications. Of the two GaAs has been the most widely studied, although interest in InP is steadily increasing.

A particular area of interest is molecular beam epitaxial growth at low substrate temperatures. Lower temperature are desirable for all semiconductor structures as redistribution of dopant atoms is inhibited. Apart from the usual problems associated with breakdown of epitaxial growth, it has been found to be impossible to produce *p*-type InP layers [1–3] at low temperature, although acceptor concentrations up to $10^{19}\ \text{cm}^{-3}$ are possible above 500 °C [2]. Liang et al. [1], using Hall effect measurements, found a maximum in the free electron concentration for growth temperatures below 250 °C. As phosphorous is preferentially included at lower temperatures, these authors assumed three types of defects, interstitial phosphorous (P_i), the phosphrous antisite (P_{In}) and the indium vacancy (V_{In}) to be present. Recent calculations [4] also predict that in phosphorous rich InP the dominant defects should be negatively charged indium vacancies and phosphorous antisites. Of these only P_{In} is expected to be a donor. Dreszer et al. [3] have confirmed the presence of this defect with Optically Detected Magnetic Resonance (ODMR). Using admittance spectroscopy, Liang et al. [1] found an activation energy for this deep level of 0.32 ± 0.05 eV, which is deep compared to most *n*-type impurity donors. For a growth temperature of 310 °C they found a defect concentration of $2 \times 10^{18}\ \text{cm}^{-3}$, suggesting a value as high as $2 \times 10^{19}\text{cm}^{-3}$ at 255 °C. Compensation by *p*-type doping should therefore be somewhat difficult. Dreszer et al. [3] found a similar concentration ($4 \times 10^{18}\ \text{cm}^{-3}$) of deep donors which they could partially compensate with Be doping for growth temperatures above 300 °C. From the temperature dependence of the Hall coefficient they found an activation energy of 220 ± 50 meV for the donor defect. Using Fourier Transform InfraRed (FTIR) spectroscopy they found a second level 110 ± 20 meV above the bottom of the conduction band. These levels were assigned to the first and second ionisation energies of the phosphorous antisite, respectively.

Positron annihilation studies [5] on low temperature MBE grown InP indicate the presence of vacancy-type defects. From a comparison with electron irradiated samples these could plausibly be identified as V_{In}. In this paper, we present positron lifetime studies on the same specimens. On annealing at 560 °C Hautojärvi et al. found a change in the characteristic defect parameter, indicating the presence of a larger defect, either a divacancy or small cluster. The results presented here not only confirm this assumption, identifying the defect as a divacancy, but show an increase in defect concentration on annealing. Electron microscopy studies on similar samples [6] show the formation of cubic α-P precipitates with a diameter between 3 and 7 nm on annealing to 680 °C. The phosphorous is assumed to condense from antisite defects and

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should therefore lead to an increase in the concentration of vacancy type defects.

Because of the nature of the measurement [7] all previous slow positron beam studies on InP [5, 8, 9] have relied on measuring the Doppler broadening of the annihilation radiation, which provides only relative defect parameters. In a typical slow positron beam positrons from a radioactive source impinge on a moderator crystal. This is usually a metal, such as tungsten, which has a negative work function for positrons. The small fraction of incident positrons ($\approx 10^{-4}$) which diffuse to the exit face before annihilating is therefore spontaneously emitted. These are then transported in vacuum and accelerated onto the target with a defined energy. However, even if the emission of the positron from the source is tagged, because its transport time to the sample is poorly defined, timing measurements at the resolution required for positrons lifetime spectroscopy (≤ 250 ps) are not possible.

In contrast to lifetime spectroscopy, which samples the local electron charge density at the annihilation site, Doppler-broadening measures the local electron momentum distribution convoluted with the instrumental resolution. Results are usually presented in terms of one or two simple parameters, conventionally called S and W, defined as the normalised intensity in arbitrarily defined regions at the center and wings of the peak respectively. In any given spectrometer, values for S and W can be attributed to different defect types, although both parameters depend non-linearly on both the resolution of the detector and the energy windows selected. Lifetime spectroscopy, on the other hand, is the technique usually employed in bulk positron annihilation experiments, where the emission of the positrons can be tagged by the coincident emission of a fiducial γ photon. The annihilation rates for positrons annihilating at different sites can easily be extracted, are more or less independent of the spectrometer resolution, and can be relatively easily attributed to specific defect types. In contrast to Doppler-broadening measurements, employing a single parameter, measured positron lifetimes can be compared directly with theoretical calculations of the annihilation rates.

Despite these drawbacks, a lot of experience has been gathered over the last two decades with continuous slow positron beams. Reliable measurements of trapping rate profiles are regularly obtained. Identification of defect types and comparison between different laboratories, however, are both less certain. Our measurements, using the pulsed positron beam in Munich [10] are more closely comparable in nature to bulk measurements using positron lifetime spectroscopy and allow, not only a more robust defect characterisation, but also direct comparison with both theory and other experiment. Extraction of depth profiles is, however, considerably more complicated and time consuming than for time-independent measurements. Both experimental techniques have their strengths in different areas and should, obviously, be seen as being complementary to each other.

The lifetimes of positrons trapped at different defects in InP are reasonably well known, both experimentally [11–13] and theoretically [14]. However, in both lifetime and Doppler-broadening measurements, absolute defect concentrations cannot, as yet, be obtained to a high degree of accuracy as the specific trapping rates to the different defects are still unknown.

1 Experimental

The three samples studied were grown by gas source MBE at Thomson-CSF, Corbeville and have previously been investigated by Hautojärvi et al. [5] using the continuous positron beam in Helsinki. All were doped with 5×10^{17} Be cm^{-3}, 1.5 μm thick and grown on semi insulating Fe doped substrates at 180 °C. Two different layers were grown at two different phosphene flow rates, 8 and 22 standard cubic centimeters per minute (sccm). A sample grown at the lowest flow rate was also annealed for 30 mins at 560 °C. Even after annealing, and irrespective of the PH_3 flow rate, the layers were n-type with a carrier concentration of 5×10^{16} cm^{-3}. The same Czochralski-grown p-type (1.2×10^{18} Zn cm^{-3}) wafer as in [5] was also measured as a reference sample.

The measurements were performed using the Munich pulsed low energy positron system [10]. As in a conventional slow positron beam [7], positrons from a 500 MBq (13 mCi) ^{22}Na source are 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 needs to be superimposed onto the beam. This is achieved by passing the continuous beam through a sequence of radio frequency bunchers and choppers, resulting in a pulse width at the target of 150 ps with a repetition frequency of 50 MHz. The annihilation quanta are detected with a BaF_2 scintillator which, in coincidence with the pulsing signal, forms the basis of a conventional positron lifetime spectrometer with a resolution of 235 ps (FWHM) and count rate of 220 cps.

The positron lifetime spectra were initially analysed in terms of a sum of exponential components, as for bulk measurements, from which the mean lifetime was calculated. Although such a model is only strictly valid for homogeneous defect distributions in bulk solids, useful semiquantitative information can be extracted. This is particularly true in the case of near saturation trapping of the positron, or the presence of a surface barrier [15], where diffusion of the positron back to the surface is suppressed.

For the reference sample and one as-grown layer, which did not exhibit saturation trapping, the spectra were also analysed in detail using a model which takes the spatial diffusion of the positron and the surface boundary condition into account [16]. In this model, positrons are assumed to be implanted with a known implantation profile and allowed to diffuse, before being trapped, escaping the sample, or annihilating, according to the one dimensional diffusion equation

$$D \frac{\partial^2 u}{\partial z^2} - [\lambda + \kappa(z)] u(z, t) = \frac{\partial u}{\partial t},$$

where $u(z, t)$ is the depth distribution of the positrons, λ the bulk annihilation rate (inverse lifetime) and $\kappa(z)$ a spatially dependent trapping rate to a defect distribution. The escape rate to the surface is given by the radiative

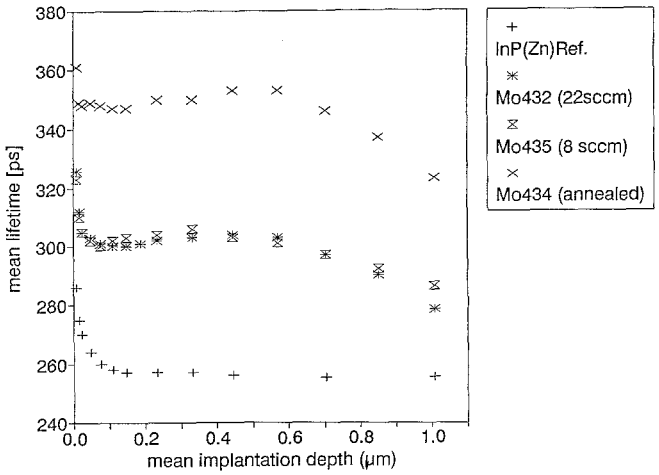


Fig. 1. Positron mean lifetime as a function of mean implantation depth (incident positron energy) for gas phase MBE-grown InP layers: (*) as-grown, PH_3 flow rate 22 sccm, (⧖) as-grown, 8 sccm, (×) 8 sccm annealed at 560 °C and (+) Cz-grown *p*-type reference sample

boundary condition

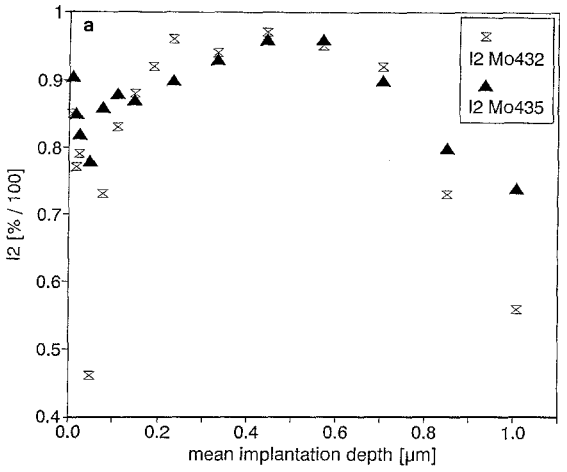
$$D\left.\frac{\partial u}{\partial z}\right|_{z=0} = vu(0, t),$$

where the surface penetration coefficient v has the dimensions of velocity and is commonly assumed to be infinite.

2 Results and discussion

The mean lifetime as a function of mean implantation depth (incident positron energy) for the different layers is shown in Fig. 1. The mean depth has been calculated from the incident positron energy according to the formula $\bar{z} = (40/\rho)E^{1.6}$ nm [7], with the energy E in keV and the density $\rho = 4.79$ g/cm^3. All the samples, including the reference wafer, exhibit reduced diffusion back to the surface, reaching a nearly constant positron lifetime for mean implantation depths greater than 150 nm (6 keV implantation energy).

At first sight, this behaviour in the Czochralski grown wafer is somewhat surprising as this specimen does not exhibit a defect component in its bulk positron lifetime spectrum [5]. Also in these beam measurements, at moderate implantation energies, only a single component of 256 ± 3 ps can be resolved. This value is towards the higher end of the range of published values for the bulk positron lifetime [11, 12] and can reasonably be attributed to the bulk positron lifetime. A similar effect is also seen in heavily doped *p*-type silicon [17, 18]. For both materials a consistent analysis in terms of the diffusion model is possible, assuming a defect-free sample and finite penetration of the surface. For InP the relevant parameters are: bulk lifetime $\tau_B = 260 \pm 2$ ps, positron diffusion coefficient $D = 1.9 \pm 0.5$ cm^2/s, and surface penetration coefficient $v = 0.5 \pm 0.1 \times 10^5$ m/s. This extremely low probability for positrons to leave the bulk of *p*-type semiconductors results from band bending at the surface,



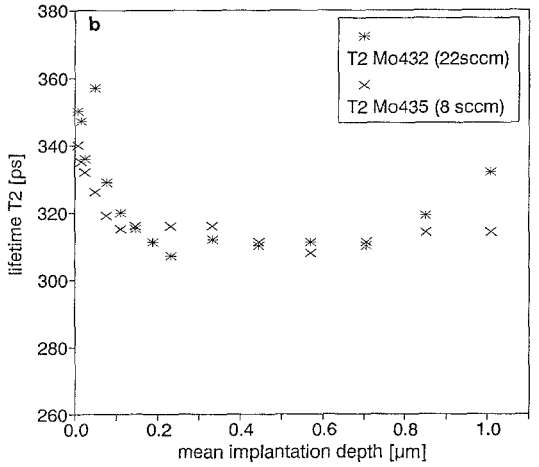


Fig. 2a, b. Intensity (**a**) and lifetime (**b**) of the defect component of the as-grown InP layers, (⧖) 22 sccm and (▲) 8 sccm

with the chemical potential for positrons in the bulk being considerably lower than at the surface.

The two as-grown layers are very similar, with a mean lifetime in the layers of around 300 ps. A two component analysis (Fig. 2) yields similar values for the intensity of the defect component and a lifetime of 312 ± 5 ps. The results from the layer grown with the higher phosphorus flux have also been analysed in terms of the diffusion model, using the material parameters from the reference wafer, to extract the trapping rate of positrons to the defect and their associated lifetime. Some error may be introduced by using the value for v obtained from *p*-type material for what is essentially an *n*-type layer, despite its heavy *p*-doping. However, because of the high trapping rate, surface effects should not introduce too great an error. For mean implantation depths above 100 nm, consistent values of 9.0 ± 1.3 GHz and 310 ± 2 ps could be obtained for the trapping rate and defect lifetime respectively.

A similar defect lifetime has been observed in electron irradiated InP [12] and as-grown material [11] and has been attributed to vacancy type defects. It is, however considerably longer than the value attributed to the

indium vacancy by Bretagnon et al. [13], which at about 267 ps is nearer to our value for the bulk positron lifetime. Theoretical calculations [14] yield lifetimes of 246, 295 and 273 ps for the bulk, V_{In} and V_P respectively. Scaling these values to our bulk lifetime gives a value for the indium vacancy in agreement with the measured defect lifetime. According to the same authors, the phosphorous vacancy should be positively charged with a binding energy for the positron of only 60 meV. Consequently, positrons should not be trapped by V_P at ambient temperature and will not be detected in this experiment. Values for the specific trapping rate to the indium vacancy used by different authors [5, 8, 9, 11–13] have been estimated by comparison with values for GaAs and range from 10^{-8} to 10^{-9} cm^3/s, depending on the charge state of the vacancy. Combining with the estimated trapping rate yields a defect concentration between 9×10^{17} and 9×10^{18} cm^{-3}. As the indium vacancy is expected to be negatively charged, the specific trapping rate should be towards the higher end of the range and, consequently, the defect concentration should be at the lower end, around 10^{18} cm^{-3}.

In the annealed sample only one component with a lifetime of 350 ± 5 ps can be resolved, indicating a higher defect concentration as all positrons are trapped at defects. The positron lifetime at this defect is shorter than that attributed to vacancy clusters in plastically deformed InP [12] but is in reasonable agreement with the theoretical value for positrons trapped at a divacancy [14]. The absence of a free positron component, however, prevents any reliable estimate of the trapping rate, except for a rough lower limit of around a hundred times the bulk annihilation rate, corresponding to a defect concentration in excess of 5×10^{19} cm^{-3}. The increase in vacancy concentration on annealing could be provided by the observed precipitation of phosphorous [6] from antisite defects.

3 Conclusions

Indium phosphide layers grown by gas source MBE have been studied by positron lifetime spectroscopy using the Munich pulsed positron beam. Our results both confirm and compliment the results from previous Doppler-broadening measurements carried out on the same samples. The as-grown samples are known to be phosphorous rich and contain a high concentration of vacancy-type defects. On annealing, phosphorous rich precipitates are formed and the concentration of free volume defects increases. Positron lifetime spectroscopy, coupled with an analysis of the positron diffusion in the layer, has identified the grown in defects to be indium vacancies at a concentration around 10^{18} cm^{-3}. The defect concentration is, in these samples, independent of the phosphorous flow rate during growth. On annealing for 30 minutes at 560 °C, the defect concentration increases to in excess of 5×10^{19} cm^{-3} with the dominant defects having a lifetime attributable to divacancies. The necessary increase in vacancy concentration could be provided by the condensation of phosphrous from antisite defects to form the observed precipitates.

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