Site Changes of Ion-Implanted Li in GaAs below 300 K

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The lattice sites of implanted Li in GaAs single crystals have been determined between 80 and 300 K by measuring channeling and blocking effects of α particles emitted in the decay of implanted radioactive ^{8}Li. Below 220 K the tetrahedral interstital site is preferentially occupied, whereas between 220 and 300 K substitutional and irregular sites are increasingly populated. These site changes are attributed to, respectively, reactions with negatively charged Ga vacancies and defect complexes in recovery stages I and II of GaAs.

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The outstanding properties of Li dopants in semiconductors, i.e., their fast diffusion, their electrical activity, and their ability to compensate deep acceptors, are intimately related to ther lattice position: For example, in Si interstitial Li is well known to act as a donor on the tetrahedral site.[1] This site was proposed for Li donors in GaAs also,[2] whereas experimentally both a donor and an acceptor character of diffused Li have been observed.[3] Therefore a direct site determination appears to be of particular relevance. By means of proton channeling, a localization of Li would be feasible via the ^{7}Li$(p,\alpha)^4$He nuclear reaction;[4] however, this ion-beam analysis technique demands a fairly high impurity concentration and suffers from radiation damage introduced by the analyzing beam.[4,5] We have chosen a different approach for the determination of the lattice location of Li in GaAs single crystals, the measurement of channeling and blocking effects of α particles emitted in the nuclear decay of implanted radioactive probes.[6] Low implementation fluences (about 10^{12} cm^{-2}) and impurity-probe concentrations (a few ppm or less) are sufficient for such a channeling technique, which makes it particularly suited to semiconductor studies.[7] The short-lived isotope ^{8}Li ($T_{1/2}$=0.84 s), which is produced by a spallation reaction with the 600-MeV proton beam from the CERN synchrocyclotron in a Ta target and subsequently implanted with 60 keV energy by means of the on-line isotope separator ISOLDE,[8] was utilized for this purpose. It decays via β^- decay into an excited state of ^{8}Be, which within 10^{-21} s breaks up into two α particles continuously distributed in energy around 1.6 MeV according to a width of that state of 1.5 MeV.[9] In spite of a recoil energy of up to 12 keV transferred to the excited ^{8}Be nucleus in the β^- decay of ^{8}Li, its recoil distance is smaller than 10^{-15} m, and thus the site of α-particle emission coincides with the position of the ^{8}Li nucleus.

An important aspect of lattice-location measurements for ion-implanted Li atoms is their potential to give insights into fundamental defect reactions in GaAs. Since lattice defects are created in the implantation process their possible interactions with the Li probes can be studied. For an explanation of the acceptor character of Li$^+$ diffused into GaAs, for instance, a reaction of interstitial Li atoms with Ga vacancies V_{Ga} has been proposed, which results in a Li displacement onto substitutional Ga sites.[3] This reaction should be favored by the Coulomb interaction, since up to triply-negative-charged states exist for V_{Ga} in the lower half of the band gap, in contrast to a reaction with an As vacancy V_{As}, which possesses neutral or positively charged states in the upper half of the band gap.[10,11] The stability range of isolated V_{Ga}, however, is not yet known unambiguously,[12] mainly because of the absence of an electron paramagnetic resonance (EPR) signal for this defect.[13] On the other hand, V_{As} could be traced by EPR and appeared to be stable up to at least 550 K,[12] whereas V_{Ga} is considered to be unstable above room temperature.[14] This is consistent with the lack of any indication for V_{Ga} in positron annihilation measurements (PAS) for as-grown material[15] and a proposed transformation of V_{Ga} into an As$_{Ga}$-V_{As} complex (where V_{As} denotes an As vacancy and As$_{Ga}$ an As antisite).[12] For electron-irradiated GaAs, on the other hand, a change in the average positron lifetime above 200 K observed by PAS has been attributed to the annealing of V_{Ga}.[16] In our lattice-location measurements we have therefore chosen implantation temperatures between 80 and 300 K, which cover this temperature range including annealing stages I and II (at 230 and 280 K, respectively), where prominent defect reactions are known to occur in GaAs.[17,18]

The implantations were performed with a well-collimated beam of ^{8}Li$^+$ ions along nonchanneled directions into Si- and Zn-doped (n- and p-type) (100)-cut GaAs crystals (1.3×10^{-3} and 4×10^{-2} Ω cm, carrier concentrations 10^{18} cm^{-3}) up to total fluences of 7×10^{11} cm^{-2} (sample a, Zn doped), 5×10^{12} cm^{-2}

(sample b, Zn doped), and 1.6×10^{13} cm^{-2} (sample c, Si doped). The experimental arrangement has been described elsewhere.[7] The emission yields of α particles not discriminated in energy were measured around $\langle 100\rangle$ and $\langle 110\rangle$ crystal axes during the implantation. In this way the radioactivity in the sample was kept in saturation by continuous implantation, the Li concentration remained as low as 10^{13} cm^{-3} throughout the measurement, and no additional impurities were introduced due to the breakup of ^{8}Be. From a consideration of projections of the diamond-type lattice along crystal axes it is evident that yield measurements around $\langle 100\rangle$ and $\langle 110\rangle$ directions are sufficient for a discrimination between substitutional (S) and tetrahedral interstitial (T) sites of the emitter atom, and also against other symmetrical interstitial sites on $\langle 111\rangle$ atomic strings [e.g., the bond center (BC), the antibonding (Q), or the hexagonal (H) site; see, e.g., Fig. 1 in Ref. 5]. Prominent dips in a $\langle 100\rangle$ direction are only possible for S and T sites; maxima in a $\langle 110\rangle$ direction only for T and H sites. For BC and Q sites directional effects are not very pronounced at all as shown by model calculations.[19] The observed $\langle 100\rangle$ and $\langle 110\rangle$ emission patterns (Fig. 1) therefore unambiguously reveal the occupancy of T and S sites at 220 and 300 K, respectively. This change in the emission anisotropies upon raising the temperature has been observed for all samples irrespective of their doping character (Fig. 2). The sharp decrease of normalized yield in the $\langle 110\rangle$ direction above 220 K to values smaller than 1, which is most pronounced for sample c, gives direct evidence for the conversion of tetrahedral interstitial into substitutional Li, whereas the slower yield increase in the $\langle 100\rangle$ direction reflects the increase of Li atoms on irregular or less-symmetric (R) sites causing only weak emission anisotropies. The temperature dependence of α-particle channeling and blocking is quite weak[20] and was neglected in the analysis; diffusion of the Li atoms can also be excluded.[3] The random fraction f_R has to be considered as including sites in damaged surroundings or in defect complexes and additionally accounts for dechanneling and low-angle scattering of the α particles. The latter contributions, however, must be rather limited, since for the implantation with the lowest fluence, f_R in total does not exceed 20% as shown below.

Within this model, respective site fractions can be calculated from the measured normalized yields $\chi^m_{\langle 100\rangle}$ and $\chi^m_{\langle 110\rangle}$ by solving the equations

$$f_T\chi^T_{\langle hkl\rangle}+f_S\chi^S_{\langle hkl\rangle}+f_R\chi^R=\chi^m_{\langle hkl\rangle}$$

under the normalization condition $f_T+f_S+f_R=1$,

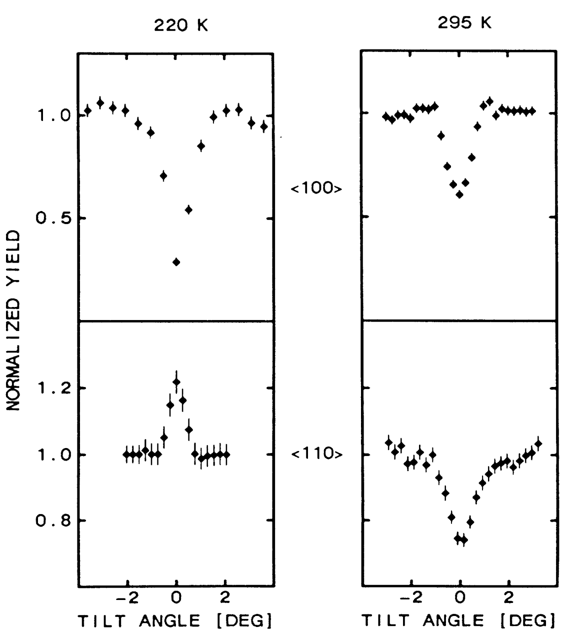

FIG. 1. Channeling and blocking effects of α particles emitted in the decay of implanted ^{8}Li in GaAs single crystals around $\langle 100\rangle$ and $\langle 110\rangle$ axes, measured at 220 K for sample a (left) and at 295 K for sample c (right).

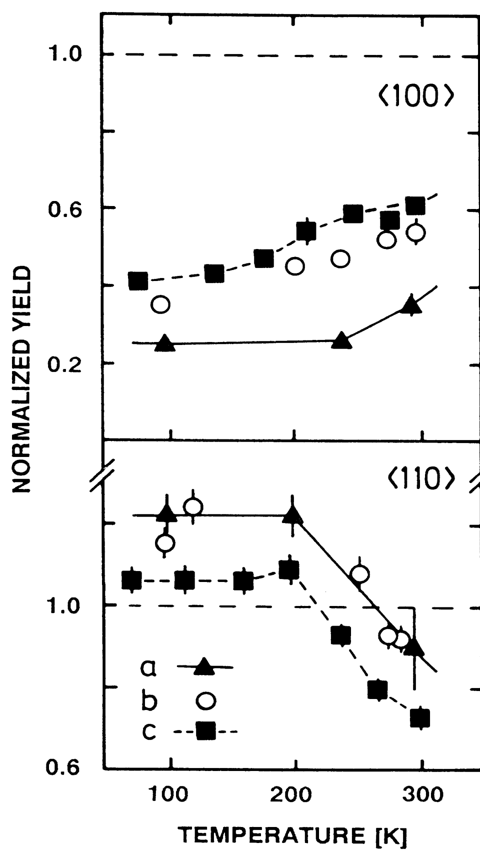

FIG. 2. Normalized emission yields of α particles emitted in the decay of ^{8}Li along $\langle 100\rangle$ and $\langle 110\rangle$ axial directions as a function of implantation temperature. The total ^{8}Li implantation fluences of samples a, b, and c increased in succession.

where $\chi^{T,S}_{\langle hkl \rangle}$ denotes the theoretically expected normalized yields for $\langle 100 \rangle$ and $\langle 110 \rangle$ directions and $\chi^R = 1$. A reasonable estimate of site populations is possible by adopting $\chi^{T,S}_{\langle hkl \rangle}$ calculated by Bech Nielsen for 1.5-MeV ^{4}He channeling in Ge,[19] since the normalized yields along low-index directions depend mainly on the atomic density, the lattice spacing along the respective atomic rows, and the vibrational amplitudes,[20] which are quite similar for Ge and GaAs. The values adopted in this way are $\chi^S_{\langle 100 \rangle} = \chi^T_{\langle 100 \rangle} = 0.095$, $\chi^S_{\langle 110 \rangle} = 0.065$, and $\chi^T_{\langle 110 \rangle} = 2.1$.[19] For the resulting site fractions, as displayed in Fig. 3, two different temperature regimes below and above 220 K can be distinguished: At the lower temperatures, f_T is the dominating well-defined fraction and is temperature independent and highest for sample a with the lowest implantation fluence. For this sample, also f_S and f_R remained constant until 220 K. A substitutional fraction of about 30% was obtained for all samples around 100 K, which for samples b and c slightly decreased up to 220 K in a way similar to f_T but in contrast to f_R, which increased considerably for those two samples. A clear positive correlation between f_R and the total implantation fluence appeared in that temperature regime. The behavior is completely different above 220 K: A sharp decrease of f_T is accompanied by an increase of f_S and also by an increase of f_R in all samples. On the whole, no major influence of the doping character was found.

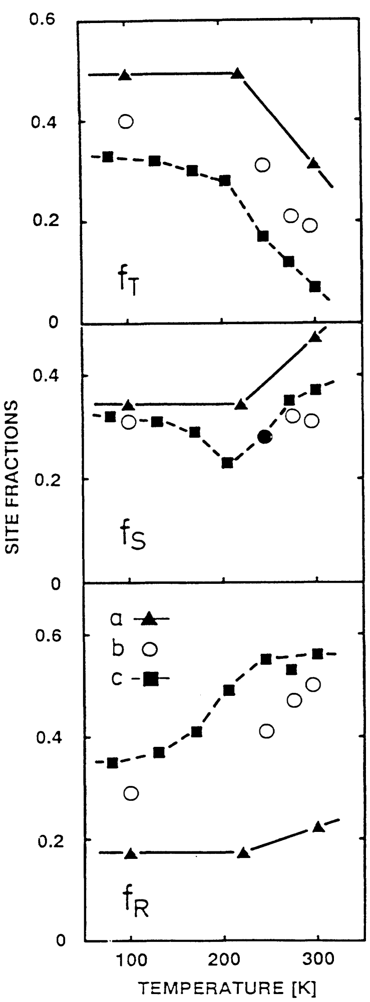

FIG. 3. Fractions of implanted Li atoms occupying tetrahedral interstitial (f_T), substitutional (f_S), and random (f_R) sites in GaAs as a function of temperature, calculated for samples a, b, and c from the $\langle 100 \rangle$ and $\langle 110 \rangle$ normalized yields displayed in Fig. 2.

The most remarkable result in our opinion is the increase of f_S above 220 K at the expense of f_T, which we attribute to a defect reaction $\mathrm{Li}_T{}^+ + V_{\mathrm{Ga}}{}^{n-} \rightarrow \mathrm{Li}_{\mathrm{Ga}}{}^{(n-1)-}$ ($n=2,3$) as proposed by Fuller and Wolfstirn.[3] In the vacancy-rich core of the displacement cascade of implanted Li ions this reaction should be favored, since the Fermi level there will be in about midgap position.[21] Thus negatively charged V_{Ga} states should be populated preferentially irrespective of the doping character of the sample. Assuming an instability of next-neighbor $\mathrm{Li}_T{}^+$-$V_{\mathrm{Ga}}{}^{n-}$ pairs already at 80 K, which seems to be reasonable in view of their Coulomb attraction and is indicated by a substitutional fraction for low implantation temperatures also, the increase of f_S above 220 K would be a result of the trapping of mobile $V_{\mathrm{Ga}}{}^{n-}$ at $\mathrm{Li}_T{}^+$. Then a migration energy of at most 0.6 eV can be estimated for $V_{\mathrm{Ga}}{}^{n-}$ assuming at least one jump of $V_{\mathrm{Ga}}{}^{n-}$ during the lifetime of the ^{8}Li nucleus and adopting a typical attempt frequency of 10^{13} s^{-1}. This interpretation is particularly tempting, since it corroborates the interpretation of the PAS results for electron-irradiated GaAs in terms of annealing of V_{Ga}, and thus may provide a key for a disclosure of the defect reactions responsible for stage-I and -II annealing. The increase of f_R in the same temperature range also at the expense of f_T is attributed to defect reactions involving more complicated defect complexes like vacancy clusters. Since a slow increase of f_R occurs already below 220 K for samples b and c implanted with higher fluences, we suggest that defect complexes like, e.g., divacancies, whose formation probability increases with ion fluence, may already be mobile and become trapped both at tetrahedral interstitial and at substitutional Li at temperatures well below stage I. The 30% substitutional Li fraction at lower temperatures is attributed to athermal processes occurring in the collision cascade during the slowing down of the implanted Li atoms.

Summarizing, direct evidence is presented for the occupancy of both tetrahedral interstitial and substitutional lattice sites by Li atoms in GaAs utilizing on-line implantation of the short-lived α emitter ^{8}Li. Furthermore, this isotope may serve as a probe for the detection of mobile $V_{\mathrm{Ga}}{}^{n-}$ via the defect reaction of $\mathrm{Li}_T{}^+ + V_{\mathrm{Ga}}{}^{n-} \rightarrow \mathrm{Li}_{\mathrm{Ga}}{}^{(n-1)-}$, which is indicated by an increase of the substitutional Li fraction to occur at $T \geqq 220$ K. It is suggested that this mobilization of $V_{Ga}{}^{n-}$ is a crucial step in stage-I and -II defect recovery in GaAs.

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