Electronic Energy Levels of Defects That Anneal in the 280-K Stage in Irradiated *n*-Type Gallium Arsenide

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Using optical-excitation minority-carrier deep-level transient spectroscopy we have studied the thermal annealing in *n*-GaAs of lattice-defect hole traps produced by 1.0-MeV proton irradiation at 120 K. We find that three hole traps, with electronic levels at 0.16 eV (of low concentration), at about 0.25 eV, and at 0.42 eV above the valence band, are removed in a thermal-annealing stage centered at about 280 K, consistent with the well known resistivity-annealing stage found at this temperature in electron-irradiated *n*-GaAs. This is the first determination of electronic energy levels of defects removed in the 280-K annealing stage of *n*-GaAs.

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The investigations by Thommen[1] on electrical-resistivity changes in *n*-type gallium arsenide irradiated at low temperatures by high-energy electrons showed removal of the irradiation-induced lattice defects in thermal-annealing stages centered at about 235, 280, and 520 K, these being denoted by him as stages I, II, and III. Other studies of resistivity and Hall effect[2,3] and positron-lifetime measurements[4,5] confirmed the removal of irradiation-induced defects in *n*-GaAs at 250-300 K and near 500 K. Majority-carrier deep-level transient-spectroscopy (DLTS) measurements on irradiated *n*-GaAs have shown that electron-trapping energy levels, called $E1$ to $E5$, lying at 0.05 to 0.9 eV below the conduction-band edge E_c, all anneal in the 500–520-K stage,[6-8] but the only irradiation-induced levels previously reported to anneal in the lower-temperature stages are that at $E_c-0.23$ eV (Ref. 9) and $E7$,[10] each of which anneals near 235 K and is of low concentration. It is clear that there must be additional electronic energy levels corresponding to defects that anneal near and below room temperature.

In capacitance-voltage studies[11] on *n*-GaAs irradiated at 85–120 K by 1.0-MeV protons we have found three stages, at 180 K (*A*), 235 K (*B*), and 280 K (*C*), of thermal annealing of irradiation-induced deep electron traps, and we have deduced that the defects which anneal in stage *C* at 280 K have electron-trapping acceptor energy levels lying near or below the middle of the GaAs band gap. By optical-excitation minority-carrier DLTS (OMCTS) applied to *n*-GaAs irradiated at 298 K by 1.0-MeV protons and quickly cooled to about 100 K, we have found[12] that the concentration of an irradiation-induced hole trap at $E_v+0.42$ eV, which we call HNI(0.42) (where HNI means "hole trap in *n*-GaAs after irradiation"), we reduced by successive temperature scans that extended to about 300 K. The OMCTS results presented here for *n*-GaAs demonstrate that the HNI(0.42) and other irradiation-induced hole traps are removed in the 280-K annealing stage *C*.

In this investigation we have used vapor-phase-epitaxy (VPE) *n*-GaAs, tin doped to near 2×10^{15} cm^{-3} (layer E212P from BDH Ltd.), and OMCTS measurements have been made by minority-carrier capacitance-transient spectroscopy, employing band-to-band optical-pulse production of holes in reverse-biased Schottky diodes.[12] The irradiations, by 1.0-MeV protons from the University of Sussex 3-MV Van de Graaff ion accelerator, were made through the gold layers of the Schottky diode samples held at temperatures close to 120 K in a cryostat that also allowed *in situ* OMCTS-DLTS measurements at 85–350 K and thermal-annealing treatments. The depth region, from the surface to about 2 μm, studied in the GaAs remained *n* type in its irradiated and irradiated-annealed states, and the optical-excitation pulse durations of 14 ms that were employed were found always to produce essentially complete saturation of the transient capacitances.

Figure 1 shows the effects of irradiation and subsequent heat treatments up to 300 K on the OMCTS spectra of the *n*-GaAs. The ordinates for each spectrum are proportional to the amplitudes of the measured capacitance transients. Spectrum *a*, obtained before irradiation, shows a significant peak near 205 K due to a grown-in hole trapping level, HNG(0.36),[12] lying at 0.36 eV above the valence-band edge. Spectrum *b* is that obtained after proton irradiation at 120 K followed by heating at 240 K for 30 min. We have found in other experiments that heating at 200–240 K following irradiation at 120 K causes changes in the OMCTS spectra, but those changes, which may be associated with the annealing stages *A* and *B*, are not considered further in this Letter. Spectra *c* to *h*, respectively, of Fig. 1 were obtained, following *b*, after 30-min heatings at temperatures of 250 to 300 K at 10° intervals.

It is seen that spectrum *b* of Fig. 1 shows irradiation-induced peaks having maxima at approximately 115

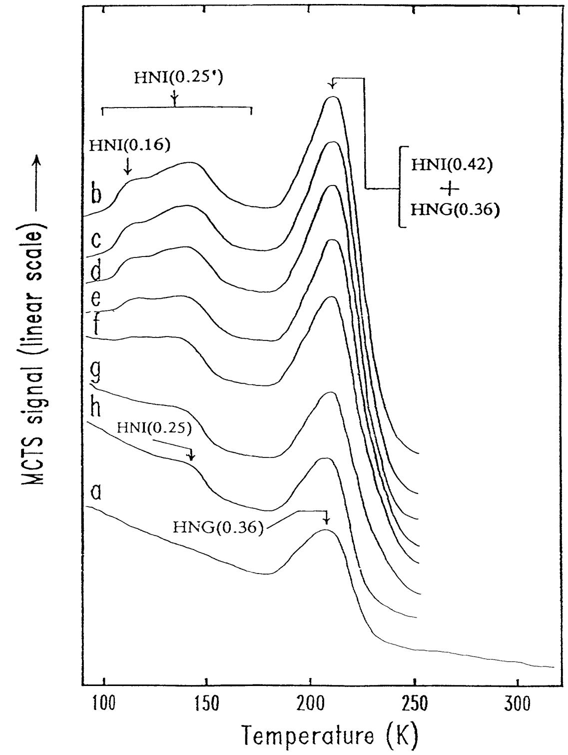

FIG. 1. OMCTS spectra for VPE *n*-GaAs: spectrum *a*, before irradiation; spectrum *b*, after 1.0-MeV proton irradiation at 120 K to a dose of 1.75×10^{11} cm^{-2} and subsequent heating for 30 min at 240 K; spectra *c*–*h*, after further thermal anneals at 250, 260, 270, 280, 290, and 300 K, respectively, each for 30 min. For clarity of presentation the spectra have been displaced with respect to each other along the ordinate axis. In obtaining these spectra, the diode was held at a reverse bias of 3 V and the signal-analyzer time constant was 28.1 ms. All the heatings following the irradiation were carried out at zero bias in the dark.

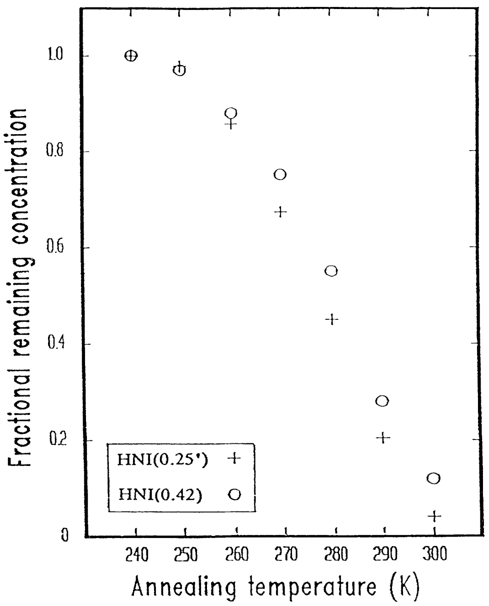

FIG. 2. Experimental data, deduced from Fig. 1 as described in the text, for the fractional concentrations of the hole trap HNI(0.25′) producing the broad OMCTS peak centered near 142 K and the hole trap HNI(0.42) producing the peak at 210 K (plusses and circles, respectively) after each of the successive isochronal, 30-min heatings at 250–300 K following 1.0-MeV proton irradiation at 120 K to a dose of 1.75×10^{11} cm^{-2} and heating for 30 min at 240 K.

(small), 142, and 210 K, the latter peak overlapping but being considerably larger than that of the grown-in trap HNG(0.36). The figure indicates that all three peaks were very much reduced by the heat treatments at 250–300 K, i.e., in a temperature range corresponding to that of the defect-annealing stage *C*.

By the standard DLTS method we have measured, without heating above 240 K, the apparent hole-emission activation energy and hole-capture cross section of the irradiation-induced 210-K OMCTS peak, and have found that they are not significantly different from those, viz., 0.42 ± 0.02 eV and $(5.4\pm0.4)\times10^{-15}$ cm^2, of the hole trap HNI(0.42) that we have observed[12] in *n*-GaAs irradiated at 298 K by 1.0-MeV protons and cooled quickly before the OMCTS measurements. We therefore identify the irradiation-induced 210-K OMCTS peak of Fig. 1 as being due to the hole trap HNI(0.42). In spectrum *h* of Fig. 1, the OMCTS peak just above 200 K is mainly due to the grown-in defect HNG(0.36) observed previously in spectrum *a*.

Considering the OMCTS peak near 142 K of spectra *b* to *h* of Fig. 1, we see that the 250–300-K heatings caused it to become both considerably weaker and considerably narrower. But neither those heat treatments nor several further hours at 300 K led to its complete removal. We find that the narrow residual peak centered at 142 K in spectrum *h* of Fig. 1 corresponds to the hole trap HNI(0.25) at $E_v+0.25$ eV [apparent hole-emission energy and hole-capture cross section, 0.25 ± 0.03 eV and $(2.5\pm0.4)\times10^{-15}$ cm^2] which we have observed[12] by OMCTS in *n*-GaAs proton irradiated at 298 K and have identified with the hole trap $H1$(0.25 eV), well known in irradiated *p*-GaAs (Refs. 8,13) and *n*-GaAs.[8,10] We interpret the broadness of the irradiation-induced OMCTS peak centered at 142 K in spectrum *b* in terms of a set of defect-related energy levels, and our annealing data as indicating that most of the defects producing those energy levels are removed by heating at 250–300 K; however, after that heat treatment, there remains the single defect energy level HNI(0.25) which is stable at 300 K. We assign to the broad peak that anneals at 250–300 K the provisional name HNI(0.25′) to indicate that it seems to have energy levels at and near that of the single level HNI(0.25).

We find that the small peak in spectrum *b* of Fig. 1 at 115 K, which was also removed by the subsequent heatings to 300 K, has an apparent hole-emisson activation energy of 0.16 ± 0.02 eV and an apparent hole-capture cross section of $(2.2 \pm 0.2) \times 10^{-17}$ cm^2; we call it HNI(0.16).

Figure 2 shows the fractional concentrations of the HNI(0.25′) and HNI(0.42) hole traps remaining after each of the successive 30-min heatings at 250–300 K. In estimating those fractional remaining concentrations we have assumed a single straight-line background for each spectrum of Fig. 1, the straight line being drawn between spectrum points corresponding to temperatures of 100 and of 245 K; from the total peak height at 142 K we have subtracted the height at 142 K of the HNI(0.25) peak (measured after heating at 300 K for 2 h) so as to obtain the strength of the HNI(0.25′) peak, and from the total peak height near 210 K we have subtracted the height at 210 K of the HNG(0.36) peak (from spectrum *a* of Fig. 1) so as to obtain the strength of the HNI(0.42) peak.

It is seen in Fig. 2 that the fractional reductions by the isochronal heatings of the irradiation-induced hole traps HNI(0.25′) and HNI(0.42) were very similar, each trap being removed in a thermal-annealing stage centered at close to 280 K.

In our previous studies[11] using capacitance-voltage measurements of the changes in the concentrations of deep electron traps in *n*-GaAs that had been irradiated by 1.0-MeV protons at 120 K, we showed that our experimental isochronal (30 min per heating) data on the removal of electron traps in the annealing stage *C* near 280 K agreed well with the results of a theoretical calculation for such isochronal annealing in a first-order annealing process having a thermal activation energy of 0.84 eV and reaction prefactor of $10^{11.6}$ s^{-1}. In the present work we find that the experimental data of Fig. 2 for the isochronal annealing of the HNI(0.25′) and HNI(0.42) hole traps are in good agreement with the experimental isochronal data obtained in our *C*-*V* electron-trap studies on the 280-K stage, and therefore match the same theoretical isochronal-annealing data. Those annealing parameters of the theoretical calculation are not significantly different from the experimental, Thommen, values[1] of first order, 0.83 ± 0.04 eV and $10^{11.6 \pm 0.6}$ s^{-1}, for the annealing near 280 K of the resistivity produced by irradiation with high-energy electrons.

We conclude that our data clearly demonstrate that the irradiation-induced hole trapping levels HNI(0.25′) and HNI(0.42), lying in the gallium arsenide band gap at about $E_v + 0.25$ eV and at $E_v + 0.42$ eV, respectively, are both removed in *n*-GaAs in the defect annealing stage observed at 280 K by resistivity measurements[1] on electron-irradiated *n*-GaAs and by our *C*-*V* measurements[11] of deep electron traps in *n*-GaAs irradiated by 1.0-MeV protons. Collisions of 1-MeV protons with lattice atoms can certainly easily cause the dual atomic displacements needed[1,14] to produce the defects that anneal in the 235- and 280-K annealing stages of electron-irradiation damage, and it is very likely that the proton-irradiation-induced electronic levels that we observe to be removed in the annealing stage *C* near 280 K are the same in kind as those produced by high-energy electrons.

We find also from the data shown in Fig. 1 that the HNI(0.16) defect is removed in the same 280-K annealing stage as the HNI(0.25′) and HNI(0.42) defects. It seems likely that HNI(0.16) is identical to the hole trap *HX*1, having apparent hole-emission energy and hole-capture cross section equal to 0.14 eV and 7×10^{-18} cm^2, observed[15] by majority-carrier DLTS studies in *p*-GaAs after irradiation by 130-keV protons at 77 K, and found to anneal in the temperature range 200–300 K.

Considering the HNI(0.42) hole trap, we have previously[12] identified this with the hole trap *H*2, at $E_v + 0.42$ eV, found in irradiated *p*-GaAs and stable at 300 K in such material.[8,13] Our present work demonstrates a reduction of the thermal-annealing activation energy of this defect from its value in *p*-GaAs to that for the defect in its more negative charge state in *n*-GaAs.

Finally, from our measured OMCTS hole-emission energies we can find the corresponding electron-trapping energies by taking account of the temperature-dependent[16] band gap of GaAs at the temperatures of the three OMCTS peaks. We deduce that a considerable part of the annealing stage centered near 280 K in irradiated *n*-GaAs is due to the removal of lattice defects having electron-trapping levels at $E_c - 1.04$ eV [the HNI(0.42) hole trap] and at about $E_c - 1.24$ eV [the HNI(0.25′) hole trap]; a smaller part of the annealing stage is caused by the removal of a defect energy level at $E_c - 1.34$ eV [the HNI(0.16) hole trap]. The magnitudes of the energy intervals between these levels and E_c explain why no corresponding majority-carrier DLTS peaks have been found: It is very unlikely indeed that an electron trapped at any such energy level could be emitted to the conduction band at a DLTS-sensitive rate at any temperature below the 280 K at which these defects are removed by thermal annealing.

Concerning the natures of defects removed in the 280-K annealing stage, we recall that the defects, *E*1 to *E*5, that anneal in the higher-temperature 500–520-K stage result from displacement of single arsenic atoms,[8,14,17] that the production of the defects that anneal in the 235- and 280-K stages requires displacement of two atoms,[1,14] that positron-lifetime experiments[4,5,18] suggest strongly that the defects annealing near and below 300 K contain vacancies, and that it has been proposed[4,5,11,18] that the defects that anneal below room temperature include defects in the gallium sublattice of the gallium arsenide. The gallium and mixed divacancies V_{Ga}-V_{Ga} and V_{Ga}-V_{As} seem therefore to be strong candidates (perhaps with various *V*-*V* separations) for the irradiation-induced hole traps observed in the present work. Another possibility is the single gallium vacancy

V_{Ga} formed by interaction between V_{Ga}-V_{As} and an arsenic interstitial;[11] theoretical studies[19,20] have suggested that gallium monovacancies indeed have electronic energy levels below midgap, including[19] $E_v+0.44$ eV, i.e., similar to our observed level at $E_v+0.42$ eV for HNI(0.42).

In summary, this work has shown that irradiation of *n*-GaAs at 120 K by 1.0-MeV protons introduces hole-trapping lattice defects that are removed in the 280-K thermal-annealing stage observed in the studies by Thommen[1] of electrical-resistivity changes in electron-irradiated *n*-GaAs and in our recent capacitance-voltage investigations[11] on proton-irradiated *n*-GaAs. The two major hole traps observed are denoted as HNI(0.25′), having a spectrum of energy levels near $E_v+0.25$ eV, i.e., near $E_c-1.24$ eV, and HNI(0.42), having a sharp level at $E_v+0.42$ eV, i.e., at $E_c-1.04$ eV. The annealing parameters of both of these agree well with those of the previous electrical-resistivity and capacitance-voltage studies. We propose that HNI(0.42) is the same as the trap *H*2 observed in irradiated *p*-GaAs and found to be stable at 300 K in that material.

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