Demonstration of gallium-defect annealing at 280 K in irradiated GaAs and $Al_xGa_{1-x}As$

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Using capacitance-voltage and deep-level transient spectroscopy measurements of electron-trap concentrations, we have compared for *n*-type $Al_{0.22}Ga_{0.78}As$ and *n*-type GaAs the thermal annealing at 85–500 K of lattice defects produced by irradiation (by 1.0-MeV protons) at 85 K. The isochronal annealing data indicate defect removal of similar magnitudes in each material in annealing stage I (near 235 K) and in annealing stage III (at 450–500 K), but that the magnitude of the defect removal in stage II (near 280 K) in the $Al_{0.22}Ga_{0.78}As$ is only about a half of the corresponding value in the GaAs. These results show that defects involving gallium atoms are removed in annealing stage II in these materials.

Because lattice defects in III-V semiconductors can have significant effects upon the electronic and optoelectronic properties of such materials, it is essential to have knowledge and understanding of their structures and behaviors. Of considerable importance in terms of defects that are unstable at 300 K in GaAs was the work of Thommen,[1] in which *n*-type GaAs was electron irradiated at or below 77 K, and the sample conductivity was then measured as a function of successive thermal annealing treatments. The conductivity was observed to increase towards its preirradiation value in three main steps, near 235, 280, and 520 K (called stages I, II, and III, respectively), each attributable to the removal and/or reconfiguration of a separate kind of defect. The production of the stage-I and -II defects was found to require a higher electron-irradiation energy than for those of stage III, thus suggesting that the former are defects produced by double displacements and that stage III is attributable to recombination in the interstitial-vacancy pairs of a single sublattice.[1,2] The defect annealing stages I and II have also been observed, by the capacitance-voltage profiling method, in *n*-type GaAs irradiated by 1.0-MeV protons.[3,4]

Studies by deep-level transient spectroscopy (DLTS) on irradiated *n*-type GaAs have shown electron traps labeled as $E1-E5$, having electronic energy levels less than 1.0 eV below the conduction-band edge, that are removed by heat treatments near 500 K,[5–9] corresponding to Thommen's annealing stage III. From the dependence of the production of $E1-E3$ on the direction of an incident irradiation electron beam with respect to crystal axes, these electron traps have been identified as defects in the arsenic sublattice.[10]

Much less information is available about the defects that anneal below room temperature. Two electron traps, detected by DLTS as levels in the upper half of the energy-band gap in irradiated *n*-type GaAs, have been observed to disappear in Thommen's stage I near 235 K,[5,11] but their combined concentration can account for only a small part of the total annealing in that temperature range. The removal near 280 K (stage II) of three hole-trapping levels has been observed in proton-irradiated *n*-type GaAs studied by optical-excitation minority carrier DLTS (OMCTS),[4,12] and these defects may account for a significant proportion of that annealing stage. Positron annihilation experiments[13] on semi-insulating GaAs electron irradiated to a high dose have shown defect annealing at 77–350 K, suggested to be due to removal of acceptor-type gallium vacancies throughout this broad temperature range. Electron paramagnetic resonance (EPR) measurements have indicated a defect suggested to be a gallium vacancy in electron-irradiated *p*-type;[14] this defect was stable at 300 K in lightly irradiated material, but somewhat unstable at 300 K when observed after a large irradiation dose, i.e., in GaAs having its Fermi energy near midgap.

In the present work, capacitance-voltage (C-V) measurements have been used to study defect annealing between 85 and 500 K in *n*-type GaAs and *n*-type $Al_xGa_{1-x}As$ ($x \simeq 0.22$) after 1.0-MeV proton irradiation at 85 K, for the purpose of revealing defect-removal processes sensitive to the elemental species of component group-III lattice atoms. We find that the defect annealing in stage II (near 280 K) is very different in the two materials, whereas that in each of the stages I and III (near 235 and 500 K, respectively) is almost independent of the elemental composition. Our results strongly suggest that stage-II defects in GaAs and $Al_xGa_{1-x}As$ are complexes involving displacements on the group-III sublattice.

Schottky barriers were fabricated for this study by the evaporative deposition of moderately transparent ($\sim$40 Å) gold Schottky contacts ($\varphi = 1$ mm) onto *n*-type epitaxial GaAs and $Al_xGa_{1-x}As$ ($x = 0.22 \pm 0.01$), with alloyed tin Ohmic contacts made to the n^+ substrates. The GaAs sample material was a vapor-phase-epitaxy- (VPE) grown, tin-doped [$n = (2-3) \times 10^{16}$ cm^{-3}], 5.0-μm epilayer (G623PH, from BDH Ltd., UK), and the $Al_{0.22}Ga_{0.78}As$ material was a metal-organic-VPE (MOVPE) epilayer, of thickness 2.0 μm, Se doped to $n = (3-4) \times 10^{16}$ cm^{-3} and capped with a thin (100-Å) *n*-type layer (CB274, provided by the III-V Semiconductor Facility at the University of Sheffield, UK). The apparent immobile-charge concentration-distance profile, $N^+(x)$, in the samples before and after irradiation and after the successive heatings was obtained, via

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capacitance-voltage measurements, using a Shandon Southern SS-367 impurity profile plotter (IPP) of capacitance test signal $\omega_C = 100$ kHz and modulation $\omega_{dC/dV} = 1$ kHz; in determination of the distance x from the Schottky contact and of the N^+ values, account was taken of the compositional dependence of the material dielectric constant.[15] A DLTS system[16] provided concentration and thermal emission information on majority-carrier trapping levels. Gallium arsenide and AlGaAs Schottky diode samples were irradiated together at 85 K by 1.0-MeV protons from the University of Sussex 3-MV Van de Graaff accelerator, and then given isochronal (15-min) heatings from 100 to 500 K in 10-K steps, with $N^+(x)$ remeasured at 85 K after each such heating.

We have found that the $N^+(x=0.5\ \mu m)$ values in both the GaAs and $Al_{0.22}Ga_{0.78}As$ decreased linearly with irradiation dose at 85 K (these decreases certainly being due to trapping of majority-carrier electrons by irradiation-induced lattice defects) over the dose range $(0-6.0)\times 10^{12}\ H^+\ cm^{-2}$, after a small initial increase in the AlGaAs that we have quantitatively determined to be due to the efficient capture of irradiation-induced holes h^+ by DX_{Se} centers.[17] In order to negate a possible effect of electron recapture on the DX_{Se} centers during the annealing treatments, all N^+ data reported here were obtained at 85 K after a 10-min sample illumination, employing a high-intensity red ($h\nu_{peak} = 1.95$ eV) light-emitting diode (LED) to produce saturating electron and hole concentrations by band-to-band transitions.

Figure 1 presents DLTS spectra from proton-irradiated GaAs and $Al_{0.22}Ga_{0.78}As$ samples. Other spectra obtained showed no DLTS peaks in the $Al_{0.22}Ga_{0.78}As$ between 20 and 100 K. Our assignments, shown, of the $E1-E4$ peaks in the $Al_{0.22}Ga_{0.78}As$ spectrum have been made by comparison with previous results on electron-irradiated $Al_xGa_{1-x}As$.[18-21] We have noted the expected stage-III annealing of $E3$ defects at 400–500 K in our GaAs samples, and by investigating the annealing of the $E1$, $E2$, and $E3/E4$ defects in the $Al_{0.22}Ga_{0.78}As$ (Fig. 2) we have found that the corresponding stage-III annealing in this material occurs at 350–500 K, this being a somewhat wider temperature range than in the GaAs.

The results of simultaneous isochronal-annealing measurements on postirradiation N^+ values in the two materials are shown by the open symbols in Fig. 3. The features of the GaAs data are clearly recognizable from those of previous studies[1,3] with Thommen's stage I near 235 K, a sharp stage II near 280 K, and stage III towards 500 K. For the $Al_{0.22}Ga_{0.78}As$, the stages I and III, very similar in temperatures and magnitudes to those in the GaAs, are evident, except that, as in Fig. 2, the AlGaAs stage III begins near 350 K. Concerning the slight reverse recoveries of the N^+ values below stage I in the two materials, preliminary experiments suggest that these are true defect-restructuring processes, rather than carrier-trapping effects, but their origin is as yet unknown.

A major observation from Fig. 3 is, however, that the magnitude of the annealing near 280 K, i.e., in stage II, in the $Al_{0.22}G_{0.78}As$ is considerably smaller than that in the GaAs.

When interpreting N^+ changes, it is important to consider the sensitivity of the C-V profiling technique to the defects present.[22] At a given temperature, in uniform n-type material well away from the Schottky contact, N^+ is equal to the net shallow donor concentration $N_d - N_a$, provided that deep levels are absent. The introduction of deep donor levels acts to increase the measured N^+ value by an amount equal to the deep donor concentration only when these levels are able to ionize rapidly enough to follow the IPP modulation signal $\omega_{dC/dV}$. Conversely, deep acceptors cause an N^+ reduction if their thermal emission rate is significantly lower than that frequency. Therefore, in order to make a quantitative comparison between rates of damage production in GaAs and $Al_{0.22}Ga_{0.78}As$, it is necessary to take account of any differences between the two materials in the electron emission rates of lattice defects at the 85-K measurement temperature. For this purpose, $N^+(x)$ profiles for both materials were recorded at a series of temperatures between 30 and 310 K after annealing to 350 K. Two large steps in the $N^+(0.5\ \mu m)$-vs-temperature plot were observed for the GaAs, these being centered near 40 and 90 K and corresponding to the levels $E1$ and $E2$, respectively. In the $Al_{0.22}Ga_{0.78}As$, comparable effects were observed only above 130 K; since $E1$ and $E2$ defects are believed to be donors,[23] this indicates that they have no influence on 85-K $N^+(x)$ measurements for the

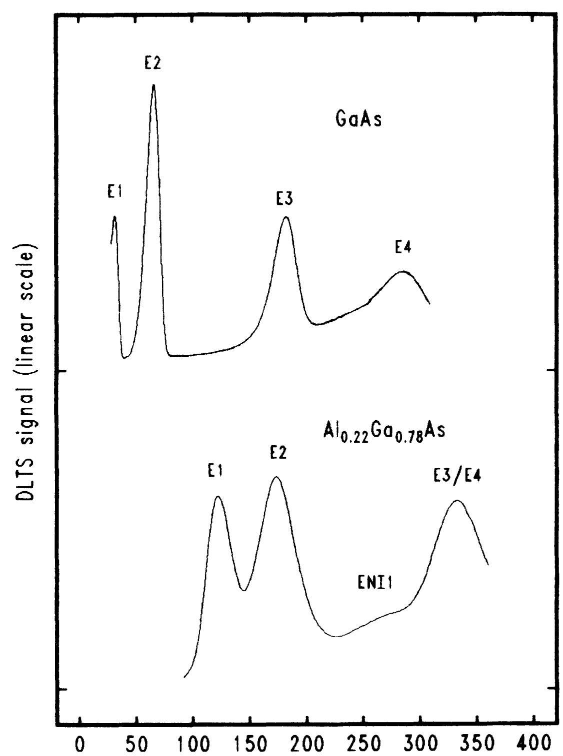

FIG. 1. DLTS spectra for n-type GaAs and n-type $Al_{0.22}Ga_{0.78}As$ after irradiation by 1.0-MeV protons at 85 K and annealing treatments near 350 K. The DLTS emission rate window was 20.2 s^{-1}. The irradiation-induced defects $E1-E4$ are shown in each case; a further trap, here labeled ENI1, also produced by the irradiation and stable at 500 K, is seen in the $Al_{0.22}Ga_{0.78}$ As spectrum.

$Al_{0.22}Ga_{0.78}As$. The total N^+ increase in the GaAs between 30 and 85 K was found to be $(0.35\pm0.05)\times10^{16}$ cm^{-3}, and the effect of correcting the GaAs data by this amount, i.e., excluding $E1$ and $E2$ from the data, is shown by the solid triangles in Fig. 3. Since the concentrations of $E1$ and $E2$ were not determined for these samples during stage-III annealing, here we omit the GaAs N^+ data points for 410–490 K; but that for 500 K is displayed as measured since we know from further experiments that $E3$ defects, and presumably therefore also $E1$ and $E2$ defects, are removed by similar heatings to 500 K. We find by the same procedure that the initial irradiation-induced rates of decrease of N^+ with dose were very similar in the GaAs and $Al_{0.22}Ga_{0.78}As$.

The significant result of this study, seen clearly in Fig. 3 by comparing the data which contain no effects of the $E1$ and $E2$ defects, i.e., square symbols ($Al_{0.22}Ga_{0.78}As$) and solid triangles (GaAs), is the strong perturbation of Thommen's annealing stage II (near 280 K in GaAs) as a result of the substitution of aluminum for gallium, and it is seen that the magnitude of the annealing near 280 K in the $Al_{0.22}Ga_{0.78}As$ is only about half of that for the GaAs. Stage I (near 235 K), on the other hand, is affected at most only slightly, and the removal of DLTS-detected levels in stage III similarly indicates a relative insensitivity of this stage to group-III atomic species.

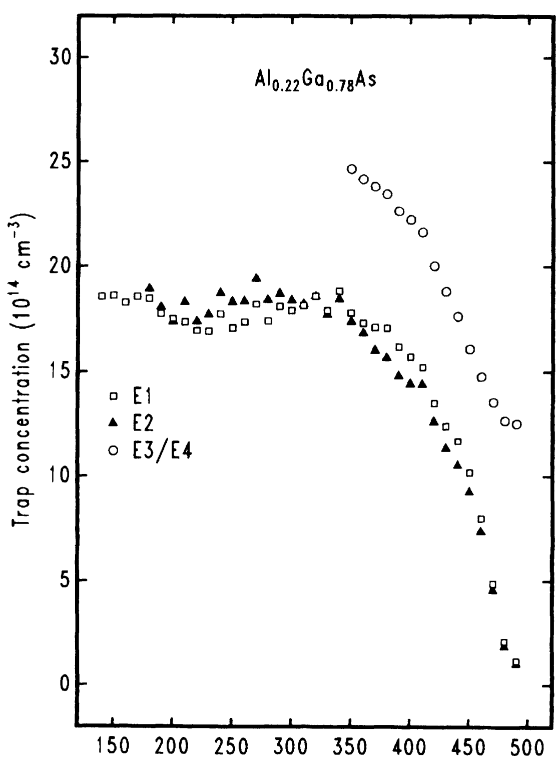

FIG. 2. Concentration values, as obtained from the DLTS peak heights, of the $E1$, $E2$, and $E3+E4$ electron traps in $Ga_{0.22}Ga_{0.78}As$, as functions of isochronal (15-min) annealing temperature after irradiation at 85 K by 1.0-MeV protons to a dose of 5.5×10^{12} $H^+ cm^{-2}$. Due to the broadness of these DLTS peaks in this material these data give underestimates of the true concentrations.

The annealing stage III in GaAs is believed to represent the recombination of arsenic interstitial-vacancy pairs,[9] and, given that each arsenic vacancy has four group-III atoms as nearest neighbors, the observed temperature broadening of the stage-III annealing in the $Al_{0.22}Ga_{0.78}As$ can be understood as due to local variations in the nearest-neighbor gallium/aluminum ratio. It is evident, however, that the much greater difference between the stage-II annealing in the two materials indicates that the stage-II defects are more directly dependent on the species of group-III atom; we reach the clear conclusion that the defects that anneal in stage II in $Al_{0.22}Ga_{0.78}As$ and in GaAs involve irradiation-displaced gallium atoms.

We note, furthermore, that annealing of a defect involving only a single gallium atom should lead to a reduction of the magnitude of the 280-K annealing by at most 22% in the $Al_{0.22}Ga_{0.78}As$ compared to that in GaAs: our data therefore indicate the involvement of more than one gallium atom per defect in the 280-K recovery. A gallium antisite-vacancy close pair (Ga_{As}-V_{Ga}) with a

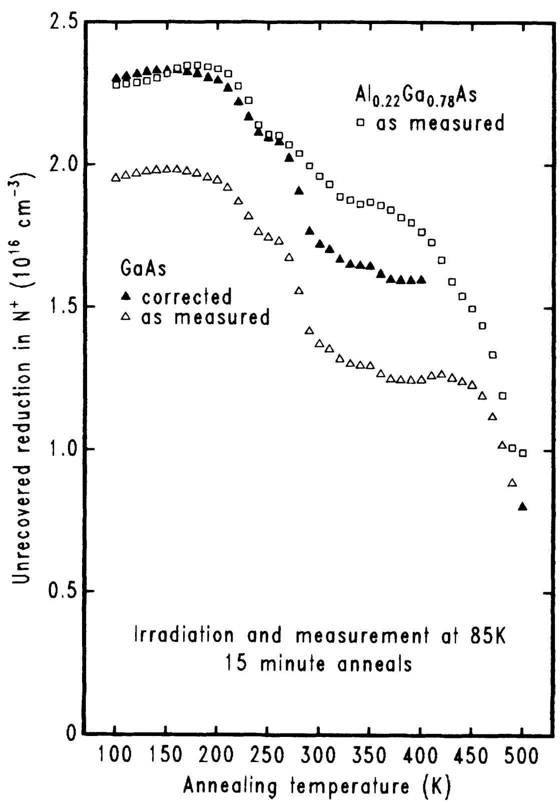

FIG. 3. Open triangles and squares: recoveries of the postillumination, 85-K values of N^+ (at 0.5 μm from the Schottky contact) in the GaAs and $Al_{0.22}Ga_{0.78}As$, respectively, as functions of isochronal (15-min) annealing temperature after simultaneous irradiations of the two materials at 85 K to a dose of 4.6×10^{12} H^+cm^{-2}. Those irradiations had caused the postillumination $N^+(0.5\ \mu m)$ values to fall from 2.70×10^{16} to 0.77×10^{16} cm^{-3} for the GaAs and from 3.39×10^{16} to 1.14×10^{16} cm^{-3} for the $Al_{0.22}Ga_{0.78}As$. Solid triangles: recovery of the postillumination N^+ values at 0.5 μm in the GaAs after correction, as described in the text, to remove the influence of the $E1$ and $E2$ defects from the GaAs plot.

nearby arsenic interstitial As_i, produced by displacement of one gallium atom and an adjacent arsenic atom, would be consistent with our data, the annealing of such a complex involving the movement of the Ga_{As} atom away from its three group-III nearest neighbors as it jumped back into its original group-III site. We suggest that this annealing reaction occurs near 280 K wherever all the three nearest neighbors of the Ga_{As} are also gallium atoms, and thus that, as we observe, the annealing in the 280-K stage will be significantly smaller in $Al_{0.22}Ga_{0.78}As$ than in GaAs. This model is in agreement with previous proposals[1,2] that the defects annealing below 300 K in GaAs involve double displacements, and that positron-lifetime experiments[13] show that they contain gallium vacancies (or negatively charged V_{Ga} complexes).

The results of the present work indicate that aluminum-related defects analogous to the stage-II gallium-related defects remain in the AlGaAs up to at least 350 K. Figure 3 shows that the total concentration of defects annealing at 350–500 K is not greatly different in the two materials, perhaps suggesting that, because of larger bond strengths, the defects involving aluminum atoms are stable even at 500 K, i.e., at a temperature significantly above that for defects involving only gallium atoms.

In summary, our experimental data comparing defect annealing in GaAs and $Al_{0.22}Ga_{0.78}As$ after irradiation at 85 K clearly demonstrate the involvement of gallium atom defects in the annealing stage II centered near 280 K, and suggest that such defects are not involved in the stage-I annealing near 235 K. Our results support the identification of stage-III annealing at 450–500 K with removal of arsenic-related defects.

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