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Optical identification of the gallium vacancy in neutron-irradiated gallium arsenide

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Gallium arsenide grown by the metallorganic-chemical-vapor-deposition method was irradiated at room temperature with fast neutrons in the fluence range 10^{12} to 3×10^{15} cm^{-2} (1.00 MeV equivalent fluence in gallium arsenide). The effects of neutron irradiation were studied by photoluminescence (PL) spectroscopy in the energy range 0.5–1.55 eV. In the samples irradiated to 3×10^{13} cm^{-2} and higher fluences, we observe a transition at 1.4745±0.0003 eV in the PL spectrum recorded at 2 K. Its intensity increases with neutron fluence. Upon increasing the temperature at which the PL is recorded, the transition shifts to higher energies, and an additional higher-energy component appears. At 20 K, the energy of the doublet is 1.4750 and 1.4786±0.0003 eV. The temperature dependence suggests that the low-energy component is a donor-acceptor pair and the high-energy one is a transition from the conduction band to the acceptor. We identify the acceptor as the gallium vacancy (V_{Ga}). We deduce its energy to be at 42.2±0.3 meV above the valence band. Replicas involving the 37-meV LO phonon were observed. Isochronal annealing was performed on samples irradiated to 1×10^{13} and 3×10^{13} cm^{-2}. Samples which were irradiated and then annealed to 500 and 550 °C exhibited the same doublet and their phonon replicas in the PL spectrum. This suggests that V_{Ga} is dissociated at 500 °C from a complex formed during neutron irradiation. The effect of neutron irradiation and of isochronal annealing on other transitions observed by PL is presented. These transitions include the sharp transition at 0.702 eV, which has been associated with the arsenic antisite defect ($\mathrm{As}_{\mathrm{Ga}}$), and the broad transition at approximately 1 eV. The modifications in the infrared PL spectrum are discussed in parallel with deep-level transient-spectroscopy data.

INTRODUCTION

Gallium arsenide (GaAs) is a direct-gap semiconductor whose gap at the Γ point is 1.5192±0.0002 eV at 4.2 K.[1] In such a material, the point defects are the vacancies, interstitials, and antisites. Amongst these point defects, the arsenic vacancy (V_{As}) is a donor and its energy is thought to be at 45 meV below the conduction band.[2,3] The arsenic and gallium interstitials As_I and Ga_I are also expected to be donors, but the gallium vacancy (V_{Ga}) is expected to be an acceptor.[4–8] The arsenic antisite ($\mathrm{As}_{\mathrm{Ga}}$) has been associated with the midgap level called $EL2$.[9] The energy of the gallium antisite ($\mathrm{Ga}_{\mathrm{As}}$) has been placed at 78 meV above the valence band.[10] To our knowledge, the Ga_I energy and the As_I energy have not been experimentally determined. In this work, we identify V_{Ga} and estimate its energy to be 42.4±0.3 meV above the valence band. Associations of these point defects give rise to more complex ones. The energies of some binary defects have been given.[11]

One problem encountered in identifying defects is that their concentration may be too low. In this case, one may increase some defects by irradiating the sample. For this reason, we study in this work the defects introduced by fast neutron irradiation. Since the neutron is a neutral particle, it interacts with the lattice through the short-range nuclear force. Thermal neutrons can cause nuclear transmutation but this process is negligible at the low-thermal neutron fluences used in this work. The primary effect of energetic neutron irradiation is to displace atoms and create vacancies and interstitials. The deflected incident neutron can interact with another lattice site and create more vacancies and interstitials. In addition, the dislodged atom, which interacts with the lattice electromagnetically, can cause further damage. Further, phonons, other native defects, interfaces, and surfaces lead to the recombination of these radiation-induced defects. Nevertheless, we expect to observe vacancies and other point defects in neutron-irradiated samples, partic-

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ularly at high fluences.

Using photoluminescence (PL) spectroscopy, we find in the irradiated samples a doublet transition (1.4745 ± 0.0003 eV at 2 K and 1.4782 ± 0.0003 eV at 10 K) whose intensity increases with fluence. The temperature dependence of the PL signal suggests that the lower-energy component is a donor-acceptor pair (DAP) transition and the higher-energy component is a transition (e-A) from the conduction band to an acceptor A. From the sharpness of the transition we deduce that the defect created is a point defect. This acceptor can only by V_{Ga}. We determine the energy of the defect created by the neutron irradiation to be 42.2 ± 0.3 meV above the valence band.

Although we study defects which are introduced by irradiation, defects are also found in as-grown samples. In the characterization by PL of samples grown by molecular-beam epitaxy, transitions were found at 1.4724 ± 0.0004 eV at 1.7 K and at 1.4763 ± 0.0004 eV at 11.6 K.[12] These transitions were attributed to a DAP and to e-A, respectively, but the shallow acceptor was not identified. Its ionization energy was determined to be 43.2 ± 0.4 meV. It is quite possible that the transitions observed in Ref. 12 are the same as those reported here. The difference is that in our samples, which were grown by the metallorganic-chemical-vapor-deposition method (MOCVD), the defect is introduced by irradiation, while in Ref. 12 it was found in unirradiated samples grown by molecular-beam epitaxy. Also, in Ref. 12, another shallow unidentified acceptor was found whose ionization energy is 25.2 ± 0.1 meV.

Defects are characterized in part by their energy and their symmetry. These properties can be considered fundamental to the lattice and should not vary from sample to sample. However, the defects can interact among themselves and their distribution in a given sample can depend on its history. Thus, the defects in samples grown by different techniques can appear very different in nature. Moreover, the detection method can determine which defects are observed. Using positron-annihilation lifetime measurements, it is observed that vacancies are primary grown-in defects in liquid-phase-encapsulated Czochralski (LEC) GaAs.[13] However, observation of these vacancies in LEC GaAs by optical techniques such as PL, to our knowledge, has not been reported. It is suspected that both gallium- and arsenic-related defects are created during electron irradiation of GaAs,[14] but considerably more information is available on defects associated with the arsenic sublattice.[11] Evidence for damage to the Ga sublattice has been given.[14] The present work provides more data on defects associated with the gallium sublattice. V_{Ga} has recently been observed by electron paramagnetic resonance (EPR) in electron-irradiated p-type GaAs.[15]

There are several reports on the effects of neutron irradiation of GaAs. Coates and Mitchell[16] studied the effect on electrical and optical properties. The development of deep-level transient spectroscopy (DLTS) revealed states within the forbidden gap. It was shown[17] that neutron irradiation introduces the U band and the $EL6$ trap. Although the nature of these traps was not given, it was found that both traps were removed after isochronal annealing between 400 and 500 °C. In another work,[18] it was confirmed that the U and $EL6$ traps anneal out between 450 and 500 °C, however, a third peak appeared after annealing. In these two publications, LEC material was used and the neutron fluence level was 3.1×10^{15} cm^{-2},[17] and 5×10^{14} to 5×10^{16} cm^{-2},[18] respectively. Using liquid-phase-epitaxy (LPE) -grown samples and fluence of 1×10^{14} cm^{-2}, it was found that neutron irradiation introduces the broad U band in LPE material,[19] but $EL6$ was not observed. After annealing to 350 °C, the intensity of the U band did not change, but at 450 °C, it was reduced by half.[19] Some of the present authors have also studied neutron damage in MOCVD GaAs by DLTS.[20] The U band and the $EL6$ trap are introduced at the lowest fluence level investigated, i.e., 10^{12} cm^{-2}, and the $EL14$ trap appears at 3×10^{14} cm^{-2}.

EPR reveals the symmetry of the defects. Using LEC material and fluences of 2×10^{15} to 2.5×10^{17} cm^{-2}, it was found that the EPR signal consists of a quadruplet attributed to the antisite $\mathrm{As}_{\mathrm{Ga}}^{+}$ and a singlet attributed to V_{Ga}^{-}.[21] It was found that the singlet signal starts to anneal out at 300 °C, and disappears completely at 450 °C.[22] The quadruplet signal begins to anneal out at 450 °C, is reduced by a factor of 10 at 600 °C, and then remains constant up to 800 °C. In another investigation,[23] it was suggested that $\mathrm{As}_{\mathrm{Ga}}$ and V_{Ga} form an association and that V_{Ga} is dissociated at 450 °C from the complex defect introduced by neutron irradiation. Using Zn- (4.6×10^{16} cm^{-3}) doped GaAs, V_{Ga} has been detected by EPR in electron-irradiated (fluence of 2×10^{16} to 1×10^{18} cm^{-2}) GaAs; it occupies trigonal symmetry and its charge state is -2.[15]

Photoluminescence spectroscopy has been used to detect $\mathrm{Ga}_{\mathrm{As}}$.[10] The transition at 702 meV has as final state a defect with tetrahedral symmetry. The authors proposed this defect to be the arsenic antisite.[24,25] The effect of neutron irradiation on this transition to the arsenic antisite is reported here. Some of the present authors have studied by PL the damage in neutron-irradiated GaAs,[26–29] but PL has not been used to study the physical processes occurring during the annealing stages. In this work, we study isochronal annealing in neutron irradiated samples by PL spectroscopy. The present work confirms the EPR finding[23] that V_{Ga} is dissociated at 450 °C from the complex defect introduced by neutron irradiation.

Another optical technique used to study deep levels is infrared-absorption spectroscopy. The absorption between 1 and 1.3 eV in LEC material contains detailed structure,[30,31] whose interpretation is still under debate. The equivocal interpretation of the transitions in the unirradiated samples obscures the physical processes occurring during neutron irradiation in LEC GaAs.[31]

As noted earlier, our experiments are performed on annealed samples. As the temperature is raised, the weakly bound binary associations get dissociated first, and those with larger binding energy are dissociated at higher temperatures. Besides discovering the kinetics of the defects in the crystal, one can in principle isolate the defects and identify them. We present the PL spectra of samples which were irradiated and annealed at different temperatures in this work.

Despite the large amount of work that exists in the literature on neutron-irradiation-induced defects in GaAs, a clear picture of the defects created by the irradiation has not emerged. This is possibly because the samples studied, for example, LEC GaAs, are not the purest available and the fluence level needed to observe an effect due to radiation is relatively high. In the MOCVD samples studied here, the lowest fluence that modified the PL spectra occurred at about 10^{13} cm^{-2}. This fluence is at least two orders of magnitude lower than that used by other authors;[21,22] moreover, we use a different detection method. The experimental conditions are more suitable in the present work which have perhaps aided in identifying the elemental defect, V_{Ga}, reported here.

ENERGY-LEVEL DIAGRAM

We show in Fig. 1 the energy-level diagram of GaAs at the Γ point. Absorption measurements[30] on semi-insulating LEC material have indicated a broad structure at approximately 1 eV. This transition is indicated as 1. Although the traps $EL3$ and the broad band U are inferred from DLTS measurements, the final states of transition 1 are not known. Sharp structures are superimposed on the broad one. The sharp features have been interpreted as transitions from $EL2$ to the states above the conduction band, such as shown in transition 2.[30] By PL, one observes both sharp and broad transitions in semi-insulating LEC material. The broad transitions (3 and 4 in Fig. 1) involve the midgap state $EL2$,[25] but the sharp transition (5 in Fig. 1) has been attributed to $EL2_{n=2} \Rightarrow EL2_{n=1}$.[24] In transition 3, the initial state is broad, contrary to transition 4 whose final state is broad. Sharp transitions from the conduction band to shallow-acceptor states and from shallow-donor states to the valence band have also been observed by PL.[10,32] In Fig. 1, we show only the transitions e-V_{Ga} (transition 6) and its DAP (transition 7) along with similar transition e-C (transition 8, conduction band to the carbon acceptor) and its DAP (transition 9). We also show in Fig. 1 a transition (indicated as 10) from the conduction band to a deep level, a hole trap, which are usually called Hn, n being an integer.[33] Transition 10 is more likely to be seen in PL than in absorption. The broad level L has been observed by DLTS but not by PL in irradiated samples.[34]

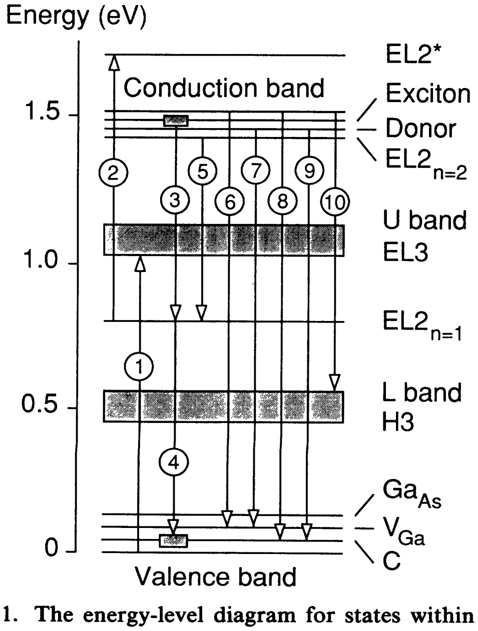

FIG. 1. The energy-level diagram for states within the forbidden zone in GaAs. The spacing of the levels is not to scale.

EXPERIMENT

The samples used in this experiment were cut from a wafer three inches in diameter grown at the Epitronics Corp, by MOCVD. The substrate was undoped LEC material. A 2-μm-thick buffer layer of undoped GaAs was deposited next. The 4-μm-thick top layer was doped with silicon to a nominal concentration in the 10^{15}-cm^{-3} range. We measured $(n_D - n_A)$ to be $(3\pm1)\times10^{15}$ cm^{-3}, and the peak mobility at 70 K to be (3.4 ± 0.1) $\text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$. The $EL2$ concentration was measured to be $(4\pm2)\times10^{13}$ cm^{-3} by the DLTS technique.

The irradiations were performed at the Fast Burst Reactor, Aberdeen Proving Ground, MD. The fluence was measured using sulfur dosimetry. The fluence values quoted here are in terms of 1 MeV equivalent fluence in silicon. Recent recalibration of the source indicates that this fluence should be multiplied by 0.96 to obtain the 1 MeV equivalent damage in GaAs.[35] The energy spectrum of the neutrons reveals that the percentage of thermal neutrons is negligible.[36] Since the effects due to nuclear transmutations are detected by PL at thermal neutron fluences of 10^{17} and 10^{18} cm^{-2},[37] we do not expect to observe transmutations at the fluences used in this work.

The PL in the infrared was recorded with a Fourier Transform Infrared Bomem spectrometer, in which the 647-nm krypton-ion laser line was the excitation, and the detectors were Ge or InSb. The PL spectra were recorded from 2 to 40 K using a Cryoindustries bath cryostat. The PL spectra in the band-gap region were also excited with a titanium sapphire laser and recorded with a Jarrell Ash 1-m single monochromator. The detector was a RCS C31034 photomultiplier. In the latter setup, the temperature was varied through a CTI Cryogenics closed cycle refrigerator.

The DLTS measurements were performed with a POLARON BIORAD DL 4600 System. The description of the method has been given.[38] The basic idea of DLTS is that upon heating a sample, electrons trapped at an impurity site can be released to the conduction band or holes to the valence band. Since our samples were n doped, we could determine electron traps, although from a change of sign of the signal, one can deduce a hole trap. The signal measured was the change in capacitance across a Schottky diode. One can measure the concentration, activation energy, and electron capture cross section of the defect with this technique. Unfortunately, the activation energy measured in DLTS is not the same as that observed in PL, because the DLTS measurements are performed at higher temperature.

We have not investigated higher fluences because of technical problems i.e., the PL signal becomes too weak to detect at fluences above 3×10^{15} cm^{-2}. Also the resistance becomes too large for DLTS work at fluences above 3×10^{14} cm^{-2}.

RESULTS AND ANALYSIS

A. Photoluminescence near the band-gap region in unirradiated samples

We show in Fig. 2 the PL spectrum near the band-gap region of an as-grown sample, at 20 K (top) and at 2 K (bottom). The features observed are as follows:[32,39]

(1) The free exciton at 1.5156 eV, which is more visible at 20 than at 2 K.

(2) The bound exciton, which at 20 K appears as a broad feature at 1.5137 eV, but which has structure at 2 K. These structures are attributed to recombinations at donor and acceptor sites.

(3) The transition *e*-*C* at 1.4931 eV.

(4) The DAP at 1.4892 eV, in which the donor is mostly likely silicon and the acceptor is carbon.

(5) The phonon replica (PR) of the *e*-*C* and DAP transitions at 1.4536 and 1.4560 eV. The phonon-assisted transitions involve the 37-meV LO phonon.[40]

Figure 2 shows the behavior of an *e*-*C* and its DAP transitions with temperature. With carbon as an acceptor in these results, we note that at 2 K, the DAP and its replica are strong in intensity, but that at 20 K, the *e*-*C* transition and its phonon replica are stronger than the DAP and its PR. This is because at higher temperatures the donors tend to be ionized, consequently the donor population decreases and that of the free carriers increases.

At 2 K, the excitonic region has structure which is shown in Fig. 3. Previous studies on MOCVD samples[39] revealed transitions at 1.5156 eV, attributed to the free exciton, at 1.5145 eV attributed to the recombination of the exciton at a donor site (D^0-X), at 1.5137 eV attributed to a donor hole transition (D^0-h), at 1.5133 eV attributed to the recombination of the exciton at an ionized donor site (D^+-X), and at 1.5125 eV attributed to the recombination of an exciton at an acceptor site (A^0-X). We observe transitions at 1.5156, 1.5145, 1.5137, and 1.5125 eV. The two strong peaks in Fig. 3 are (A^0-X) and (D^0-X).

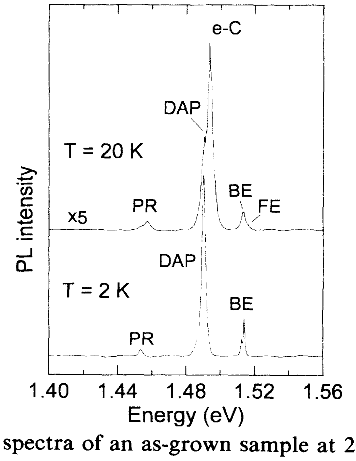

FIG. 2. PL spectra of an as-grown sample at 20 K (top) and at 2 K (bottom). The symbols are described in the text. The upper curve has been multiplied by five.

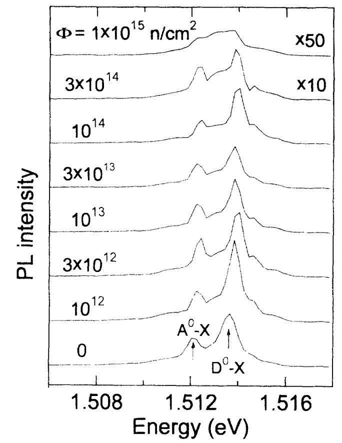

FIG. 3. The 2-K PL spectrum in relative intensity units, in the excitonic region as a function of neutron irradiation fluence Φ.

B. Effect of neutron irradiation on the PL spectrum near the band-gap region

The effect of neutron irradiation on the excitonic region is shown in Fig. 3. We observe subtle relative inten-

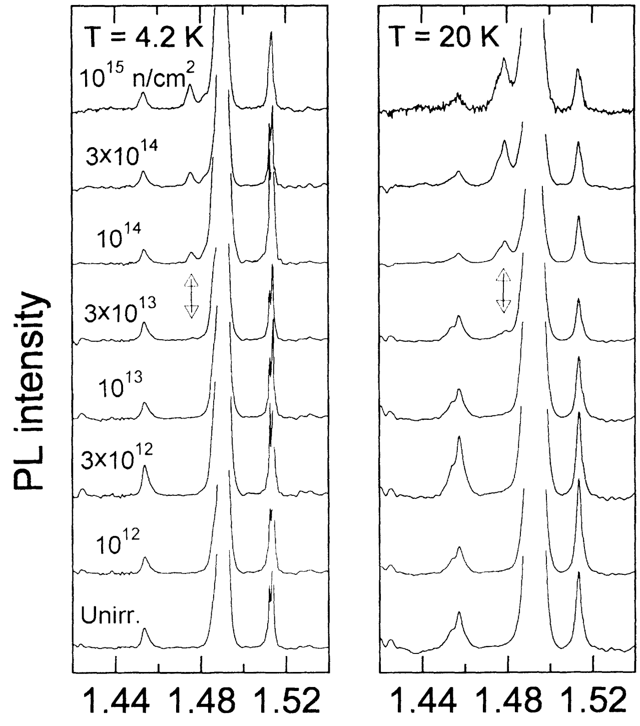

FIG. 4. Effect of neutron irradiation on the PL spectrum at 4.2 K (left) and at 20 K (right). The peak that appears at 1.4745 eV at a fluence of at least 3×10^{13} cm^{-2} (indicated by an arrow in the figure at left) is a radiation-induced defect. At 20 K the transition is a doublet. The fluences indicated also apply to the spectra on the same horizontal line at right.

sity changes with radiation. No additional peaks are observed. The absolute intensity decreases markedly at higher fluences. PL intensity changes in neutron-irradiated GaAs have been discussed recently.[20]

We show in Fig. 4 the effect of neutron irradiation on the PL spectrum near the band-gap region. The spectra were recorded at 4.2 and 20 K. At a fluence of 3×10^{13} cm^{-2} and higher a peak is observed at 1.475 eV which gets stronger relative to the other peaks as the fluence increases. This peak is indicated by an arrow in Fig. 4, and it is a singlet at 4.2 K. However, at 20 K, this new transition is a doublet, with the component at 1.4786 eV being much stronger than that at 1.4750 eV. The difference in energy of the doublet and the temperature dependence suggest that the low-energy component is a DAP. Further details on the temperature dependence are given in the section on annealed samples. At higher fluences, we also observe a weak feature at 1.482 eV in the PL spectra recorded at 4.2 K. By working with *n*-type GaAs doped with silicon to 10^{16} cm^{-3}, this peak, though undetectable in the unirradiated samples, gains intensity as the fluence is increased. Its measured energy in the latter sample of 1.4824 eV corresponds well with the DAP transition in which the acceptor is silicon ($\mathrm{Si_{As}}$).[32] Further work is in progress.

C. PL spectrum in the 0.50–0.87-eV infrared region

The main contribution of this work is the identification of V_{Ga} as determined by PL in the band-gap region. Due to the variety of defects that can form by irradiation, and since these defects may be detected optically, we have recorded the PL spectrum in the infrared region.

Figure 5 shows the PL spectrum in the region 0.5–0.87 eV in an as-grown as well as in irradiated GaAs samples. A broad feature with a maximum at about 0.61 eV is observed. This broad feature consists of transitions at 0.61 and 0.68 eV from a shallow donor state to the midgap native defect $EL2^0$ and from the midgap state to an acceptor state, respectively.[24] These are transitions 3 and 4, respectively, in Fig. 1. The noise that appears at 0.56 eV comes from the low response of the system in this energy range. The optical system response goes through a zero at 0.56 eV due to a beam-splitter absorption. Superimposed on this continuum are four sharp transitions separated by 37 meV, the strongest of which is at 0.702 eV. These are LO phonon-assisted transitions, and the zero phonon line, barely visible in our spectra, occurs at about 0.740 eV. These four LO phonon-assisted transitions are better seen in the sample which was irradiated to 3×10^{14} cm^{-2}. The peak at 0.702 eV has been attributed to the $EL^0_{n=2}$ to $EL^0_{n=1}$ transition.[24] This feature has been described as "the sharpest signature of $EL2$."[24] Another sequence of transitions separated by 11 meV is also observed; this energy corresponds to the transverse-acoustic phonon at the X point of the Brillouin zone (TA_X).[41] These TA-assisted transitions are indicated by arrows in the spectrum obtained from the sample irradiated to 1×10^{12} cm^{-2}. Although the absolute intensities of the PL spectra are not given in Fig. 5, we observe that the PL intensity tends to increase at lower fluences before decreasing at higher fluence. Similar behavior has been reported.[20] The shape of the transitions does not seem to be affected.

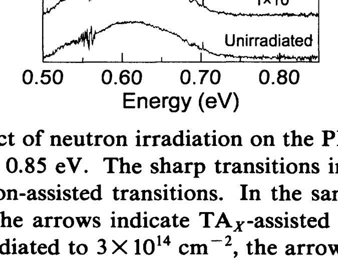

FIG. 5. Effect of neutron irradiation on the PL spectrum between 0.50 and 0.85 eV. The sharp transitions indicated by arrows are phonon-assisted transitions. In the sample irradiated to 10^{12} cm^{-2}, the arrows indicate TA_X-assisted transitions. In the sample irradiated to 3×10^{14} cm^{-2}, the arrows indicate LO-assisted transitions.

D. PL spectrum in the 0.8–1.1-eV infrared region

The PL spectrum of the unirradiated sample is shown in Fig. 6. A very weak broad signal appears at approximately 1 eV. The increased noise that appears at high energy is due to the weak system response in this energy range. The effect of neutron irradiation on the PL spectrum is also shown in Fig. 6. The weak broad peak that appeared in the unirradiated sample is barely visible at a fluence of 3×10^{12} cm^{-2}, suggesting that a deep level may be removed by neutron irradiation. However, a distinct broad feature appears at about 1.03 eV at higher fluences. It is particularly strong at a fluence of 3×10^{13} cm^{-2}. At still higher fluences, its intensity decreases, and its maximum seems to shift to lower energies. This suggests that neutron irradiation is restructuring the level at approximately 0.5 eV above the valence band, or that transition 10 in Fig. 1 is sensitive to neutron irradiation. Other evidence that neutron irradiation restructures deep levels has been presented.[20]

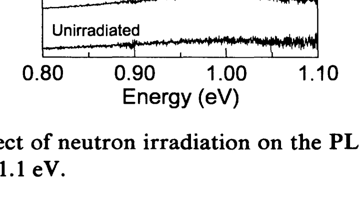

FIG. 6. Effect of neutron irradiation on the PL spectrum between 0.8 and 1.1 eV.

Absorption in semi-insulating samples of GaAs has been observed at 1.039 eV.[30,31] One could hypothesize that in the PL process, electrons in the conduction band reach the state at 1.039 eV optically or through radiationless transition, and then a photon having 1.039 eV is emitted. From our results, this would mean that the irradiation is increasing the defect concentration whose energy is approximately at 1 eV. However, it was observed that the optical absorption decreased as a function of neutron fluence in LEC material, which led to the conclusion that neutron irradiation destroyed some traps, and attributed to $EL2$.[31] Our results indicate the opposite effect, that is, the peak at 1.03 eV is strongest at a fluence of 3×10^{13} cm^{-2}. We thus retain the idea that in the PL experiments, the transition at about 1 eV corresponds to a transition from the conduction band to a state created by the neutron irradiation at approximately 0.5 eV above the valence band. This idea is confirmed by DLTS results, as discussed below.

We do not observe any change in the PL spectra between 1.1 and 1.4 eV with irradiation.

EXPERIMENTS ON ANNEALED SAMPLES

We annealed the samples for 30 min at temperatures varying from 50–550 °C in steps of 50 °C. Higher anneal temperatures were not used to avoid evaporation of the arsenic atoms. We show in Figs. 7(a) and 7(b) the effect of annealing on the PL spectrum of an unirradiated sample and on a sample irradiated to 10^{13} cm^{-2}, respectively. Referring to Fig. 7(a), we do not observe any signal at 1.4746 eV after annealing to 550 °C, although the intensity tends to weaken. In contrast, in Fig. 7(b), after annealing to 500 °C, we observe a peak at 1.4746 eV and its phonon replica (PR) at about 1.440 eV. Its temperature dependence (see Fig. 8 and Table I) suggests a DAP transition for the low-energy component and an e-A transition for the high-energy one. Moreover, the energy of the acceptor state coincides with that induced by neutron irradiation at fluences greater than 3×10^{13} cm^{-2} as shown in Fig. 4. Thus the new peak observed in Fig. 7(b) must be attributed to the neutron irradiation and not to the annealing.

The data presented in Table I are very similar to that given in Ref. 12 for the acceptor in the sample labeled B.

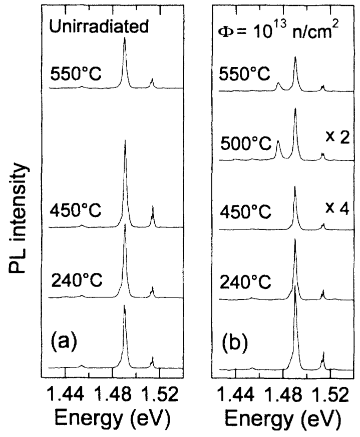

FIG. 7. Effect of isochronal annealing on the PL spectrum at 4.2 K of an (a) as-grown GaAs sample and (b) a GaAs sample irradiated with neutron to a fluence of 1×10^{13} cm^{-2}. The peak at 1.4745 eV appears only in samples which were irradiated and annealed to 500 K and above.

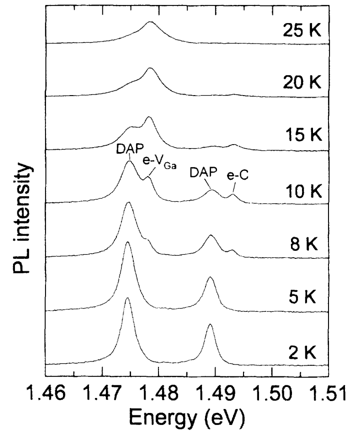

FIG. 8. The effect of temperature on the PL transition at 1.4745 eV (2 K) induced by neutron irradiation at a fluence of 10^{13} cm^{-2}. The sample was annealed to 500 °C. The transition at 1.4891 eV (2 K) is attributed to the carbon impurity.

TABLE I. The energy values (eV) obtained by PL, of transitions to the carbon and V_{Ga} acceptor states.

Temperature (K)	D^0-V_{Ga}	e-V_{Ga}	D^0-C	e-C
0[a]	1.4748±0.0005	1.4785±0.0005	1.4893±0.0005	1.4932±0.0005
2	1.4745±0.0003		1.4891±0.0003	
5	1.4746±0.0003		1.4891±0.0003	
8	1.4747±0.0003		1.4892±0.0003	1.4931±0.0003
10	1.4748±0.0003	1.4782±0.0003	1.4893±0.0003	1.4932±0.0003
15	1.4750±0.0003	1.4785±0.0003	1.4896±0.0003	1.4932±0.0003
20	1.4750±0.0003	1.4786±0.0003	1.4892±0.0003	1.4934±0.0003
25	1.47480±0.0003	1.4787±0.0003		

[a] The value at $T=0$ K has been obtained by extrapolation.

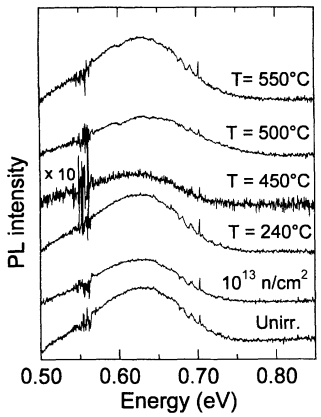

FIG. 9. The effect of annealing on the PL spectrum of a sample irradiated to 10^{13} cm^{-2} in the range 0.5–0.85 eV. Lowest trace is for an unirradiated sample.

To summarize our data, first there is a slight shift to higher energies of the low-energy component as the temperature is increased. At higher temperatures, the occupation number of the DAP high-energy levels increases, and thus the shape of the transition is deformed to favor the high-energy side. Second, the transition *e*-*A* also shifts to higher energies as the temperature is raised. This is due to increase in the kinetic energy of the electrons with temperature. Third, the *e*-*A* transition appears at higher temperatures consistent with the fact that the donors tend to be ionized at higher temperatures. We remark that the transitions to the carbon acceptor behave in similar fashion and details of these transitions have appeared.[42]

To complete our analysis of the transition at 1.4745 eV, we have obtained PL spectra at 2 K in which the laser power was varied. We observed that as the power increases, the transition shifts to the blue as was the case when the temperature was increased but the power was constant. The blue shift confirms the DAP nature of the transition. In addition, we observed that the 1.4745-eV transition saturates more quickly than the 1.4893-eV transition. At low powers, the DAP at 1.4745 eV in which V_{Ga} is the acceptor is stronger than the DAP at 1.4893 eV in which *C* is the acceptor (Fig. 8), but at higher powers, DA(V_{Ga})P is weaker than DA(*C*)P (Fig. 7). The saturation of a DAP depends on the acceptor concentration and on the lifetime of the transition. The latter factor depends on the distance between the donor and acceptor. At the moment we cannot analyze the power dependence of the PL intensity quantitatively.

We observe that neutron irradiation has an effect on the excitonic structure. As shown in Figs. 3 and 7(b), the transition called (*A*-*X*) is enhanced in both irradiated and in irradiated and annealed samples. This confirms that neutron irradiation is introducing acceptor states.

We show in Fig. 9 the very weak effect of annealing on the infrared PL spectrum between 0.50 and 0.85 eV. Assuming that the transition at 0.702 eV is a signature of $\mathrm{As}_{\mathrm{Ga}}^{+}$, i.e., of *EL*2,[24] we note that neutron irradiation does not affect *EL*2 in our samples in the fluence range studied here.

We show in Fig. 10 the effect of annealing on the infrared spectrum between 0.8 and 1.1 eV. We note that the peak at about 1 eV is enhanced by the annealing. Similar to the peak at 1.4745 eV of Fig. 7(b) it persists after annealing to 550 °C.

RESULTS OF DLTS EXPERIMENTS

The DLTS spectra of unirradiated samples have been published.[20,38] We find in the DLTS spectra of unirradiated samples two peaks, called *EL*2 and *EL*12. In recording a DLTS signal, the temperature was scanned from 100 to 450 K, which led to some annealing. We show in Fig. 11 the DLTS signal from a sample irradiated to 10^{13} cm^{-2} and annealed to 240 °C for 30 min. Figure 11 shows six curves corresponding to different rate windows. The method of analyzing the raw data has been presented.[38] At such low annealing temperatures, the spectra of unannealed and unirradiated samples are essentially the same, except for the tail on the low-temperature side of the *EL*12 peak (see Fig. 11).

The peak at 780 meV has been called *EL*2. It is known that this trap involves the $\mathrm{As}_{\mathrm{Ga}}^{+}$ defect,[34] but it may also contain another point defect, most likely As_I.[43] On irradiation in the fluence range studied here, its concentra-

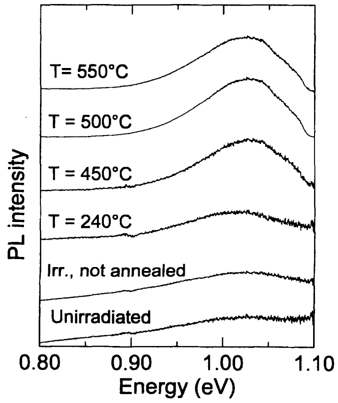

FIG. 10. The effect of annealing on the PL spectrum of a sample irradiated to 10^{13} cm^{-2} in the range 0.8–1.1 eV. Lowest trace is for an unirradiated sample.

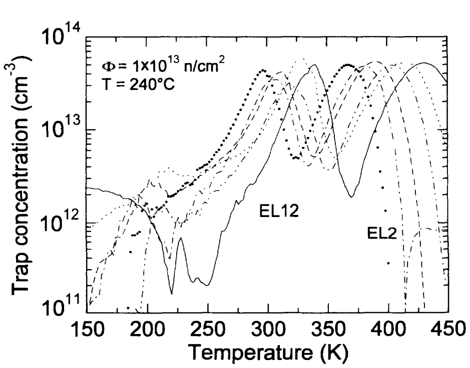

FIG. 11. DLTS signal from a sample irradiated to 10^{13} cm^{-2} and annealed to 240 °C. The rate windows were 1000, 400, 200, 80, 50, and 20 s^{-1}.

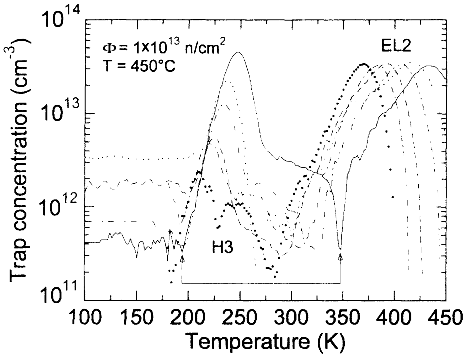

FIG. 12. DLTS signal from a sample irradiated to 10^{13} cm^{-2} and annealed to 450 °C. The signal that appears between 170 and 345 K, i.e., between the arrows, is reversed in sign, suggesting it is a hole trap. The rate windows were the same as in Fig. 11.

tion changes by at most a factor of 2. It has also been shown that its concentration is independent of annealing up to 870 °C.[34] We thus conclude that the defects induced by neutron irradiation at a fluence of 10^{13} cm^{-2} are not related to $EL2$. The peak at 0.770 eV has been labeled $EL12$.[9] Our studies show that it is a surface-related trap.[38]

In the irradiated samples, we observe $EL2$, $EL12$, and the U band, $EL6$, and $EL14$. The concentration of these defects as a function of fluence for our samples has been reported earlier for our samples.[20]

The effects of annealing at 450 °C on the DLTS signal are shown in Fig. 12. At the annealing temperature of 450 °C, a hole trap is observed. We calculate that its energy is 0.50±0.04 eV above the valence band, implying that it is $H3$.[33] The observation of this hole trap supports the interpretation of the broad IR PL peak at 1.03 eV as a transition from the conduction band to a state at about 0.5 eV above the valence band. Annealing at higher temperatures removes this hole trap, but another broad electron trap appears. Its large breadth renders its analysis difficult (Fig. 13 in the temperature range 200–325 K). We observe that $EL2$ is not affected by temperature annealing up to 550 °C, consistent with previous measurements.[34,44]

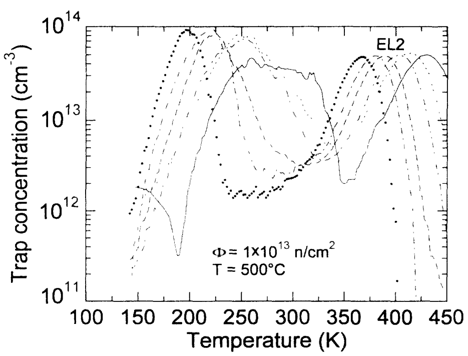

FIG. 13. DLTS signal from a sample irradiated to 10^{13} cm^{-2} and annealed to 500 °C. Annealing at this temperature reintroduces a signal due to an electron trap (the signal at lower temperatures).

DISCUSSION

There are both sharp as well as broad peaks in the PL spectra of neutron-irradiated GaAs. The features shown in Figs. 2 and 3, whose half-width are of the order of a few meV's belong to the first category. Figure 5 shows both sharp features, e.g., that at 0.702 eV, and broad features, e.g., that at 0.61 eV. The half-width of the latter is of the order of 100 meV. The peak that appears in Fig. 8, i.e., after neutron irradiation and annealing, has a full width at half maximum, simply denoted as the width, of 2.6 meV, and is therefore to be described as sharp. This line is very likely due to a point defect, because the DAP transition involving carbon in Fig. 8 has a similar width. Also, the equally sharp transition at 0.702 eV has been attributed to the point defect ${\rm As}_{\rm Ga}^{+}$ and we measure its width to be 1.3 meV. This width is also comparable to the widths of the PL peaks in the excitonic region as shown in Fig. 3. Indeed, we attribute the peak in Fig. 8 to $V_{\rm Ga}$ because the other point defects $V_{\rm As}$, ${\rm Ga}_I$, and ${\rm As}_I$, are donors[4–8] and the defect ${\rm Ga}_{\rm As}$ has been identified as an acceptor.[10] In these measurements, the instrumental resolution was nominally 0.5 meV. The widths quoted contain instrumental broadening. Other complex associations, such as $V_{\rm Ga}+{\rm Ga}_{\rm As}$, are acceptors,[45] but these are excluded because their optical signature is expected to be broad.

We measure the energy of $V_{\rm Ga}$ to be 42.2±0.3 meV above the valence band. It is also known that $V_{\rm As}$ has its energy at about 45 meV below the conduction band. One could hypothesize that the transition observed at 1.4745±0.0003 meV is $(V_{\rm As}\text{-}h)$. However, the separation between the transition observed at 1.4745±0.0003 eV and its companion which appears at higher temperatures is 3.4±0.6 meV at 10 K. This separation is typical of that between the conduction band and shallow donors in GaAs, as determined by the bound exciton transitions. We maintain that the transition at 1.4745±0.0003 eV involves a shallow donor and an acceptor and not a deep donor and the valence band.

A sharp peak at 1.03 eV has also been observed in infrared absorption.[30] That work[30] shows that a sharp peak at 1.039 eV is superimposed on the broad peak centered at approximately 1.039 eV. The sharp line is called the zero phonon line and it is associated with a transition from $EL2$ to a state above the conduction band (transition 2 in Fig. 1). We do not observe the sharp zero phonon line in this PL work. Energy considerations should allow it since the energy of the laser excitation used (1.919 eV) in this work is larger than the energy (1.779 eV) of the level called $EL2^*$ in Fig. 1. However, momentum conservation might forbid it because absorption of the incident 1.919-eV photon in PL does not take place at the Γ point.

The peak at 1.03 eV in the IR PL spectrum of unirradiated as well as irradiated samples has a width of about 100 meV, and is therefore broad, suggesting that it is more complex than a point defect. We recall that signals in PL tend to originate at the conduction band and those in IR absorption at the valence band. It is unusual for absorption to originate at midgap states. It is surprising that the broad transition observed in PL, namely, that in Figs. 6 and 10, coincides with the broad one observed in absorption.[30,31] Our results on PL suggest that the broad transition observed in infrared absorption at about 1 eV could also originate at a complex defect like $H3$, in which case the final state is the conduction band. Identification of the broad peak at 1.03 eV is not possible at present, and neutron irradiation does not give further clues. As pointed out earlier, the PL intensities at 1.4745 and 1.03 eV in neutron-irradiated GaAs increase on annealing at 500 °C. We have interpreted the peak at 1.4745 eV as due to V_{Ga}. The origin of the IR peak is not known. One key unanswered question is whether the growth of these structures on annealing is due to the dissociation of one or more types of complex defects.

Both the simple and complex defects observed by DLTS have been described as sharp and broad. In particular, the U band is broad and it has been interpreted as a complex trap.[19] The other traps that we observe are in general sharper than the U band.

The appearance in DLTS of a hole trap in samples which have been irradiated and annealed at 450 °C precedes the appearance in PL of V_{Ga} in the same samples annealed at 500 °C. One possibility is that $H3$ is a chemical association involving V_{Ga}, for example,

$$\mathrm{As}_{\mathrm{Ga}}^{+}-V_{\mathrm{Ga}}^{-}$$

or

$$\mathrm{Ga}_I-V_{\mathrm{Ga}} \ .$$

Although it has been proposed that the first association is formed in neutron-irradiated LEC GaAs (Ref. 23) and it may be related to $EL2$, we show that the midgap state, as monitored by PL at 0.702 eV or by the DLTS peak having an activation energy of 780±40 meV ($EL2$), is not sensitive to neutron irradiation in the fluence range studied here. Thus, V_{Ga} is not associated with the midgap state $EL2$. The second association, which is an acceptor, has been proposed in electron-irradiated GaAs.[14] To verify that $H3$ contains Ga_I, one should monitor Ga_I. However, its energy is not known at present. Besides these binary defects, more complex ones are also possible.

V_{Ga} has been observed by EPR.[15] In that work, its symmetry (trigonal) and charge state (-2) have been given. We cannot determine either of these properties from our experiments.

The energetic neutron creates a vacancy and an interstitial simultaneously. Although we have identified V_{Ga}, one should in principle observe V_{As}, As_I, and Ga_I. The fact that we have not observed all these could be due to defect-dependent factors such as (1) the recombination rate, (2) the diffusion rate, (3) the transition probability, and (4) accessibility of the transition energy. Also, purer samples without LEC substrates might yield higher signal-to-noise ratio in the infrared PL spectra and thus give more information on these defects.

SUMMARY

(1) The transitions that appear in the PL spectrum at 1.4745±0.0003 (2 K) and 1.4782±0.0003 eV (10 K) in neutron-irradiated samples suggest that the first is a DAP in which the acceptor is V_{Ga}, and the second is a transition from the conduction band to V_{Ga}.

(2) The same transitions appear in the PL spectrum of a sample irradiated to 10^{13} cm^{-2} and annealed to at least 500 °C. This suggests that V_{Ga} is dissociated from a complex at 500 °C.

(3) DLTS experiments reveal that a hole trap $H3$ whose activation energy is 0.504±0.040 eV is created in irradiated samples annealed to 450 °C.

(4) The transitions at 1.4745 and 1.03 eV in the PL spectra of neutron-irradiated GaAs increase on annealing the samples to 500 °C. The identification of the broad peak at 1.03 eV is not known.

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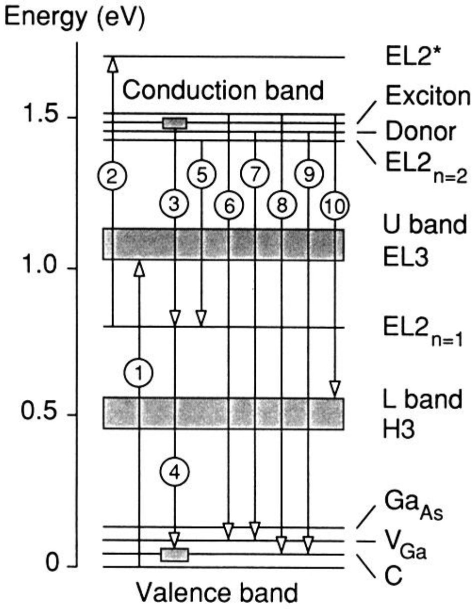

FIG. 1. The energy-level diagram for states within the forbidden zone in GaAs. The spacing of the levels is not to scale.