RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 11 15 APRIL 1988-I

Neutron irradiation effects on the infrared absorption of the *EL*2 defect in GaAs: New interpretation for the intracenter transition

M. O. Manasreh
Systran Corporation, 4126 Linden Avenue, Dayton, Ohio 45432

D. W. Fischer
Air Force Wright Aeronautical Laboratories, Materials Laboratory (AFWAL/MLPO),
Wright-Patterson Air Force Base, Ohio 45433-6533

B. C. Covington
Department of Physics, Sam Houston State University, Huntsville, Texas 77341

(Received 12 January 1988)

The effect of neutron irradiation on the optical properties of the *EL*2 center in semi-insulating GaAs was studied using the infrared absorption technique. The results show that the absorption band known as the intracenter transition between 1.03 and 1.27 eV is decreased by neutron irradiation. This absorption band is interpreted as a charge-transfer transition between the $\mathrm{As_{Ga}}$ antisite and an X component(s) assuming that $EL2 \equiv \mathrm{As_{Ga}}+X$. The neutron irradiation increases the $\mathrm{As_{Ga}}$ antisite concentration and reduces the *EL*2 concentration. The reduction of the *EL*2 concentration is due to the decrease of the X-component concentration. The zero-phonon line observed at 1.039 eV may not be an internal optical excitation within the isolated $\mathrm{As_{Ga}}$ antisite.

There are several debates regarding the identification of the intrinsic mid-gap defect known as *EL*2 in semi-insulating GaAs. One of the oldest controversies arises from the resemblance between the electron-paramagnetic resonance (EPR) spectrum of the *EL*2 center in its normal state and that of the isolated $\mathrm{As_{Ga}}$ antisite defect.[1] Recent controversies involve the assignment of the zero-phonon line[2-6] (ZPL) in the infrared (IR) absorption and the method[7-11] of transforming the *EL*2 center from the normal state ($EL2^0$) to the metastable configuration ($EL2^*$).

The information provided by the different experimental techniques has so far been unable to give a complete picture of *EL*2. Part of the difficulty in identifying the atomic configuration of *EL*2 is that no direct experimental observation of $EL2^*$ has been reported. Since optical, electrical, or paramagnetic properties of $EL2^*$ have not been observed, its microscopic structure is still speculative in nature. Several models[12-17] have been proposed to account for the experimental observations reported for *EL*2. Most of these models rely on the atomic displacement which occurs during the transformation of $EL2^0$ to $EL2^*$. Nevertheless, the theoretical and experimental consensus is that *EL*2 involves a complex defect of which the $\mathrm{As_{Ga}}$ antisite is an essential component.

The near IR absorption is one of the most complicated aspects of the *EL*2 defect. It contains different absorption bands corresponding to various optical excitations.

The purpose of this Rapid Communication is to report new experimental results on the effects of neutron irradiation on the optical properties of *EL*2. A new interpretation for the absorption band known as the intracenter transition will be suggested. It is also speculated that the ZPL may not arise from the isolated $\mathrm{As_{Ga}}$ antisite.

Three single crystals of semi-insulating GaAs were cut from a boule grown by the liquid-encapsulated Czochralski technique. The IR absorption measurements were obtained using a CARY 2300 spectrophotometer. A closed-cycle refrigerator was used to cool the samples in the dark to 9.5 K. The monochromatic spectrophotometer light was weak enough ($\sim 5\times10^{-5}$ W/cm^2) so that a noticeable photoquenching effect is not induced. The *EL*2 defect was quenched by an external 100-W quartz-halogen lamp. Two of the samples were neutron irradiated at the Texas A&M University Research Reactor in a flux of 4.3×10^{12} n cm^{-2}s^{-1} for certain periods of time as indicated in Table I. The impurities introduced by neutron transmutation doping are also shown in Table I.

The IR absorption spectra of *EL*2 before and after photoquenching are shown in Fig. 1 for the three samples. The *EL*2 absorption spectra are superimposed on a background and residual absorptions. The background absorption is increased as the neutron irradiation dose is increased and it is considered as being due to the induced irradiation damage. The residual absorption after a complete photoquenching of *EL*2 is observed even before neutron irradiation [see Fig. 1(c)] and found to be sample dependent. Its magnitude depends on the postgrowth annealing. This residual absorption is not observed in p-type GaAs samples, and we speculate that it is due to the isolated $\mathrm{As_{Ga}}$ antisite. This assumption seems quite reasonable because it has been shown previously that the antisite concentration increases with the amount of neutron irradiation[1] similar to the increase in residual absorption as shown in Fig. 1 (spectra presented by broken lines) and Table I. It should be pointed out that other defects such as *EL*0 may be involved in the residual absorption. The IR absorption of *EL*0 has never been reported and we be-

TABLE I. Characteristics of the semi-insulating samples used in the present study. Samples were cut from the same boule. All samples are $12\times12\times1.8$ mm^3.

	Sample number		
	G101[a]	G102	G103
Irradiation time (s)	···	3.679×10^2	3.679×10^3
[Ge] (cm^{-3})[b]	···	5.0×10^{13}	5.0×10^{14}
[Se] (cm^{-3})[b]	···	7.714×10^{13}	7.691×10^{14}
Relative concentration of *EL*2[c]	1	0.938	0.786
Relative integrated area of total *EL*2[d]	1	0.963 ± 0.010	0.858 ± 0.010
Relative integrated area of As$_{\mathrm{Ga}}$[e]	1	6.0 ± 0.3	72 ± 2

[a] Control sample.

[b] Impurities were introduced by neutron transmutation doping.

[c] The concentrations of *EL*2 were calculated using Martin's curve (Ref. 21).

[d] The total integrated areas of *EL*2 absorption were obtained between 6000 and 11 800 cm^{-1} from Fig. 2.

[e] The total integrated areas of As$_{\mathrm{Ga}}$ were obtained from Fig. 1 after *EL*2 is completely quenched. Area was measured under broad absorption between 6000 and 11 780 cm^{-1}.

lieve that *EL*0 is IR inactive in this region.

An apparent shift (sharp increase of the IR absorption near the band edge) in the band-edge position toward lower energy is observed for the sample G103. This phenomenon is found to be severe in the IR absorption measurements of samples irradiated for a period of time larger than 3.679×10^4 s. Although the IR absorption measurements are difficult to perform for samples with high neutron irradiation doses, the EPR measurements[1,18-20] confirm the presence of large isolated As$_{\mathrm{Ga}}$ antisite concentrations ($\sim10^{18}$ cm^{-3}).

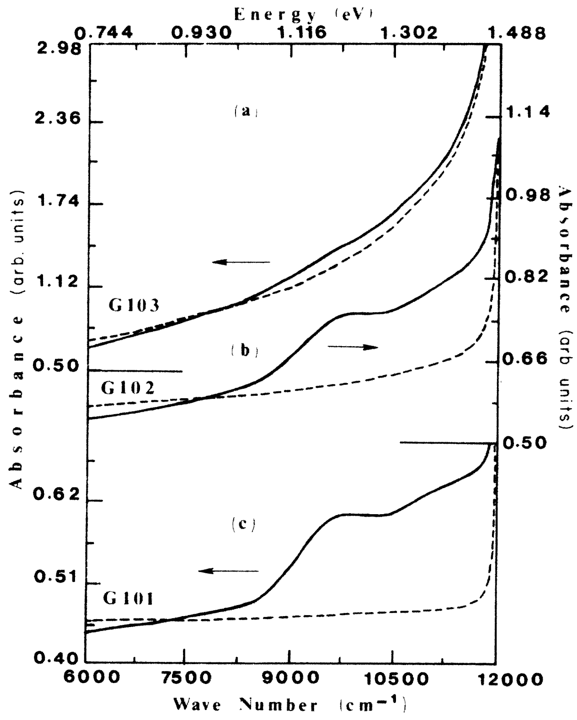

FIG. 1. The IR absorption spectra of *EL*2 before (solid lines) and after (broken lines) photoquenching at 9.5 K. The samples were neutron irradiated in a flux of 4.3×10^{12} n cm^{-2} s^{-1} for (a) 3.679×10^3 s, sample G103, (b) 3.679×10^2 s, sample G102, and (c) no irradiation, control sample G101. The broken line spectra are believed to be due primarily to the isolated As$_{\mathrm{Ga}}$ antisite photoionization.

The spectra obtained after photoquenching were subtracted from the spectra obtained before photoquenching for each sample (see Fig. 1) and the results are shown in Fig. 2. It is clear that the neutron irradiation decreases the *EL*2 concentration (Fig. 2) while it increases the isolated As$_{\mathrm{Ga}}$ antisite concentration.[1,18-20] The latter is in-

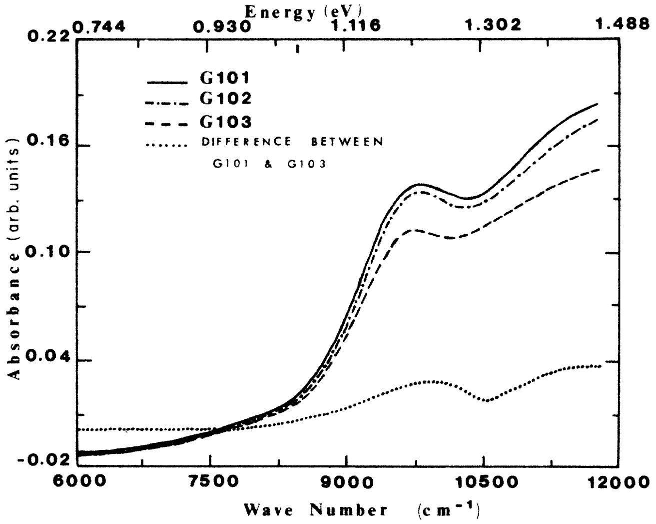

FIG. 2. The *EL*2 IR absorption difference spectra for the three samples. These curves were obtained by subtracting the spectra after photoquenching from the spectra taken before photoquenching. The *EL*2 concentration is decreased by increasing the neutron irradiation doses. The dotted curve is the result of subtracting the G103 spectrum from the G101 spectrum.

ferred from the dramatic increase of the residual absorption after $EL2$ is completely quenched (see Fig. 1). The increase of the isolated antisites by neutron irradiation has been reported previously using the EPR technique.

A careful examination of Table I shows that the relative concentration of $EL2$ as calculated from Martin's calibration curve[21] is different from the relative total integrated area (which is proportional to the defect population[22]) obtained from Fig. 2 especially for sample G103. Two important points can be extracted from this observation. First, Martin's calibration curve, which is questioned by Gatos and Lagowski,[23] may not present an accurate estimation for the $EL2$ concentration. Second, unlike photon illumination[24] the neutron irradiation affects $EL2^0$ in a nonlinear fashion. To clarify the latter point, we subtracted the G103 spectrum from the G101 spectrum and plotted the results in Fig. 2. The presence of the peak at ~1.24 eV after the subtraction indicates that the neutron irradiation affects the absorption band between 1.03 and 1.27 eV more than it affects other optical excitations in the $EL2$ absorption spectrum. A similar behavior is observed in a sample (with the same irradiation dose as G103) obtained from a different vendor. The peak at 1.24 eV was not observed when any two spectra in Fig. 1 of Ref. 24 were subtracted.

We speculate that the IR absorption which remains (residual absorption) after complete photoquenching of $EL2$ as shown in Fig. 1 is related to the isolated As_{Ga} antisite. In addition, the increase of the residual absorption which is pronounced for G103 (see Fig. 1 and Table I) above 0.75 eV is a characteristic of electron photoionization absorption. It is not clear whether the upward shift of the quenched spectra in the lower photon energy region is due to free-carrier absorption[25] or hole-photoionization absorption.[26] There are two points which support the speculation offered above. First, the isolated As_{Ga} antisite is the dominant defect that may give rise to the IR absorption above midgap (for a review, see Ref. 17). Second, the residual absorption after photoquenching of $EL2$ is increased by neutron irradiation. This picture is in good agreement with previous observations[1,18,19,27] in which an increase of the antisites concentration is achieved by neutron irradiation.

The general consensus is that $EL2 \equiv As_{Ga} + X$, where X is still a matter of controversy. Two recent attempts[16,17] have been made to identify the X component(s). The model proposed by von Bardeleben *et al.*[16] identifies X as a movable arsenic interstitial (As_i) which is revised to a split interstitial[28] for the $EL2^*$ configuration. This model is supported by the optically detected electron-nuclear double resonance.[29] However, an acceptor defect (impurity) is needed for this model[30] which is speculated to be intrinsic in nature[31] such as an arsenic vacancy. The other attempt[17] identifies X as a divacancy which is supported by the electron irradiation, and plastic deformations combined with thermal annealing.[32] It is obvious from the above discussion that $EL2$ may be more complicated than a simple pair defect. In fact, the complicated IR absorption spectrum of $EL2$ may reflect such complexities.

The absorption band between 1.03 and 1.27 eV (we will refer to this band as AB for simplicity) has been the subject of numerous studies.[2-11,24,33] It contains a broad peak at 1.18 eV, a ZPL at 1.039 eV, and phonon replicas separated by 11 meV. The AB was interpreted as a transition from $EL2$ to the L minimum of the conduction band,[34-36] an intracenter transition within the As_{Ga} antisite,[6,37] and an intracenter transition within the gallium vacancy (V_{Ga}).[17] It has been shown[38] that the AB cannot be related to V_{Ga} and that the ZPL may not be associated[4] with the broad peak at 1.18 eV.

As mentioned earlier, the neutron irradiation increases the isolated As_{Ga} antisite concentration and decreases the $EL2$ concentration. The generation of the isolated antisites and consumption of interstitials and vacancies were discussed previously[1] in more detail. Based on the results of the relative integrated areas of $EL2$ and As_{Ga} (see Table I), the rate of As_{Ga} antisite generation is much higher than the rate of X component destruction (reduction of $EL2$). If $EL2$ is a complex involving As_{Ga} and an X component(s) and if X is to be identified[16] as As_i, then the reduction of the $EL2$ concentration is the result of a decrease in As_i concentration. This processes is accompanied by a reduction of the AB signal as shown in Fig. 2. This behavior leads us to propose that the AB is a charge-transfer transition between the As_{Ga} and As_i defects. The present experimental results do not rule out any charge-transfer transitions between As_{Ga} and vacancies. We are not aware of any previously reported measurements for charge-transfer transitions between defects in GaAs. However, very recently[39] energy-transfer processes between defects were reported for GaP system. In addition, recent theoretical calculations[40] predict different possibilities of charge-transfer transitions between As_{Ga} and As_i in support of the present interpretation of the AB.

The present results are in disagreement with the interpretation of the AB as being an intracenter transition within the isolated As_{Ga} antisite.[6,37] This is because neither the AB nor the ZPL were observed in the residual absorption (the residual absorption is interpreted by us as the isolated As_{Ga} photoionization absorption) even for the sample G103 which contains more isolated As_{Ga} antisite than the control sample by a factor of 72 (see Table I). The absence of the ZPL from the residual absorption (As_{Ga} absorption) of sample G103 casts doubt on the interpretation of the ZPL as being A_1 to T_2 transition within the isolated As_{Ga} antisite of a T_d symmetry[6] and lends support for the ZPL as being a transition within an orthorhomnic complex.[5] In addition, a multiplet structure was observed in the ZPL in the absence of any uniaxial stresses.[24,33] This fine structure is qualitatively similar to the structure observed[41] in the ZPL of Se and Cr complex in GaAs. These experimental results along with the recent experimental observations[42] of the temperature dependence of the activation energy for thermal recovery of $EL2$ seem to support the speculation that $EL2$ is more complex than a simple pair defect.

In conclusion, the present results show for the first time that the neutron irradiation reduces the $EL2$ concentration. The absorption band between 1.03 and 1.27 eV was interpreted as a charge-transfer transition between the constituent atoms of $EL2$. We also interpreted the residual absorption which remains after $EL2$ is completely quenched as a photoionization absorption of the isolated $\mathrm{As_{Ga}}$ antisite. More experimental measurements (in particular, thermal annealing) are needed to evaluate the effect of various defects introduced by neutron irradiation on the *EL*2 center.

---

[1] E. R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider, and T. Wosinski, J. Appl. Phys. **53**, 6140 (1982); E. R. Weber and J. Schneider, in *Proceedings of the 12th International Conference on Defects in Semiconductors*, edited by C. A. J. Ammerlann [Physica **116B+C**, 398 (1983)].

[2] M. Skowronski, D. C. Lin, J. Lagowski, L. M. Pawlowicz, K. Y. Ko, and H. C. Gatos, in *Microscopic Identification of Electronic Defects in Semiconductors*, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (Materials Research Society, Pittsburgh, 1985), p. 207.

[3] J. Lagowski and H. C. Gatos, in *Proceedings of the 13th International Conference on Defects in Semiconductors*, edited by L. C. Kimerling and J. M. Parsey (AIME, New York, 1985), p. 73.

[4] Y. Mochizuki and T. Ikoma, Phys. Rev. Lett. **59**, 590 (1987); Mater. Sci. Forum **10–12**, 323 (1986).

[5] T. Figielski and T. Wosinski, Phys. Rev. B **36**, 1269 (1987); T. Figielski, Mater. Sci. Forum **10–12**, 341 (1986).

[6] M. Kaminska, M. Skowronski, and W. Kusko, Phys. Rev. Lett. **55**, 2204 (1985).

[7] J. C. Bourgoin and M. Lannoo, Rev. Phys. Appl. (to be published).

[8] M. Skowronski, J. Lagowski, and H. C. Gatos, Phys. Rev. B **32**, 4264 (1985).

[9] M. Levinson and J. A. Kafalas, Phys. Rev. B **35**, 9383 (1987).

[10] L. Samuelson and P. Omling, Phys. Rev. B **34**, 5603 (1986).

[11] F. Fuchs and B. Dischler, Appl. Phys. Lett. **51**, 2115 (1987).

[12] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 2340 (1985).

[13] M. Levinson, Phys. Rev. B **28**, 3660 (1983).

[14] T. Ikoma and Y. Mochizuki, Jpn. J. Appl. Phys. **24**, L935 (1985).

[15] T. Figielski, E. Kaczmarek, and T. Wosinski, Appl. Phys. A **38**, 253 (1985).

[16] H. J. von Bardeleben, D. Stiévenard, J. C. Bourgoin, and A. Huber, Appl. Phys. Lett. **47**, 970 (1985); H. J. von Bardeleben, D. Stiévenard, D. Deresmes, A. Huber, and J. C. Bourgoin, Phys. Rev. B **34**, 7192 (1986).

[17] J. F. Wager and J. A. Van Vechten, Phys. Rev. B **35**, 2330 (1987).

[18] R. Wörner, U. Kaufmann, and J. Schneider, Appl. Phys. Lett. **40**, 141 (1982).

[19] J. Schneider and U. Kaufmann, Solid State Commun. **44**, 285 (1982).

[20] M. O. Manasreh, P. F. McDonald, S. A. Kivlighn, J. T. Minton, and B. C. Covington, Solid State Commun. **65**, 1267 (1988).

[21] G. M. Martin, Appl. Phys. Lett. **39**, 747 (1981).

[22] C. Struart Kelley, Phys. Rev. B **6**, 4112 (1972); T. H. Keil, Phys. Rev. **140**, A601 (1965).

[23] H. C. Gatos and J. Lagowski, in *Microscopic Identification of Electronic Defects in Semiconductors*, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (Materials Research Society, Pittsburgh, 1985), p. 153.

[24] M. O. Manasreh and B. C. Covington, Phys. Rev. B **36**, 2730 (1987).

[25] M. Tajima, H. Saito, T. Iino, and K. Ishida, Jpn. J. Appl. Phys. Lett. **27**, L101 (1988).

[26] B. Dischler, F. Fuchs, and U. Kaufmann, Appl. Phys. Lett. **48**, 1282 (1986).

[27] W. T. Read, Jr., *Dislocations in Crystals* (McGraw-Hill, New York, 1953).

[28] C. Delerue, M. Lannoo, D. Stiévenard, H. J. von Bardeleben, and J. C. Bourgoin, Phys. Rev. Lett. **59**, 2875 (1987); D. Stiévenard and H. J. von Bardeleben, Rev. Phys. Appl. (to be published); H. J. von Bardeleben, J. C. Bourgoin, D. Stiévenard, and M. Lannoo, in Proceedings of the 14th International Symposium on GaAs and Related Compounds, Heraklin, Crete, 1987 (unpublished).

[29] B. K. Meyer, D. M. Hofmann, J. R. Niklas, and J.-M. Spaeth, Phys. Rev. B **36**, 1332 (1987).

[30] G. A. Baraff and M. Schlüter, Phys. Rev. B **35**, 5929 (1987); **35**, 6154 (1987).

[31] B. K. Meyer, D. M. Hofmann, and J.-M. Spaeth, in Materials Research Society Symposium E, Boston, 1987 (unpublished).

[32] T. Haga, M. Suezawa, and K. Sumino, in Materials Research Society, Symposium E, Boston, 1987 (unpublished).

[33] M. O. Manasreh and B. C. Covington, Phys. Rev. B **35**, 2524 (1987).

[34] A. Chantre, G. Vincent, and D. Bois, Phys. Rev. B **23**, 5335 (1981).

[35] M. Tajima, Jpn. J. Appl. Phys. **26**, L885 (1987).

[36] M. Tajima, T. Iino, and K. Ishida, Jpn. J. Appl. Phys. **26**, L1060 (1987).

[37] M. Kaminska, M. Skowronski, J. Lagowski, J. M. Parsey, and H. C. Gatos, Appl. Phys. Lett. **43**, 302 (1983).

[38] M. O. Manasreh, Phys. Rev. B **37**, 2722 (1988).

[39] W. M. Chen, M. Golewski, and B. Monemar, Phys. Rev. B **36**, 7755 (1987).

[40] G. A. Baraff, M. Lannoo, and M. Schlüter, in Materials Research Society Symposium E, Boston, 1987 (unpublished).

[41] Y. Fujiwara, Y. Kita, Y. Tonami, T. Nishino, and Y. Hamakawa, J. Phys. Soc. Jpn **55**, 3741 (1986).

[42] D. W. Fischer, Phys. Rev. B **37**, 2968 (1988).