Comments

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Comment on "Identification of a defect in a semiconductor: *EL*2 in GaAs"

H. C. Gatos and J. Lagowski
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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We find it necessary to comment on the paper by von Bardeleben *et al.* [Phys. Rev. B **34**, 7192 (1986)] as it presents a new *EL*2 model based on questionable experimental data which are in conflict with well-established characteristics of this deep midgap level responsible for the semi-insulating characteristics of GaAs.

Following are the specific reasons for this present comment. First, the GaAs material employed in the subject paper[1] was very abnormal, as it contained an unexplainably low and normally unattainable *EL*2 concentration. Second, there are fundamental differences between the universally accepted annealing behavior of *EL*2 and that reported in the subject paper. Third, the determination of the *EL*2 concentration was carried out with an experimental approach known to be susceptible to interfacial effects and artifacts. Fourth, in the light of the results presented a serious doubt remains as to whether or not the defect studied was indeed *EL*2.

The authors of Ref. 1 employed "especially grown samples in order to allow coupled EPR and deep-level transient spectroscopy (DLTS) measurements on the same samples." They state that the concentration of *EL*2 in these samples ranges from $(1-3)\times10^{15}$ cm^{-3} and that these samples were taken from ingots grown "in a way identical to the growth of semi-insulating materials." Under no circumstances can GaAs crystals grown from the melt be considered representative or typical if the as-grown *EL*2 concentration is as low as the above values.[2–5] Universally reported *EL*2 concentrations in GaAs grown from the melt exceed 10^{16} cm^{-3}: $(1-5)\times10^{16}$ cm^{-3} for the horizontal Bridgman (HB) method,[2] $(1-3)\times10^{16}$ cm^{-3} for liquid-encapsulated Czochralski (LEC) method,[3–4] and $(3-7)\times10^{16}$ cm^{-3} for the heat-exchange method (HEM).[5]

A low concentration of *EL*2 can be obtained in crystals grown from Ga-rich melts.[2] In such atypical crystals, however, the presence of arsenic interstitials becomes thermodynamically completely unfavorable. Virtually *EL*2-free crystals can also be obtained by quenching GaAs from temperatures (about 1200 °C) near the solidification point. Subsequent annealing at 850 °C of such crystals reestablishes the normal *EL*2 concentration values in the 10^{16}-cm^{-3} range.[6] In fundamental contrast, von Bardeleben *et al.* report *EL*2 annihilation during 850 °C annealing.

In Table I we have summarized the effects of 850 °C annealing on the *EL*2 concentration for four types of melt-grown GaAs crystals. The results were obtained in our laboratory, using the ingot annealing technique; they are representative of voluminous results in the literature (see Refs. 3,4, and 7–9). The *EL*2 concentrations were determined by optical-absorption[10] and DLTS measure-

TABLE I. Effects of 850 °C whole-Ingot annealing on *EL*2 concentration in melt-grown GaAs.

Growth method	*EL*2 concentration (cm^{-3}) As grown DLTS	As grown ir absorption	After 30-min annealing DLTS	After 30-min annealing ir absorption
LEC	1.2×10^{16}	1.2×10^{16}	1.6×10^{16}	1.5×10^{16}
HB	2.5×10^{16}	2.4×10^{16}	2.5×10^{16}	2.5×10^{16}
HEM	4.5×10^{16}	4.2×10^{16}	4.5×10^{16}	4.3×10^{16}
LEC; Ref. 1[a]	$(1-3)\times10^{15}$		$(0.5-5)\times10^{14}$[a]	

[a]10-min annealing at 850 °C with Si_3N_4 encapsulation.

ments (employing Au diodes) for conducting n-type material and by optical absorption for semi-insulating material. It is seen that short-term annealing at 850 °C increases or causes no change in the $EL2$ concentration. Similar behavior has been found in and reported by a large number of laboratories (Refs. 3, 4, and 7–9, and references therein). In fact, since 850 °C annealing does not affect adversely the $EL2$ concentration, this thermal treatment is now used by commercial producers to improve the homogeneity and mobility of melt-grown semi-insulating GaAs crystals.[11] von Bardeleben *et al.* attributed the inconsistency between their results and those in the literature to uncertainties in the optical-absorption method used for the determination of $EL2$ concentration. It is clear from Table I, however, that this inconsistency persists regardless of the method employed for the determination of $EL2$.

The low concentration and the annealing behavior at 850 °C reported in the subject paper are not commonly related to $EL2$. It is quite possible that von Bardeleben *et al.* were studying instead other midgap levels which are present in LEC GaAs at concentrations in the 10^{15}-cm^{-3} range.[12] All of these levels are subject to photoquenching like $EL2$. Actually, $EL2$ can be readily distinguished from them by its emission-rate signature[2] $e^{-1}T^2 = 3.53\times10^{-8}\exp\,[(0.815\text{ eV})/kT]s^{-1}$ and the 1.039-eV zero-phonon absorption line.[13] In the subject paper the emission-rate data (Fig. 11) cover a range which is much too narrow for reliable relevant determinations. Employing these limited data we obtain an activation energy of 0.9 eV which is not that characteristic of $EL2$ (i.e., 0.815 eV).

Employing Al Schottky barriers, von Bardeleben *et al.* observed enhancement and change in the shape of the DLTS peak during low-temperature annealing (95–130 °C). They took this observation as evidence of the mobile character of the X element (proposed to be arsenic interstitial As_i) of the $EL2$ complex $As_{Ga}+X$. However, it is well documented in the recent literature that Al Schottky barriers on GaAs are extremely susceptible to metal-semiconductor reactions which manifest themselves as changes in the magnitude, position, and shape of the DLTS peak.[14] Adverse interfacial phenomena due to Si_3N_4 capping should also be considered,[15] particularly since the samples were not etched after annealing, and prior to the deposition of the Schottky barrier. Experimental artifacts associated with such measurements can obscure the actual deep-level behavior. Our laboratory results obtained over a number of years on several thousands of GaAs samples from hundreds of commercial and laboratory-grown ingots have demonstrated (using Au and Al Schottky diodes) that low-temperature annealing has no effect on the $EL2$ concentration in melt-grown crystals. On occasion, we have observed abnormally low values of $EL2$ concentrations; however, the origin of these abnormal values has been invariably traced to poor-quality diodes.

Finally, we must address the argument of von Bardeleben *et al.* that gallium vacancies are not present in GaAs grown under arsenic-rich (i.e., gallium-deficient) conditions, since they "would trap As_i." Since vacancies are fundamental thermodynamic species, it is our opinion that this argument is naive, incorrect, and in obvious contradiction to basic principles of defect thermodynamics in compound semiconductors.[16,17] For example, the thermodynamic consideration of Ref. 14 strongly favors vacancies over interstitials in accounting for the nonstoichiometry of III-V semiconductor compounds.

Among the $EL2$ models advanced thus far those involving the arsenic antisite As_{Ga} and vacancies (as the X element) seem to attract at this time the greatest attention.[18,19] Their favorable position rests on rigorous theoretical calculations which support the $EL2$ metastability.[19,20] However, no single model (among those proposed) can account for all the experimental characteristics of the $EL2$; it is clear that the search for the perfect $EL2$ model must continue. Thus, the purpose of our Comment is not to discourage the type of research reported in the subject paper. Rather, our Comment cautions against acceptance of questionable experimental data which can readily impede progress towards arriving at a working model of $EL2$.

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