

In-diffusing divacancies as sources of acceptors in thermally annealed GaAs

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We suggest that annealing GaAs samples at high temperatures encourages the relatively rapid in-diffusion of divacancies which either are acceptors themselves or quickly dissociate into acceptors. Rapid quenching to room temperature freezes in these defects and results in altered electrical properties for the samples. A simple model, fit to some sparse existing data, yields a 950 °C estimate of $(3-5) \times 10^{-7} \text{ cm}^2/\text{s}$ for the diffusivity of the divacancy. When combined with other existing data, obtained at lower temperatures, on the in-diffusion of a defect with a level at $E_c-0.23 \text{ eV}$ and tentatively identified as the divacancy, we find the diffusivity of the divacancy to be given by $(3 \times 10^{-3}) \exp(-0.94 \text{ eV}/kT) \text{ cm}^2/\text{s}$ over the temperature range 250–950 °C.

The room-temperature electrical properties of GaAs can be altered significantly by a long high-temperature anneal followed by a quench to room temperature.¹⁻⁵ The major reason for the observed changes is believed to be an alteration in the balance of native defects present in the samples as a result of the anneal/quench. Indeed, for annealing temperatures in excess of 950 °C it has been demonstrated^{1,2} that the dominant native defect EL2 dissociates. This can result in a drop in the net carrier concentration¹ and a conversion of GaAs from semi-insulating to *p* type. Even a 950 °C anneal, which leaves EL2 intact, can decrease the electron-hole concentration.^{3,4} In such situations, where EL2 is not responsible for the observed changes, it is unclear which native defects are involved. We suggest that a prime candidate is the divacancy which should rapidly diffuse into GaAs and might subsequently act as a source for the rich defect structure observed.³ In the following we present a model based on the in-diffusing divacancy that purports to account for some data obtained after long anneals.

Asom *et al.*⁴ annealed Bridgman-grown, *n*-type, GaAs samples of dimension $0.5 \times 0.5 \times 1.0 \text{ cm}^3$ at 850, 950, and 1050 °C in As_4 overpressure for times ranging from 30 min to 192 h followed by a fast air quench (30 °C/s) to room temperature. Sections taken from the centers of the annealed samples were then characterized by deep-level transient spectroscopy (DLTS), photoluminescence (PL), and temperature-dependent Hall effect measurements. Experimental results and inferences that are of particular interest to us concern their As-rich samples annealed at 950 °C:

(1) For times longer than a few hours both the net free-carrier concentration ($n-p$) and the mobility decreased monotonically with time due to the introduction of *significantly charged acceptors*.

(2) The decrease in net free-carrier concentration saturated at about $2.4 \times 10^{16} \text{ cm}^{-3}$ after about 30 h independent of the initial electron concentration which ranged from 1×10^{16} to $2 \times 10^{17} \text{ cm}^{-3}$. Thus, some samples converted to high-resistivity *p* type.

(3) No new ionization levels in the band gap due to donors or acceptors were detected.

(4) During the first few hours of annealing the electrical changes were more complex suggesting loss of acceptors and perhaps also of donors. We do not explore this regime in any detail.

(5) The EL2 concentration, as determined by DLTS, remained essentially constant at $1.8 \times 10^{16} \text{ cm}^{-3}$.

Items (2) and (5) together suggest that the final concentration of the added acceptors ranged from about $2.4 \times 10^{16} \text{ cm}^{-3}$ (in those samples which remained *n*-type and thus in which EL2 remained neutral) to at least $4.2 \times 10^{16} \text{ cm}^{-3}$ (in those samples in which EL2 became completely ionized). Consequently the magnitude of the acceptor saturation concentration will be of less interest to us than the fact that saturation occurred.

We believe that because of the ultimately large acceptor concentration and because of the enormously long time required to attain this saturation concentration the acceptor does not originate within the sample through reactions of defects already there. We do suggest that diffusion into the sample from the surface is the key to the understanding of the acceptor.

Recalling that measurements⁴ were performed on sections taken from the centers of samples the in-diffusing defect must have a diffusivity on the order of 10^{-7} – $10^{-6} \text{ cm}^2/\text{s}$ at 950 °C. This is much larger than the diffusivity of V_{Ga} which is $6.0 \times 10^{-12} \text{ cm}^2/\text{s}$ at 950 °C. It is probably also larger than the diffusivity of V_{As} which, unfortunately, is not well known. (Recent determinations^{7,8} indicate it to be on the order of $10^{-14} \text{ cm}^2/\text{s}$ at 500 °C, about four orders of magnitude larger than that of V_{Ga} .) Fortunately for our purposes the As_4 overpressure used during the anneals should have suppressed the introduction of isolated V_{As} into the samples. Furthermore, since isolated vacancies would be expected to flow into the samples at steady rates (due to the steady evaporation of As or Ga from the surfaces) their bulk concentration (and, therefore, the concentration of associated acceptors) would not saturate but would continue to increase with time. The in-diffusion of the divacancy $V_{\text{Ga}}V_{\text{As}}$, however, should occur rapidly since its motion simply involves a hop of a nearest-neighbor As or Ga into the divacancy⁹ and its concentration should

saturate at a temperature-dependent value. Once in the sample it might undergo defect reactions resulting in acceptors such as V_{Ga} or $V_{\text{Ga}}\text{Ga}_{\text{As}}$.

There also remains the possibility that the acceptor is associated with an impurity that originates somewhere in the (unspecified) annealing system. Based on available information we cannot rule out this possibility but trust that if such were the case problems would have arisen frequently in the past with GaAs wafers annealed in the same system. Thus we focus attention on the divacancy.

Specifically two possible models involving the divacancy are formulated as follows. Upon annealing at 950 °C the surface concentration of divacancies rises quickly to the bulk equilibrium value, $[V_{\text{Ga}}V_{\text{As}}]_0$. The divacancies then diffuse into the sample from all sides with constant diffusivity D . A straightforward solution of the diffusion equation yields a divacancy concentration at the center of the sample of dimension $L \times L \times 2L$ at time t of

$$[V_{\text{Ga}}V_{\text{As}}] = [V_{\text{Ga}}V_{\text{As}}]_0 [1 - f(\tau)^2 f(\tau/4)] \quad (1)$$

where

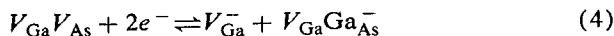
$$f(\tau) = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(n\frac{\pi}{2}\right) e^{-n^2\tau} \quad (2)$$

with

$$\tau = \pi^2 D t / L^2. \quad (3)$$

In model I we assume the divacancy itself to be a singly charged acceptor. Evidence supporting this assumption is meager. Theoretical arguments^{10,11} suggest that the divacancy has several electronic levels in the band gap while electron irradiation experiments^{12,13} point to its having a level at $E_c - 0.23$ eV; its charge states are apparently unknown. If it is singly charged then the net charged acceptor concentration is simply $[A] = [V_{\text{Ga}}V_{\text{As}}]$ as given in Eq. (1).

In model II we assume, on the basis of Baraff and Schlüter's¹⁴ study of defect reactions and Look *et al.*'s³ thermal recycling experiments, that once the divacancies enter the sample the following reaction rapidly equilibrates at 950 °C under near-intrinsic conditions:



so that

$$[V_{\text{Ga}}V_{\text{As}}] = K [V_{\text{Ga}}^-] [V_{\text{Ga}}\text{Ga}_{\text{As}}^-] \quad (5)$$

where K is a temperature-dependent equilibrium constant.

The net charged acceptor concentration in this model is then

$$\begin{aligned} [A] &= [V_{\text{Ga}}^-] + [V_{\text{Ga}}\text{Ga}_{\text{As}}^-] \\ &= [A]_0 [1 - f(\tau)^2 f(\tau/4)]^{1/2}, \end{aligned} \quad (6)$$

where

$$[A]_0 = 2\{[V_{\text{Ga}}V_{\text{As}}]_0/K\}^{1/2}. \quad (7)$$

Because the data show the introduction of *singly* charged acceptors and DLTS showed no new traps in the upper half of the band gap⁴ we have assumed that the concentration of V_{As} , a defect that can readily communi-

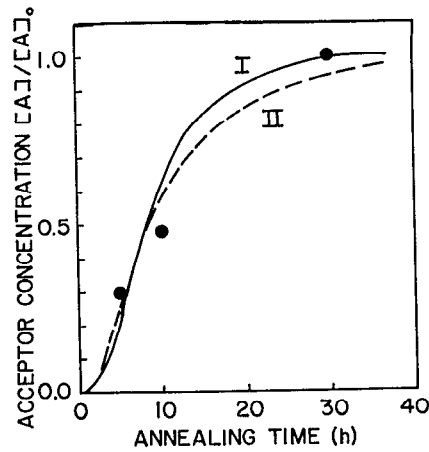


Fig. 1. The fraction of acceptors, introduced into a GaAs sample as a result of the assumed in-diffusion of divacancies, depicted as a function of time. In model I the divacancies are assumed to be acceptors; in model II they are assumed to dissociate into acceptors. The data were obtained from Ref. 4.

cate¹⁴ with $V_{\text{Ga}}\text{Ga}_{\text{As}}$, is negligible. Furthermore, in model II we have taken the divacancy to be neutral although it is sufficient to assume its concentration to be too small to be noticed.

We show in Fig. 1 the curves of $[A]/[A]_0$ generated from models I (II) with $L = 0.5$ cm using $D = 5 \times 10^{-7}$ cm²/s (3×10^{-7} cm²/s), and plot the rather limited amount of data published for the 950 °C anneal/quench. These data (Fig. 1 of Ref. 4) were obtained on samples in which the carrier concentration (n), initially $n_0 = 2.3 \times 10^{16}$ cm⁻³, dropped to approximately zero after 30 h; we take $[A]/[A]_0 = (n_0 - n)/n_0$. To the extent that the fitted values of D are representative of divacancy diffusion either model is reasonable.

We note from Fig. 1 that several hours must pass before the effect of the in-diffusing divacancies occurs at the centers of the samples. This is in accord with the measurements where Asom *et al.*'s⁴ stage II (acceptor addition) took several hours to become manifest.

Unfortunately, to our knowledge, little is known with certainty about the divacancy.^{13,15} Assuming it to have a level at $E_c - 0.23$ eV (Refs. 12 and 13) another recent experiment is very relevant. Dubonos and Koveshnikov¹⁶ studied the in-diffusion of a defect (DL5 in their notation) with this electronic level into GaAs samples during anneals at temperatures up to 350 °C following exposure to an Ar plasma. They deduced its diffusivity to be $0.12 \exp(-1.14 \text{ eV}/kT)$ cm²/s. We have approximately fitted their published diffusion profiles (which are exponential) to complementary error functions to extract the diffusion coefficients presented in Fig. 2. These values, and our 950 °C value determined above, are well fitted by

$$D = (3.0 \times 10^{-3}) e^{-0.94 \text{ eV}/kT} \text{ cm}^2/\text{s} \quad (8)$$

as shown.

We might compare these values with the diffusivity of isolated vacancies in silicon, which also migrate by nearest-

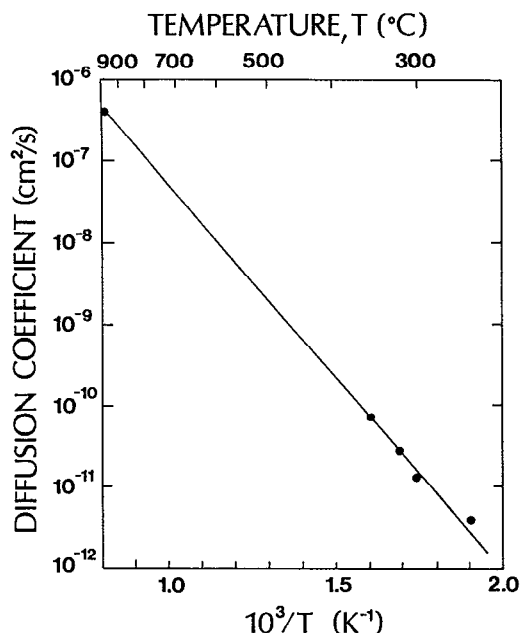


Fig. 2. The diffusion coefficient of what is purported to be the divacancy in GaAs. The isolated high-temperature datum point follows from fits discussed in the present paper; the remaining low temperature data come from fits to diffusion profiles, given in Ref. 16, of a defect with a level at $E_c - 0.23$ eV. The equation of the line is $D = (3.0 \times 10^{-3}) \exp(-0.94 \text{ eV/kT}) \text{ cm}^2/\text{s}$.

neighbor hopping. Masters and Gorey¹⁷ indirectly deduced the result $10 \exp(-1.47 \text{ eV/kT}) \text{ cm}^2/\text{s}$. Over the temperature range 250–950 °C these values are within about two orders of magnitude of those in Eq. (8).

In yet another experiment, that may be relevant to the divacancy, Boncek and Rode⁵ annealed semi-insulating GaAs wafers in a helium ambient at 830 and 885 °C for times ranging from 22 to 60 h followed by a slow cool (30–40 °C/min) to room temperature. The wafers, 380 or 510 μm thick, were from ingots grown either by the Bridgman or the liquid-encapsulated Czochralski method. After the annealing treatment samples $6 \times 6 \text{ mm}^2$ were characterized by van der Pauw resistivity and Hall effect measurements.

All their samples converted to p type with the loss of EL2 and the addition of deep acceptors with an ionization

level at $E_v + 0.150$ eV. The saturation concentration of these acceptors, attained in under 22 h, was significantly larger than that required by the measurements of Asom *et al.*⁴ Possibly the use of As_4 overpressure during the anneal in the latter case inhibited the formation of divacancies on the surface. Boncek and Rode⁵ also report that semi-insulating behavior was retained after annealing if a SiN encapsulating layer was used. Again, the build-up of divacancies might be prevented by this cap.

To what extent the other differences between the two resistivity experiments^{4,5} are due to different parameters such as annealing temperature, cooling rate, melt composition used in growing the crystals, ambient annealing gas, etc. is unclear. Certainly additional studies are needed to further characterize the new acceptor(s).

In conclusion, it appears that the divacancy, so far an elusive native defect in GaAs, might be studied by focusing attention on the associated acceptors. Even without further study it would seem prudent to be alert to the possibility of in-diffusing divacancies when annealing GaAs at high temperatures. Since they presumably diffuse very rapidly their effect is not limited to the vicinity of the sample surface.

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