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B. Ziebro

Joseph W. Hemskey

Wright State University - Main Campus, joseph.hemskey@wright.edu

David C. Look

Wright State University - Main Campus, david.look@wright.edu

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Defect models in electron-irradiated *n*-type GaAs

B. Ziebro, J. W. Hemsky, and D. C. Look

Department of Physics, Wright State University, Dayton, Ohio 45435

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1 MeV electron irradiation has been performed in degenerate, *n*-type ($n \approx 2 \times 10^{17} \text{ cm}^{-3}$), molecular beam epitaxial GaAs layers, and Hall effect measurements have been carried out during the irradiation in order to get accurate defect production data. The results have been fitted with statistical models, and are most consistent with the usual *E1* ($E_C - 0.045 \text{ eV}$) and *E2* ($E_C - 0.15 \text{ eV}$) levels being the $(-/0)$ and $(0/+)$ transitions of the As vacancy, respectively. Also, an acceptor well below $E_C - 0.15 \text{ eV}$ is produced at a much higher rate than that of *E1* and *E2*.

I. INTRODUCTION

Over the last few years, an understanding of the defects in GaAs has become more important. These defects, which can greatly affect the electrical and optical properties of the material, may be present as a result of growth conditions, or also as a result of irradiation with high energy particles. For example, irradiation with 1 MeV electrons will produce intrinsic defects such as vacancies, interstitials, and possibly antisites.¹⁻³ In as-grown material, such intrinsic defects may interact among themselves, or with impurities to form complex defects. However, it is first necessary to understand the simple defects before the complex ones can be identified. Another motivation for studying the effects of electron irradiation is the wealth of space applications for GaAs devices, because the damage caused by protons, neutrons, and gamma rays in space can often be usefully simulated by 1 MeV electron irradiation.⁴

Much work has been done in an effort to identify the defects produced in GaAs by electron irradiation, and the situation is summarized in recent review articles.¹⁻³ The most widely studied defects are electron traps, usually designated as *E1* (at $E_C - 0.045 \text{ eV}$), *E2* (at $E_C - 0.15 \text{ eV}$), and *E3* (at $E_C - 0.29 \text{ eV}$). However, even these traps have not been firmly identified, although they are generally thought to be related to the As vacancy V_{As} . One problem here is that V_{As} would naively be expected to be a donor, but yet the Fermi level continuously drops during irradiation of *n*-type GaAs. Thus, there should be acceptors, below midgap, which are being produced at a higher rate than *E1* and *E2* combined, or else *E1* and/or *E2* must themselves be acceptors. Recently this problem has been studied by Hall effect measurements^{5,6} in pure GaAs, but not in heavily doped material.

To further investigate these effects, we have designed and constructed an *in situ* Hall effect apparatus which allows continuous measurements while the electron beam is on; thus, very detailed defect production rate data may be obtained.⁷ The donor and acceptor production rates are obtained through a solution of the charge-balance equation, corrected for degeneracy using the Ehrenberg approximation. We have chosen samples of high enough concentration that the Fermi level ϵ_F is near the conduction band

edge, so that ϵ_F may be swept through *E1* and *E2* during the irradiation.

II. EXPERIMENT

For this experiment, the 1 MeV electrons were produced by a van de Graaff generator and traveled through a short span of air to hit the sample. Typical current densities were $0.4 \mu\text{A}/\text{cm}^2$. The entire configuration has been described elsewhere,⁷ and therefore a detailed description will not be given here. The material studied was an *n*-type molecular beam epitaxial (MBE) layer, doped with Si at about $2 \times 10^{17} \text{ cm}^{-3}$ to put ϵ_F close to the conduction band edge. This concentration is also important for metal-semiconductor field-effect transistor applications. Thick samples ($10 \mu\text{m}$) were used in order to minimize the severity of surface and interface free carrier depletion effects, which typically totaled $0.1\text{--}0.5 \mu\text{m}$ (Ref. 8) for the conditions of this study. Although small, these corrections were included for completeness. All irradiations were performed at room temperature.

III. THEORY

It is well known that shallow impurities in semiconductors, such as Si in GaAs (at $E_C - 0.006 \text{ eV}$), can form an energy band at high concentrations and produce a second conduction mechanism.⁹ As the concentration is further increased, this band can overlap the conduction band and the electrons in the two bands are indistinguishable. Lowney¹⁰ has shown that for a hydrogenic donor concentration greater than $1 \times 10^{17} \text{ cm}^{-3}$ in GaAs, neither a bound state nor an impurity band exists at 300 K. This idea is supported by the lack of free carrier freeze-out, even at 4 K. Thus, we assume that each Si atom provides an electron which takes part in the conduction.

The measured carrier concentrations are related to physical parameters by means of statistical theory. The energy distribution function for electrons in an energy band is

$$f(\epsilon) = 1/1 + e^{(\epsilon - \epsilon_F)/kT}, \quad (1)$$

where ϵ_F is the Fermi energy. In this work, we will measure all energies from the valence band. The distribution function for defects or impurities is often assumed to be of the form⁸

$$f(\epsilon) = 1/1 + Ke^{(\epsilon - \epsilon_F)/kT}, \quad (2)$$

where K is a degeneracy factor. To apply these expressions we must find ϵ_F , which is done by solving the charge balance equation:⁸

$$n + \sum_k N_{Ak}^- = p + \sum_k N_{Dk}^+ \quad (3)$$

where N_{Ak} and N_{Dk} denote particular acceptor and donor concentrations, respectively. For single donors, i.e., centers that are either neutral or have a single, positive charge, the unoccupied state density (that of the charged state) can be written as

$$N_D^+ = N_D/1 + \frac{g_{D1}}{g_{D0}} e^{(-\epsilon_{D1} + \epsilon_F)/kT}, \quad (4)$$

where N_D is the number of donors, ϵ_{D1} is the energy of the donor level measured from the valence band, and the g 's are the degeneracies of the occupied (g_1) and unoccupied (g_0) states, respectively. Similarly, the number of charged (or occupied in this case) acceptors can be written

$$N_A^- = N_A/1 + \frac{g_{A0}}{g_{A1}} e^{(\epsilon_{A1} - \epsilon_F)/kT}, \quad (5)$$

where N_A is the number of acceptors, and ϵ_{A1} is again measured from the valence band. Therefore, the charge balance equation becomes (for a system with one single acceptor state and one single donor state)

$$\begin{aligned} n + N_A/1 + \frac{g_{A0}}{g_{A1}} e^{(\epsilon_{A1} - \epsilon_F)/kT} \\ = p + N_D/1 + \frac{g_{D1}}{g_{D0}} e^{(-\epsilon_{D1} + \epsilon_F)/kT}, \end{aligned} \quad (6)$$

where n and p can also be related to ϵ_F . The form of the charge balance equation given above can be used to obtain production rates for donors and acceptors being produced by the irradiation. The procedure is to assume that the number of donors or acceptors produced is the product of a production rate (τ) and the irradiation dose (ϕ), so that Eq. (6) becomes

$$\begin{aligned} n + \phi\tau_A/1 + \frac{g_{A0}}{g_{A1}} e^{(\epsilon_{A1} - \epsilon_F)/kT} \\ = p + \phi\tau_D/1 + \frac{g_{D1}}{g_{D0}} e^{(-\epsilon_{D1} + \epsilon_F)/kT}. \end{aligned} \quad (7)$$

Similar forms of the charge balance equation can be written for systems with other combinations of donors and acceptors, including multiple charge states of the same defect.⁸

The carrier concentrations found during irradiation need to be corrected for two factors before inclusion in the charge balance equation. The first factor is the Hall r factor, which usually varies between 1.0 and 1.3 for GaAs.⁸

Once the experimental Hall concentration n_H and Hall mobility μ_H are found, it is possible to do a numerical solution of the Boltzmann equation, using the Brooks-Herring formula for the ionized impurity scattering rate, and find r .^{11,12} In this study, a computer program was used to numerically solve the Boltzmann transport equation, and all data fits were made to carrier concentrations corrected for the Hall r factor, even though these corrections were typically small, with r ranging from a low of 1.04 to a high of 1.23.

The second correction, which can be important for thin samples, is due to the transfer of free carriers from the conductive layer to surface and interface (layer/substrate) acceptor states.^{8,13} The relevant surface and interface potentials needed to calculate this depletion effect are known for the MBE GaAs layers used in our study: $\phi_s = -0.7$ V for an oxidized surface,¹⁴ and $\phi_i = -0.95$ V for a GaAs layer grown directly on a semi-insulating substrate.¹⁵ An iteration with respect to the variable n was used to calculate the effective sample thickness $d_{\text{eff}} = d - w_s - w_i$, where d is the metallurgical thickness and w_s and w_i the depletion thicknesses, which are functions of n . The corrected concentration n is then given by

$$n = \frac{rn_H d}{d_{\text{eff}}}. \quad (8)$$

However, it should be noted that the r and d_{eff}/d corrections were nearly always less than 15%.

A third correction, which is sometimes necessary, involves the relative sizes of the beam current I_b and the sample current I_s used for the Hall measurements. In this case, $I_b/I_s < 10^{-4}$ and thus the beam current is inconsequential.

IV. RESULTS

If $E1$ and $E2$ are indeed two charge states of V_{As} , then there are three reasonable choices for their donor or acceptor nature. The first is that of a double donor (DD) with $E1$ and $E2$ representing the $(0/+)$ and $(+/++)$ transitions, respectively. The second possibility is that of a single donor state and a single acceptor state (SD/SA), with $E1$ as the $(-/0)$ transition and $E2$ the $(0/+)$ transition. Finally, we must consider the double acceptor (DA) model, with the transitions $(--/-)$ and $(-/0)$ for $E1$ and $E2$, respectively. For each model, the corrected carrier concentration data were used to find the production rates for the $E1$ and $E2$ levels, as well as that of an acceptor state, arbitrarily taken to be 0.1 eV above the valence band (close to the theoretical position of the gallium vacancy, V_{Ga}). However, our results do not determine the acceptor energy except to place it well below $E_C - 0.15$ eV. The correct form of the charge balance equation was then used to perform a least squares fit for the production rates. As an example, if $E1$ and $E2$ represent a double acceptor, then the charge balance equation would be written

FIG. 1. The free electron concentration n (circles) and ionized defect and impurity concentration N_I (triangles) as a function of electron fluence ϕ . The solid line through the circles is a theoretical fit of n vs ϕ with τ_E floating, and the dotted line is for τ_E fixed at 1.5 cm^{-1} . The solid lines through the triangles are theoretical fits of N_I vs ϕ for a single shallow acceptor (SSA) and double shallow acceptor (DSA), respectively. All theoretical fits in this figure are based on V_{As} having double donor nature with the fitting parameters given in Table I.

$$n + \tau_E \phi / 1 + \frac{g_0}{g_1} e^{(\epsilon_1 - \epsilon_F)/kT} + \frac{g_2}{g_1} e^{(\epsilon_1 - \epsilon_2 + \epsilon_F)/kT} + 2\tau_E \phi / 1 + \frac{g_0}{g_2} e^{(\epsilon_2 - 2\epsilon_F)/kT} + \frac{g_1}{g_2} e^{(\epsilon_2 - \epsilon_1 - \epsilon_F)/kT} + \tau_A \phi + N_{As} = p + N_{Ds}, \quad (9)$$

where $\epsilon_1 = 1.424 - 0.15 = 1.274 \text{ eV}$ would be the energy at 296 K necessary to bring an electron from the valence band onto the neutral V_{As} , making it V_{As}^- , and $\epsilon_2 = 1.274 + (1.424 - 0.045) = 2.653 \text{ eV}$ would be the energy of the two-electron system after a second electron was added, making V_{As}^{2-} . The relevant degeneracies would be $g_0 = 6$, $g_1 = 15$, and $g_2 = 20$, since the V_{As}^0 , V_{As}^- , and V_{As}^{2-} states have 1, 2, and 3 electrons, respectively, in a six-fold degenerate T_2 state. Also, in Eq. (9), τ_E would be the production rate of both $E1$ and $E2$ (each a transition related to V_{As}), τ_A the production rate of the acceptor (assumed to be at $E_V + 0.1 \text{ eV}$), and N_{Ds} and N_{As} the donor (Si) and acceptor (C) concentrations, respectively, of the material before irradi-

FIG. 2. Symbols same as in Fig. 1, but all theoretical fits based on V_{As} having single donor/single acceptor nature with the fitting parameters given in Table I.

FIG. 3. Symbols same as in Fig. 1, but all theoretical fits based on V_{As} having double acceptor nature with the fitting parameters given in Table I.

ation. Actually, because of the high Si doping ($> 2 \times 10^{17} \text{ cm}^{-3}$), not all the Si atoms would be expected to be ionized even though their energy level is very close ($< 0.006 \text{ eV}$) to the conduction band (CB). The situation is even more complicated because the CB is distorted by the high Si concentration. To roughly account for these effects, we assumed that the CB was rigidly shifted downward by 0.015 eV ¹⁶ and that the Si states were then present at $E_C - 0 \text{ eV}$, rather than $E_C - 0.006 \text{ eV}$. This latter assumption was justified by the lack of carrier freezeout, even at 4 K. For the DD and SD/SA cases, similar charge balance equations were used, but with different Fermi factors and degeneracies.

The data, shown in Figs. 1–3, were fitted to Eq. (9) (or the analogs for the DD and SD/SA cases) either by allowing both τ_E and τ_A to float or by holding τ_E at 1.5 cm^{-1} (approximately the literature value²) and floating only τ_A . In each figure, the solid line through the n vs ϕ points represents the best fit for both τ_E and τ_A floating, while the dashed line is for fixed $\tau_E = 1.5 \text{ cm}^{-1}$ and only τ_A floating. The best fit parameters as well as a sum of squares (SSQ) are given in Table I. Here we have assumed that τ_A represents a single acceptor; for the double acceptor case, τ_A must be divided by 2. As can be seen in the figures and from the SSQ values, all of the dashed lines ($\tau_E \approx 1.5 \text{ cm}^{-1}$) give poor fits, and all of the solid lines good fits, with the SD/SA fit having the lowest SSQ of the three possibilities. Further information may be obtained by analyzing the mobility data μ vs ϕ . From the n vs ϕ fits, we can

TABLE I. Fitting parameters used in Figs. 1–3. The SSQ is a relative measure of the goodness of fit.

Figure	Case	Solid lines			Dashed lines		
		τ_E	$a\tau_A$	SSQ	τ_E	$a\tau_A$	SSQ
1	double donor	0.38	1.80	0.0264	1.50	2.53	0.984
2	single donor/ single acceptor	0.55	1.37	0.0138	1.50	1.19	0.536
3	double acceptor	0.63	0.85	0.0744	1.50	0.06	0.197

^aValues assuming that τ_A represents a single acceptor. If A is really a double acceptor, then the τ_A values should be divided by 2.

determine the charged fractions of V_{As} and the acceptor at a particular ϕ , sum these fractions to determine the total ionized concentration N_I (remembering to weigh the various fractions by Z^2 , where Z is the charge), and compare this N_I with that found from a Boltzmann equation analysis of the experimental μ value at the same ϕ . For each case (DD, SD/SA, DA) we have determined N_I vs ϕ under two different assumptions: (1) the shallow acceptor created by the irradiation is singly charged (SSA); and (2) it is doubly charged (DSA). It is possible that this acceptor could even be triply charged, as has been suggested for the defect V_{Ga} , but we did not include this possibility in the figures. The best fit of N_I vs ϕ is also for the SD/SA case, with the assumption that the irradiation acceptor A is doubly charged. Thus, both the n vs ϕ and N_I vs ϕ curves can be explained if $E1$ is the $(-/0)$ transition, and $E2$ the $(0/+)$ transition of a V_{As} -related defect, having a production rate of 0.6 cm^{-1} , and A is a doubly charged acceptor, with a production rate of 0.7 cm^{-1} . The good fits for the SD/SA case do not of course totally exclude the other cases because all of the n vs ϕ fits were reasonably good, and the μ vs ϕ data could be influenced by irradiation-induced inhomogeneity.

V. DISCUSSION

The SD/SA case seems to give the best fits to both the n vs ϕ and N_I vs ϕ data, although not overwhelmingly so. However, there are additional negative factors regarding the other two cases. For example, the $(+/++)$ transition of the DD case might be expected to have an energy much larger than $E_C - 0.15 \text{ eV}$, since the electron must come from the deep A_1 state which is usually assigned an energy quite close to the valence band.¹⁷ Also, the AA case is doubtful on the basis of the capture cross section of $E1$, $2 \times 10^{-15} \text{ cm}^2$, which seems much too large for a $(--/-)$ transition, in which an electron is being captured on an already negative center. It is somewhat disturbing, however, that the τ_E 's for all three cases are well below the values of $1.5\text{--}2.0 \text{ cm}^{-1}$ measured by earlier DLTS and Hall effect measurements.^{2,5} The same holds for the value of τ_A , which was found to be about 4 cm^{-1} for a single shallow acceptor (or 2 cm^{-1} for a double shallow acceptor) in a Hall effect study.⁵ The answer could lie in the fact that most of these earlier studies were performed on much purer GaAs samples ($n \sim 10^{14}\text{--}10^{15} \text{ cm}^{-3}$) compared with the 10^{17} cm^{-3} samples being considered here. Indeed, electron loss rates $\Delta n / \Delta \phi$ of $0.5\text{--}5.0 \text{ cm}^{-1}$ have been reported in the literature,³ and some of this variation may arise from differences in materials although measurement conditions, such as beam current density, could also be important. It is tempting to normalize our τ_E value of 0.55 cm^{-1} to the

accepted value of 1.5 cm^{-1} , which would then bring τ_A to 1.9 cm^{-1} , close to the previously measured value; however, we can find no obvious justification for this procedure. In spite of our lower values of τ_E and τ_A , one central point should not be missed, namely, that the acceptor center A (represented by τ_A) is being produced at a higher rate than that of $E1$ and $E2$, which were previously thought to be the dominant electron irradiation centers. This was also the central message of an earlier Hall effect study in which it was suggested that A may be related to Ga sublattice damage,⁵ although the production of V_{As} with the subsequent hopping transition $V_{As} \rightarrow V_{Ga}Ga_{As}$ cannot be ruled out.¹⁸

In summary, we have shown that an acceptor well below $E_C - 0.15 \text{ eV}$ is being produced at a high rate in degenerate, n -type GaAs. By fitting n vs ϕ and N_I vs ϕ to statistical models, it appears most likely that $E1$ is the $(-/0)$ transition and $E2$ the $(0/+)$ transition of V_{As} , and that the irradiation acceptor is doubly charged. However, these conclusions are not absolute, and the final model must await further studies.

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