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Identification of the arsenic-antisite–arsenic-vacancy complex in electron-irradiated GaAs

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We report the observation by electron paramagnetic resonance of a new irradiation-induced defect in *n*-type GaAs. It is characterized by the spin Hamiltonian parameters $S = \frac{1}{2}$, $g = 1.97 \pm 0.06$, $A = 0.068 \pm 0.004\ \mathrm{cm^{-1}}$, $I = \frac{3}{2}$ (100%) and attributed to the complex formed by an arsenic-antisite defect and an arsenic vacancy on a first-nearest-neighbor position $\mathrm{As_{Ga}As_3}V_{\mathrm{As}}$. We consider it to be the precursor defect to the isolated antisite defect $\mathrm{As_{Ga}As_4}$, which is subsequently formed by the trapping of a mobile arsenic interstitial by this complex. Contrary to this last defect, the level associated with the $0 \rightarrow +$ transition of the antisite-vacancy complex is shallow with an ionization energy $E \leq 0.35$ eV from the conduction band.

INTRODUCTION

Since its first detection by electron paramagnetic resonance (EPR) in chromium-doped GaAs (Ref. 1), the arsenic-antisite defect $\mathrm{As_{Ga}}$ has been found to be omnipresent in the $10^{16}\ \mathrm{cm^{-3}}$ concentration range in GaAs grown by the liquid-encapsulated Czochralski (LEC) or the horizontal Bridgman technique.[2,3] As the ligand hyperfine structure of this defect is not resolved, its first-nearest-neighbor structure has been deduced by scaling of the corresponding parameters of the phosphorus antisite defect $P_{\mathrm{Ga}}\mathrm{P_4}$ in GaP, for which this interaction has been resolved.[4] Subsequently, optically detected electron-nuclear double resonance (ODENDOR) studies have been performed on $\mathrm{As_{Ga}}$ defects in as-grown semi-insulating and plastically deformed GaAs; it was deduced that in these samples two different $\mathrm{As_{Ga}}$ complexes existed.[5]

Arsenic-antisite defects have also been observed in electron-irradiated GaAs.[6-8] No ENDOR studies have been performed on antisite defects in electron-irradiated GaAs. Surprisingly, their introduction rates R in the case of *n*-type GaAs doped with group-IV or group-VI elements and in the case of semi-insulating or *p*-type GaAs are very different, whereas in the first case R is as high as $1\ \mathrm{cm^{-1}}$, it is only $10^{-2}\ \mathrm{cm^{-1}}$ in the second case.[7,8] Even though this difference in the introduction rates has not been explained up to now, it suggests strongly that the creation mechanisms are not the same in the two cases. Anyhow, the primary radiation defects are Frenkel pairs in the gallium and arsenic sublattices. Thus, any radiation-induced defect will depend on their stability. Recently, it has been proposed that the atomic arrangement of the gallium vacancy has a structural bistability, which can lead to the formation of the arsenic-antisite–arsenic-vacancy complex,[9] a defect not observed up to now.

In this paper we report the study of arsenic-antisite defects in electron-irradiated *n*-type GaAs, a case where its introduction rate is close to that predicted for primary defects. We observed a new arsenic-antisite defect complex which we relate to this structural instability of the gallium vacancy. Further, our results give evidence that the arsenic-antisite defect created subsequently to the new defect complex is the isolated $\mathrm{As_{Ga}As_4}$ defect.

EXPERIMENTAL PROCEDURE

The measurements were performed on LEC-grown, Si-doped ($1 \times 10^{17}\ \mathrm{cm^{-3}}$) *n*-type GaAs. The samples were irradiated at room temperature with electrons of 1.5 MeV energy up to a dose of $2 \times 10^{17}\ \mathrm{cm^2}$. The EPR measurements were performed at $T = 16$ K with a *X*-band spectrometer.

RESULTS

After a first electron dose of $3 \times 10^{16}\ \mathrm{cm^{-2}}$, the samples were partially compensated and the free carriers were frozen out for temperatures below 100 K, making low-temperature EPR measurements possible. From deep-level transient spectroscopy (DLTS) studies on similar samples, we know that the Fermi level in this case is pinned to that of the radiation-induced $E3$ electron trap at $E_c - 0.35$ eV.[10] In thermal equilibrium at 16 K the samples showed one dominant and new EPR spectrum (Fig. 1); it corresponds to an isotropic quadruplet of equal inten-

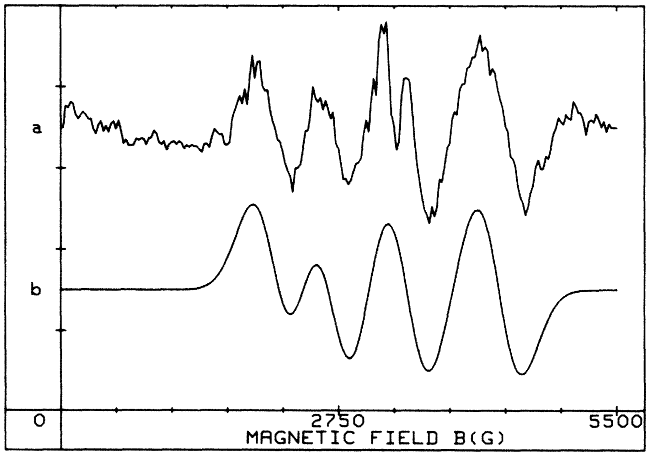

FIG. 1. Curve *a*, EPR spectrum of electron-irradiated *n*-type GaAs; $T = 16$ K, $\mathbf{B} \parallel [110]$ thermal equilibrium; curve *b*, simulated $\mathrm{As_{Ga}As_3V_{As}}$ spectrum (Breit-Rabi formula) with the parameters $g = 1.97$, $A = 6.80 \times 10^{-2}\ \mathrm{cm^{-1}}$, linewidth of 450 G.

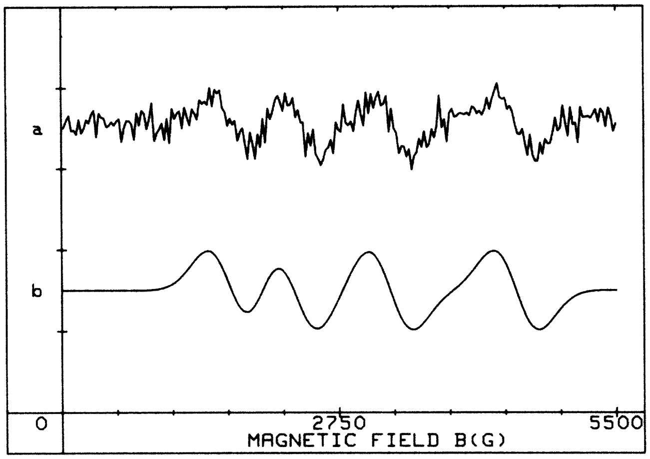

FIG. 2. Curve *a*, Photo-EPR spectrum of electron-irradiated *n*-type GaAs; $T=16$ K, $B\parallel[110]$; photoexcitation $E=1.24$ eV; curve *b*, simulated $\mathrm{As_{Ga}As_4}$ spectrum (Breit-Rabi formula) with the parameters $g=2.03$, $A=8.90\times10^{-2}\ \mathrm{cm^{-1}}$, linewidth 450 G.

sity. Superposed on this is a single-line background spectrum at $g=2$. The spectrum can be described by the spin Hamiltonian

$$H=\beta g\mathbf{S}\cdot\mathbf{B}+A\mathbf{I}\cdot\mathbf{S}\ ,$$

with $S=\frac{1}{2}$, $I=\frac{3}{2}$ (100%), $g=1.97\pm0.06$, $A=(6.80\pm0.40)\times10^{-2}\ \mathrm{cm^{-1}}$; the peak-to-peak linewidth is 450 G. A similar spectrum has very recently been observed by optical absorption (magnetic circular dichroism EPR) measurements.[11] The spectrum observed by us is similar to the EPR spectrum of the antisite $\mathrm{As_{Ga}As_4}$ in electron-irradiated GaAs,[8] besides a strongly reduced central hyperfine interaction. Under photoexcitation with an energy $E=1.24$ eV, an additional spectrum is superposed, the parameters of which identify it as that of the $\mathrm{As_{Ga}As_4}$ defect (Fig. 2). After an additional electron dose of 2×10^{16} $\mathrm{cm^{-2}}$, the samples are further compensated and the free carriers are now frozen out at $T=270$ K, that is the Fermi level is pinned by the $E4$ electron trap at $E_c-0.76$ eV.[10] Then at thermal equilibrium at 16 K only the EPR spectrum of the $\mathrm{As_{Ga}As_4}$ defect is observed. However, under band-to-band photoexcitation the new antisite spectrum is superposed, but with a reduced intensity as compared to the case after the first electron dose. Still further electron irradiation leads to samples which are semi-insulating at room temperature, in which only the EPR spectrum of the $\mathrm{As_{Ga}As_4}$ defect is observed and photoexcitation no longer induces the new spectrum.

DISCUSSION

The spin Hamiltonian parameters with, in particular, the central hyperfine constant of $6.80\times10^{-2}\ \mathrm{cm^{-1}}$ lead us to attribute the new EPR spectrum to an arsenic-antisite defect with only three nearest arsenic neighbors, that is the complex $\mathrm{As_{Ga}As_3}X$ involving an unknown defect X on the nearest-neighbor site. Indeed, in the case of GaP, where the ligand hyperfine structure is resolved in the EPR spectrum, it has been shown that electron irradiation of *n*-type material leads to the formation in the initial stage of the irradiation of the isomorphic $\mathrm{P_{Ga}P_3}X$ defect.[12,13] From the characteristics of its EPR spectrum the spin Hamiltonian parameter A of the equivalent $\mathrm{As_{Ga}As_3}X$ defect had been predicted by proper scaling to $6.86\times10^{-2}\ \mathrm{cm^{-1}}$;[7] as can been seen in Fig. 1, they correspond to those of our new EPR spectrum. The nature of the joint defect X involved in the complex has not been determined in the case of GaP. This can be done in our case since the electron-irradiation-induced defects in *n*-type GaAs have been studied in great detail:[10] First, the introduction rate $R=1$ $\mathrm{cm^{-1}}$ of the $\mathrm{As_{Ga}As_3}X$ defect is close to the theoretical one and experimentally determined one for the total defect introduction in one sublattice; this strongly suggests that it is a *primary* irradiation defect and excludes X to be an impurity-related defect. Second, similar to the case of GaP, the $\mathrm{As_{Ga}As_3}X$ complex is only observed in the early stage of irradiation; larger irradiation doses lead to the disappearance of the $\mathrm{As_{Ga}As_3}X$ defect and its replacement by the $\mathrm{As_{Ga}As_4}$ defect. From these two observations we attribute X to the V_{As} defect. As concerns the formation mechanism of these two defects it has been argued[14] that antisite defects are already present in the as-grown samples and their observation by EPR is only due to a shift of the Fermi level. We believe that for many reasons this model, which has been refuted[15] in the case of GaP is also unacceptable in the case of GaAs; indeed, these defects, in spite of their high concentration, have never been detected by any experimental technique in as-grown samples, in particular, their nonobservation by DLTS is a strong objection. Identical concentrations of the two defects, which additionally should be proportional to the donor doping concentration, is equally difficult to understand. On the contrary, all observations are simply explained in the model of irradiation-induced defects: Electron irradiation produces primary Frenkel pairs in the Ga and As sublattices. The gallium vacancies V_{Ga} are unstable in *n*-type GaAs under the irradiation conditions and transform by the jump of one arsenic atom into the nearest-neighbor gallium vacancy:

$$\mathrm{Ga_{Ga}As_4}\rightarrow V_{\mathrm{Ga}}\mathrm{As_4}+\mathrm{Ga}_i\rightarrow\mathrm{As_{Ga}As_3}V_{\mathrm{As}}+\mathrm{Ga}_i\ .$$

As concerns the subsequent defect evolution under further electron irradiation, it has been shown that electron irradiation also creates arsenic interstitials As_i,[10] which are mobile and therefore can interact with the $\mathrm{As_{Ga}As_3}V_{\mathrm{As}}$ complexes, resulting in the formation of isolated $\mathrm{As_{Ga}As_4}$ defects. The concentration of the two antisite defects will thus strongly depend on the irradiation conditions. This model explains simply the observed introduction rates for the $\mathrm{As_{Ga}As_4}$ defects: Evidently, the $\mathrm{As_{Ga}As_4}$ production at a rate of 1 $\mathrm{cm^{-1}}$ depends on the formation of the precursor defect $\mathrm{As_{Ga}As_3}V_{\mathrm{As}}$. If this defect is not created any longer, the second formation mechanism for $\mathrm{As_{Ga}As_4}$ defects which we have proposed recently can become predominant.[8] It is based on a replacement interaction between mobile arsenic interstitials and gallium-substituted defects. However, our model does not agree with the theoretical predictions[9] in two points: In Ref. 9, V_{Ga} is predicted to be stable in the negative and neutral charge states, which will be expected in n-type material.[16] Second, the wave function of the $As_{Ga}As_3V_{As}$ complex with the paramagnetic As_{Ga} ion located at the V_{Ga} site, has been calculated to be strongly V_{As}-like. At this time two answers can be given: First, even in n-type material the V_{Ga} charge state under the irradiation conditions, that is in the presence of free holes and electrons, is not known. Second, a displacement of the As_{Ga} ion from the V_{Ga} site in the V_{Ga}-V_{As} direction, which will render the wave function As_{Ga}-like,[9] is not excluded from the experimental results.

Our observations allow us to estimate the energy level positions in the gap of the $0 \rightarrow +$ and $+ \rightarrow 2+$ transitions of the $As_{Ga}As_3V_{As}$ defect. Indeed, EPR observation in thermal equilibrium of the paramagnetic + charge state As_{Ga}^{+} with the Fermi level pinned by $E3$ situates the $0 \rightarrow +$ transition closer or equal to 0.35 eV from the conduction band. Nonobservation in thermal equilibrium in samples with the Fermi level pinned by $E4$ situates the $+ \rightarrow 2+$ transition between 0.35 and 0.76 eV from the conduction band. From this an interesting problem arises, whether the $E4$ defect, for which the orientation dependence of its introduction rate has not yet been determined, corresponds to the $As_{Ga}As_3V_{As}$ defect, which is a defect in the gallium sublattice.

In conclusion, we have detected a new EPR spectrum in electron-irradiated n-type GaAs, which we attribute to the arsenic-antisite–arsenic-vacancy complex on nearest-neighbor sites, resulting from a rearrangement of the gallium vacancy, which has been predicted to be a bistable system.[9] The equilibrium position of the paramagnetic As ion is not necessarily the Ga site.[9] For further electron doses this defect transforms into the $As_{Ga}As_4$ defect, which we interprete as being due to the trapping of mobile As_i, simultaneously created by the electron irradiation.

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