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Identification of the arsenic vacancy defect in electron-irradiated GaAs

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We report the systematic observation of a new electron-paramagnetic-resonance spectrum in a wide series of electron-irradiated GaAs crystals. The spectrum consists of a partially resolved multiplet of 700-G linewidth and an effective g factor of 2.00 for $\mathbf{B}\parallel[001]$ and 2.04 for $\mathbf{B}\parallel[110]$. Comparison of its production behavior, photoexcitation spectrum, observability up to $T=70$ K and its thermal annealing at $T=500$ K with previous results obtained by capacitance spectroscopy, lead us to attribute it to the arsenic vacancy perturbed by a distribution of arsenic interstitials ($V_{As}^{-}-As_i$). The experimental spectrum is well simulated in this model with the spin-Hamiltonian parameters $S=1$, $g_{\parallel}(V_{As}\text{-}As_i)=2.00$, $g_{\perp}(V_{As}\text{-}As_i)=2.02$, and $D=0.04$ cm^{-1}.

I. INTRODUCTION

Intrinsic defects in III-V compound semiconductors have been the subject of active research—both theoretically and experimentally–in recent years.[1,2] As concerns the most widely studied compounds GaAs and InP, the application of the electron-paramagnetic-resonance (EPR) technique has led to the identification of three intrinsic defects: the anion antisite defects As_{Ga} (Ref. 3) and P_{In} (Ref. 4) as well as the anion vacancy defect in InP, V_P.[5] When the intrinsic defect concentration in as-grown crystals is too low as compared to the sensitivity of the experimental technique, irradiation with electrons (of 1-MeV energy) is an adequate means for the formation of simple intrinsic defects. Electron-irradiated samples of n- and p-type GaAs have been widely studied by deep-level transient spectroscopy (DLTS) and the main electron and hole traps, created by 1-MeV irradiation, have been attributed to defects in the arsenic sublattice;[6] in particular, the defects associated with the electron traps $E1, \ldots, E5$ are attributed to a distribution of V_{As}-As_i pairs, which anneal at $T=500$ K through the As_i mobility.[6]

We have recently undertaken an EPR study of the As_{Ga} formation by electron irradiation in lightly doped and undoped GaAs.[7] Our results, which showed both a threshold and a saturation for the As_{Ga} formation, were interpreted by the interaction of radiation-induced mobile arsenic interstitials, dissociated from their vacancy, with gallium substituted defects D_{Ga}. In this study, which concerns a variety of different samples, we observe systematically, besides the As_{Ga} defect, a new paramagnetic defect, which is the subject of this paper.

II. EXPERIMENTAL

Two series of liquid-encapsulated Czochralski-grown single crystals have been studied: (i) grown from melts of different stoichiometries, Ga rich ([Ga]/[As] = 1.24), stoichiometric ([Ga]/[As] = 1.015), As rich ([Ga]/[As] = 0.97). (ii) n-type (1×10^{16} cm^{-3}) Sn-doped, -undoped semi-insulating, and -undoped p-type samples. The predominant contaminants, as determined by secondary ion mass spectroscopy and infrared absorption, are Si, S, and C in concentrations of 10^{16} cm^{-3} and B in the 10^{15}–10^{17}-cm^{-3} range.

The electron irradiations were performed at $T=300$ K with 1-MeV electrons at doses ranging from 5×10^{16} cm^{-2} up to 7×10^{17} cm^{-2}. The EPR measurements were done with an X-band spectrometer in the 4- to 100-K temperature range. The samples were photoexcited *in situ* with photons in the 0.8 to 2-μm wavelength range.

III. RESULTS

After a first does of 5×10^{16} e cm^{-2} all samples were semi-insulating at $T=4$ K. At thermal equilibrium at this temperature all of them—with the exception of the Ga-rich p-type sample—presented one dominant EPR spectrum, that of the As_{Ga} defect. Under *in situ* photoexcitation ($E=1.20$ eV, $P=1$ mW), however, a new EPR spectrum appears in all samples, whose intensity is comparable to that of the As_{Ga} defect (Fig. 1). The particular line shape (Fig. 2)

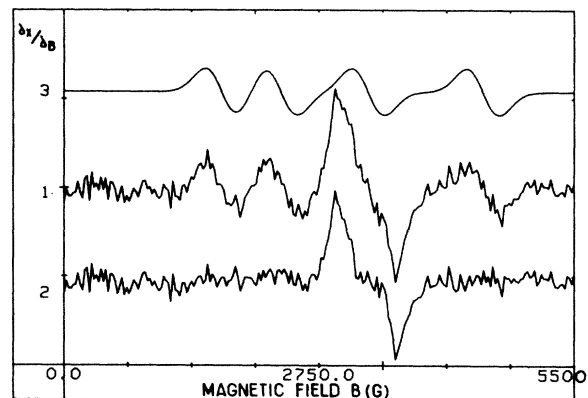

FIG. 1. Photo EPR spectrum of a semi-insulating GaAs sample after irradiation with electrons of 1 MeV at a dose of 7×10^{17} cm^{-2}; $T=16$ K, $\mathbf{B}\parallel[001]$, photoexcitation $E=1.2$ eV, $P=1$ mW (1); the same spectrum after substraction of the As_{Ga} spectrum (3) is shown in (2).

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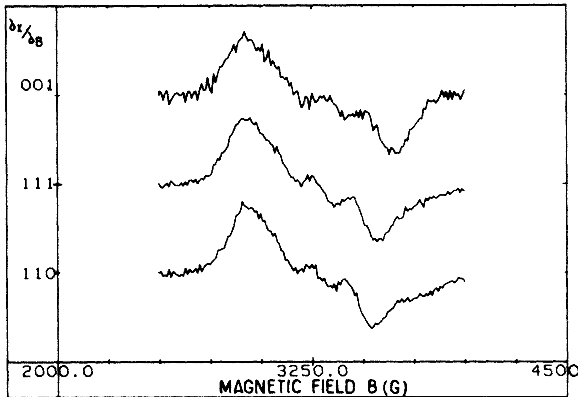

FIG. 2. Angular variation of the EPR spectrum of V_{As}^{-}-As_i for $\mathbf{B} \parallel (001)$, $\mathbf{B} \parallel [110]$, $\mathbf{B} \parallel [111]$, $T = 4$ K.

shows it to be a partially resolved multiplet of at least three overlapping lines. The EPR spectrum is slightly anisotropic and has an overall peak-to-peak linewidth of 720 G for $\mathbf{B} \parallel [001]$ and 680 G for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$; the effective g factors for the center of gravity are $g_{\mathbf{B} \parallel [001]} = 2.00$ and $g_{\mathbf{B} \parallel [110]} = 2.04$. The spectrum can be observed under photoexcitation up to a temperature of 70 K. Contrary to the As_{Ga} defect observed in as-grown semi-insulating samples, which is related to the $EL2^{+}$ defect, the As_{Ga} defect formed by e^{-} irradiation shows no photoinduced metastable behavior.[8] The new defect is created in all types of samples, stoichiometric or not, n type, p type, or semi-insulating, without any electron dose threshold. Further, its intensity does not saturate up to the highest electron dose used (7×10^{17} cm^{-2}) (Fig. 3). Its apparent introduction rate is 10^{-2} cm^{-1}; however, this value is a lower limit only, as it corresponds to the stationary concentration obtained for a specific photoexcitation.

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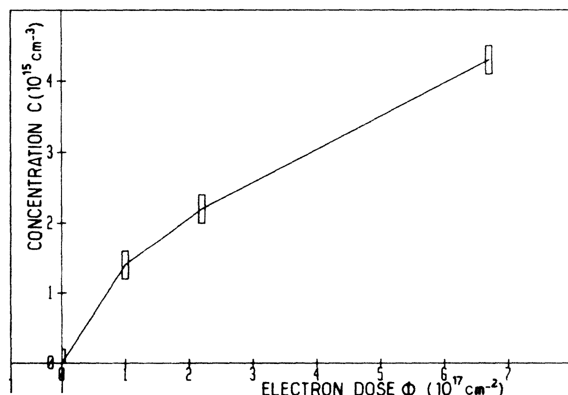

FIG. 3. Steady-state concentration of the V_{As}^{-}-As_i defect vs electron dose.

IV. DISCUSSION

As the defect, whose EPR spectrum we observe, presents a simple linear creation behavior with electron dose—absence of threshold and saturation—and is created with the same introduction rate in all five different types of materials studied, in which the only impurities present at this concentration (B, Si, S, C) vary from one sample to another, we must attribute this defect to a primary intrinsic defect, that is, vacancies V_{Ga}, V_{As}, interstitials Ga_i, As_i, or Frenkel pairs V_{As}-As_i, V_{Ga}-Ga_i. As we will show in the following, only V_{As}-As_i defects are compatible with all experimental results. It has been shown that the E defects observed by DLTS in 1-MeV room-temperature electron-irradiated GaAs all belong to the As sublattice, whereas no defect belonging to the Ga sublattice has been observed.[6] A possible explanation for this might be the opposite charge state of V_{Ga} and Ga_i defects in semi-insulating and n-type material, giving rise to a Coulomb attraction.[9] It has been further demonstrated by DLTS that the annealing stage at 500 K, where the E defects disappear, corresponds to the annealing of these V_{As}-As_i defects.[6]

A further indication is given by the fact that the EPR spectrum is not observable in thermal equilibrium in semi-insulating samples: Whereas the V_{Ga} is expected to have two paramagnetic charge states V_{Ga}^{2+}, V_{Ga}^{0} in the lower half of the energy gap with V_{Ga}^{0} being the stable charge state in semi-insulating material, the V_{As} defect should introduce gap states in the upper half of the energy gap and will be expected to be in the nonparamagnetic charge state V_{As}^{+} in semi-insulating material;[9] photoexcitation at 4 K will lead to the population of the $V_{As}^{0}, V_{As}^{-}, V_{As}^{2-}$ charge states, depending on the respective electron and hole capture cross sections and excitation conditions. The observability of the EPR spectrum at temperatures as high as 70 K excludes the V_{As}^{2-} charge state associated with the $E1$ defect,[10] which has a thermal ionization energy of 45 meV. Further, the attribu-

tion of the new defect to arsenic Frenkel pairs allows also an understanding of the observed anisotropy of the EPR spectrum in a simple manner: The used irradiation conditions are expected to lead to a broad distribution of Frenkel pairs as concerns their distance and orientation in the lattice. The modeling of the experimental spectrum in this picture, that is, a substitutional paramagnetic defect V_{As}^{-}, with a spin $S=1$, in noncubic symmetry, arising from the presence of associated defects As_i on one of the 24 sec- and third-nearest-neighbor interstitial sites and described by the spin Hamiltonian

$$H=\beta\mathbf{B}\cdot\overline{\overline{\mathbf{g}}}\cdot\mathbf{S}+D[S_z^2-1/3S(S+1)]+E(S_x^2-S_y^2) ,$$

gives a satisfactory fit with the following parameters (Fig. 4):

$$g_{\parallel}(V_{As}\text{-}As_i)=2.00,\quad g_{\perp}(V_{As}\text{-}As_i)=2.02 ,$$

$$D=4\times10^{-2}\ \mathrm{cm}^{-1},\quad E=0,\quad B=250\ \mathrm{G} ,$$

where the g tensor for each of the 24 pair configurations (V_{As}-As_i) has been assumed to have axial symmetry around the (V_{As}-As_i) axis. Due to the low resolution of the experimental spectrum only one set of g,D values has been used for the two pair configurations. The experimental observation that the spectrum does not collapse for $\mathbf{B}\parallel[111]$ or $\mathbf{B}\parallel[001]$ excludes all first-neighbor pair configurations. The validity of this model has been further tested by a measurement at a second microwave frequency (35 GHz).

A singly negative V_{As} defect has four electrons in the highest electron states; two of them occupy a lower a_2 state, the two other being in the triplet state t_2^2. Contrary to the isoelectronic defect V_{Si}^{0} in silicon, but in accordance with the case of the neutral cation vacancy in GaP,[11] which has a spin $S=\frac{3}{2}$, the two spins of the t_2 electrons are aligned parallel and give rise to a $^3P_2$ ground state, which will further split in the lowered symmetry.

In conclusion, our EPR results in electron-irradiated GaAs have shown the existence of a new spectrum, whose characteristics are consistent with its attribution to a vacancy defect. Its creation behavior versus electron dose and type of material, its thermal annealing at $T=500$ K, and its pho-

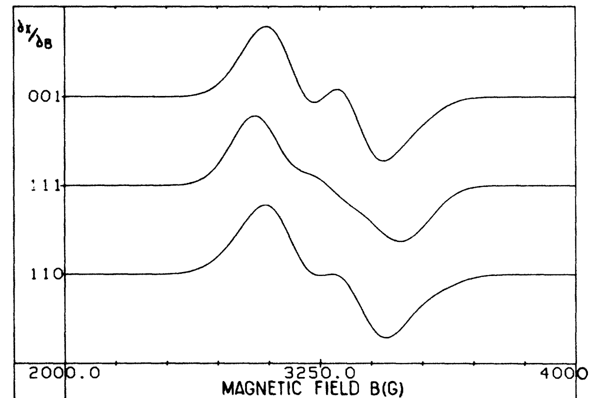

FIG. 4. Computer-simulated EPR spectra for the three orientations $\mathbf{B}\parallel[001]$, $\mathbf{B}\parallel[111]$, $\mathbf{B}\parallel[110]$; parameters are given in the text.

toexcitation response in semi-insulating samples allow its identification with the V_{As}^{-} defect. The observed spin-1 state shows the importance of many-electron effects for the electronic structure of this defect. The intermediate charge state V_{As}^{0} could not be observed for the lowest photoexcitation intensities used.

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