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Electron-paramagnetic-resonance study of GaAs grown by low-temperature molecular-beam epitaxy

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Electron-paramagnetic-resonance results demonstrate an arsenic-antisite related deep donor defect to be the dominant native defect in GaAs layers grown by low-temperature molecular-beam epitaxy (LTMBE). This defect is different from the *EL2*-related native arsenic-antisite defect. The thermal-equilibrium concentration of $3 \times 10^{18} \text{ cm}^{-3}$ ionized As_{Ga} defects directly shows the additional presence of unidentified acceptor defects in the same concentration range. The defect distribution in GaAs grown by LTMBE is unstable under thermal annealing at $T \approx 500^\circ\text{C}$.

GaAs layers grown by low-temperature molecular-beam epitaxy (LTMBE) have recently been shown to have highly improved properties as buffer layers in both modulation-doped field-effect transistor (MODFET) and metal-semiconductor field-effect transistor (MESFET) devices as compared to conventionally grown ($T \approx 600^\circ\text{C}$) GaAs layers.¹ They eliminate backgating and reduce both the sidegating and the light sensitivity of these devices. The modifications of the electrical and optical properties of these undoped LTMBE layers are due to a drastic change in the native-defect concentrations. Whereas conventional layers are characterized by native defects in the 10^{14}-cm^{-3} concentration range,^{2,3} results on layers grown at 200°C indicate native defects at concentration higher than 10^{19} cm^{-3} .^{4,5} Among them, only the arsenic-antisite has, to our knowledge, been identified.^{4,6,7} In fact, arsenic-antisite defects have been studied before by magnetic-resonance techniques and one of the main results is that there is not just one arsenic-antisite defect, but that at least, three different arsenic-antisite-related defects can exist in GaAs;⁸⁻¹⁰ they are distinguished by their central hyperfine interactions and different excited states;^{11,12} their exact different local atomic configuration are unknown. We report in this paper electron-paramagnetic-resonance (EPR) results on the arsenic-antisite defect in LTMBE layers, and demonstrate that they are different from the *EL2*-related As_{Ga} defect. We have further investigated the thermal stability of these defects in the $200\text{--}600^\circ\text{C}$ temperature range. Our results demonstrate first a rearrangement of the local atomic defect configuration at temperatures as low as 400°C . Further annealing at higher temperature ($T > 450^\circ\text{C}$) then leads to a 90% annihilation of the As_{Ga} defects. These results are extremely surprising when

compared to those obtained for the *EL2*-related As_{Ga} , for which a high thermal stability ($\approx 950^\circ\text{C}$) in bulk liquid-encapsulated Czochralski (LEC) samples has been reported.¹³

Recent Hall-effect measurements⁵ have also given a first insight into the electrical compensation in these LTMBE layers. Temperature-dependent Hall data were fitted with a high concentration N_D of deep donors with a thermal ionization energy of 0.75 eV, as expected for *EL2*-like As_{Ga} defects, but were also fitted with a low concentration of native acceptors N_A with $N_A/N_D \sim 10^{-4}$. Our EPR results, which concern the singly ionized As_{Ga} defect, are inconsistent with this model, as they indicate a native acceptor concentration in the 10^{18}-cm^{-3} range. These differences will be discussed later.

The MBE layers used in this study were grown in a Varian 360 system under normal As-stabilized conditions at a growth rate of $0.8 \mu\text{m/h}$ at a temperature of 200°C on undoped semi-insulating GaAs substrates. The layer thickness was $15 \mu\text{m}$. The EPR measurements were performed with an *X*-band spectrometer under both thermal equilibrium conditions and after various optical excitation. Absolute spin concentrations were determined with a NBS standard sample. Isochronal thermal annealings of the samples for 15 min in the $300\text{--}600^\circ\text{C}$ temperature range were performed in an open furnace under a flowing argon stream between GaAs proximity wafers. Typical sample dimensions were $4 \times 8 \times 0.5 \text{ mm}^3$. Similar samples had been previously studied by optical-absorption⁷ and Hall-effect measurements.⁵

When the samples were cooled under thermal equilibrium conditions to 4 K, they showed one four-line EPR

spectrum (Fig. 1), with the following parameters: isotropic g factor $g=2.04\pm0.01$ and isotropic central hyperfine interaction $A=(866\pm13)\times10^{-4}\text{ cm}^{-1}$, with a nuclear spin $I=\frac{3}{2}$ of 100% isotopic abundance. This spectrum is attributed to an arsenic-antisite defect in the paramagnetic $1+$ charge state; by comparison with an $\text{Al}_2\text{O}_3\text{:Cr}$ standard sample, the spin concentration is determined to $3\times10^{18}\text{ cm}^{-3}$. The spectrum is well fitted by the Breit-Rabi formula¹⁴ [Fig. 1(b)], which indicates that no additional spectrum is observed under these conditions. To prove definitely that the EPR spectrum is exclusively originating from the MBE layer, on one sample this layer has been polished away. No EPR signal was observed at 4 K in the substrate without the layer. The As_{Ga} spectrum is not saturated up to microwave powers of 100 mW. The parameters of the spectrum do not vary with the microwave power P for $0.2\leq P\leq100\text{ mW}$. The peak to peak linewidth is 400 G. The value of the central hyperfine interaction demonstrates in agreement with the short spin-lattice relaxation time at 4 K that the As_{Ga} defect is different from the EL2-related one, which has an A value of $(890\pm10)\times10^{-4}\text{ cm}^{-1}$,⁸ and due to long spin-lattice relaxation times can generally not be observed at 4 K. However, its EPR parameters are close with those of the As_{Ga} defect generated by electron irradiation in n -type GaAs. That defect, due to its formation mechanism^{9,10} as well as its simple magnetic circular dichroism spectrum¹¹ had been attributed to the isolated As_{Ga} ;¹⁵ the EL2-related As_{Ga} must then correspond to a different defect complex, as has been proposed before.¹⁶ A further fingerprint of the EL2-related As_{Ga} defect is its metastability under near-infrared photoexcitation ($E\sim1.2\text{ eV}$). In agreement with previous results on the electron irradiated As_{Ga} ,^{15,17} the native As_{Ga} defect in LTMBE GaAs is not photoquenchable at all. On the contrary, 1.2-eV photoexcitation leads to a persistent increase of up to 50% in the As_{Ga}^+ concentration. We have further determined the spectral dependence of the optically induced As_{Ga}^+ concentration increase in the

0.5–1.5-eV energy range: from a threshold energy $E=0.6\text{ eV}$, its concentration is increased for all photon energies up to 1.5 eV.

The optically induced increase in the As_{Ga}^+ concentration must be due to photoionization of either As_{Ga}^0 to the conduction band or $\text{As}_{\text{Ga}}^{2+}$ to the valence band. From previous optical-absorption studies on similar samples grown under identical conditions, we know that most of the As_{Ga} defects are present in the neutral charge state under thermal equilibrium condition ($N_D^0\sim3\times10^{19}\text{ cm}^{-3}$);⁷ thus the Fermi level is blocked in these samples on the $0/+$ level of the As_{Ga} defect. In this case, the dominant photoionization process for photon energies of $\geq0.6\text{ eV}$ will be $\text{As}_{\text{Ga}}^0\rightarrow\text{As}_{\text{Ga}}^++e^-$, where the free electron is trapped on the electron traps. The position of the $0/+$ level in the gap has been shown before for the electron-irradiation-induced As_{Ga} to be shifted to the conduction band¹⁶ as compared to the EL2-related $0/+$ level, which is at $E_c-0.76\text{ eV}$. The photoionization threshold of 0.6 eV observed in our LTMBE samples confirms these results and situates the $0/+$ As_{Ga} level in this case at $\lesssim E_c-0.6\text{ eV}$. However, it should be noted that the Hall-effect donor is at $E_c-0.75\text{ eV}$.⁷

Our EPR results demonstrate further the presence of both additional donor and acceptor defects in the 10^{18} cm^{-3} concentration range in these low-temperature-grown layers. From the As_{Ga}^+ concentration of $3\times10^{18}\text{ cm}^{-3}$ in thermal equilibrium, a lower limit for the total acceptor concentration below the Fermi level must be $3\times10^{18}\text{ cm}^{-3}$. This value apparently disagrees with the electrical compensation model based on Hall-effect measurements, where from a fitting procedure an acceptor concentration of $7\times10^{-14}\text{ cm}^{-3}$ had been proposed;⁵ these issues are discussed below. As a result of the expected low degree of contamination during the MBE growth process, which for $\sim600^\circ\text{C}$ growth temperatures gives rise to extrinsic acceptor (C, Zn) contaminations in the $10^{14}\text{--}10^{15}\text{ cm}^{-3}$ range, the native acceptor compensating the As_{Ga} donor is expected to be of intrinsic nature. The Ga_{As} and the V_{Ga} seem to be the most probable candidates.

The optically induced photoionization of As_{Ga}^0 , which is stable at 4 K, shows the additional presence of shallow electron traps in the 10^{18} cm^{-3} concentration range. In agreement with a previous observation,^{4,6} we find two partial thermal annealing stages for this process at 50 and 100 K corresponding to the thermally activated re-emission of the photocaptured electrons from these donors; they are shallower than the $\text{As}_{\text{Ga}}^{0/+}$ level; their thermal ionization energy can be roughly estimated from the thermal annealing stages to $\sim100\text{ meV}$. The previous attribution^{4,6} of the photoionization process to the valence-band- $\text{As}_{\text{Ga}}^{2+}$ transition and the corresponding thermal annealing steps at 50 and 100 K to hole emission from acceptor states does not apply in our case on the basis of our combined optical-absorption and EPR results.

We have further studied the thermal stability of the As_{Ga} defects for annealings in the $300\text{--}600^\circ\text{C}$ temperature range. From the optical-absorption studies⁷ as well

FIG. 1. EPR spectrum of a 15- μm -thick LTMBE GaAs layer at $T=4\text{ K}$: (a) experimental spectrum; (b) simulated As_{Ga}^+ spectrum with $g=2.04$, $A=866\times10^{-4}\text{ cm}^{-1}$, $\Delta B_{pp}=400\text{ G}$.

as the Hall-effect results⁵ a drastic change in the defect concentration after annealing at temperatures higher than 450°C has been reported. Further, the lattice parameter of the LTMBE material, which shows an increase of $\sim 0.1\%$ as compared to the LEC-grown substrate material, has also been reported to decrease after annealing at 450°C to that of the substrate material.^{4,6} Our EPR results of 15-min isochronal anneal are given in Table I and Fig. 2: after a 300°C anneal, the thermal equilibrium values of the As_{Ga}^+ defect—concentration and EPR parameters—are unchanged. The additional 400°C anneal increases the As_{Ga}^+ concentration by $\sim 10\%$; but now the hyperfine interaction constant of the totality of the As_{Ga}^+ ions has changed to $877 \times 10^{-4} \text{ cm}^{-1}$. Nevertheless, a low-temperature photoexcitation shows still no metastability of this defect. The anneal at 500°C then reduces the As_{Ga}^+ concentration by a factor of 6 and the 600°C anneal by an additional factor of 4 without further change in the hyperfine interaction.

Since $[\text{As}_{\text{Ga}}^+] \approx N_A$, it follows that N_A decreases from 3×10^{18} to $1.5 \times 10^{17} \text{ cm}^{-3}$ after a 600°C anneal. However, the Hall-effect⁵ and absorption⁷ results show that $[\text{As}_{\text{Ga}}]$ itself decreases by about a factor of 10–20. The data from the three different experiments correlate well as a function of annealing temperature, as shown in Fig. 2. Note that the decrease in N_A is in qualitative agreement with the results of Ref. 4. Note also that a similar low thermal stability of the EL2-related As_{Ga} defect has been reported before,¹⁸ but only for the near-surface regions (a few μm).

We now return to the apparent discrepancy between the EPR results reported here, which are consistent with an acceptor concentration of N_A of $3 \times 10^{18} \text{ cm}^{-3}$ in unannealed material, and the temperature-dependent Hall-effect results,⁵ which are best fitted with

FIG. 2. Variation of the ionized As_{Ga}^+ concentration (—) as well as the neutral As_{Ga}^0 concentration (---) (after Ref. 7) and the total donor concentration (---) (after Ref. 5) as a function of isochronal annealing.

perature, then $N_D \sim 2 \times 10^{21} \text{ cm}^{-3}$, which is clearly impossible and also disagrees strongly with the N_D values ($\sim 3 \times 10^{18} \text{ cm}^{-3}$) measured by both absorption⁷ and Hall effect⁵ in annealed samples. There are two possible resolutions to this discrepancy. The first involves the fact that the majority of 200°C, MBE-grown GaAs layers are known to contain large concentrations of pyramidal-shaped defects.¹⁹ It is quite possible that such defects could be decorated with acceptors (perhaps V_{Ga}) close to the valence band, and thus induce a charge transfer ($\text{As}_{\text{Ga}}^0 + V_{\text{Ga}}^0 \rightarrow \text{As}_{\text{Ga}}^+ + V_{\text{Ga}}^-$) for As_{Ga} centers in the vicinity of the pyramidal defects. The EPR results could be explained if about 10% of the total As_{Ga} ($3 \times 10^{19} \text{ cm}^{-3}$ in unannealed material) participated in the charge exchange. The Hall and absorption experiments would be

donor defects in the 10^{18} cm^{-3} range have been found. The As_{Ga} defect is unstable for 450°C thermal annealing; the unexpected low thermal stability of the As_{Ga} defects in LTMBE GaAs—contrary to the *EL2*-related As_{Ga} de-

fect in melt-grown GaAs—leads to the previously reported^{5,7} modification of the electrical and optical properties of this material after thermal annealing in this temperature range.

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