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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 AsGa 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 $T \gtrsim 500 \text{°C}$.

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 ($T \approx 600 \text{°C}$) GaAs layers. 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 $10^{14} \text{cm}^{-3}$ concentration range, results on layers grown at 200°C indicate native defects at concentration higher than $10^{15} \text{cm}^{-3}$. Among them, only the arsenic-antisite has, to our knowledge, been identified. 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: they are distinguished by their central hyperfine interactions and different excited states; 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 AsGa defect. We have further investigated the thermal stability of these defects in the 200–600°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 ($T > 450 \text{°C}$) then leads to a 90% annihilation of the AsGa defects. These results are extremely surprising when compared to those obtained for the EL2-related AsGa defect, for which a high thermal stability ($\gtrsim 950 \text{°C}$) in bulk liquid-encapsulated Czochralski (LEC) samples has been reported.

Recent Hall-effect measurements 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 AsGa 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 AsGa defect, are inconsistent with this model, as they indicate a native acceptor concentration in the $10^{15} \text{cm}^{-3}$ 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 μm/h at a temperature of 200°C on undoped semi-insulating GaAs substrates. The layer thickness was 15 μm. The EPR measurements were performed with a 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 300–600°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-absorption and Hall-effect measurements.

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 $g = 2.04 \pm 0.01$ and isotropic central hyperfine interaction $A = (866 \pm 13) \times 10^{-4}$ cm$^{-1}$, with a nuclear spin $I = \frac{1}{2}$ of 100% isotopic abundance. This spectrum is attributed to an arsenic-antisite defect in the paramagnetic 1+ charge state; by comparison with an Al$_2$O$_3$-Cr standard sample, the spin concentration is determined to $3 \times 10^{18}$ cm$^{-3}$. The spectrum is well fitted by the Breit-Rabi formula$^{14}$ [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 $0.2 \leq P \leq 100$ 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 $(890 \pm 10) \times 10^{-4}$ cm$^{-1}$, 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 spectrum$^{11}$ had been attributed to the isolated As$_{Ga}$$^{12}$, the EL2-related As$_{Ga}$ must then correspond to a different defect complex, as has been proposed before.$^{16}$ A further fingerprint of the EL2-related As$_{Ga}$ defect is its metastability under near-infrared photoexcitation ($E \sim 1.2$ eV). In agreement with previous results on the electron irradiated As$_{Ga}$$^{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 $E = 0.6$ 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$_{Ga}^+$ to the conduction band or As$_{Ga}^{2+}$ 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 ($N_0^0 \sim 3 \times 10^{19}$ 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 $\gtrsim 0.6$ eV will be As$_{Ga}^0 \rightarrow$ As$_{Ga}^+ + e^-$, 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 band$^{16}$ as compared to the EL2-related 0/+ level, which is at $E_c - 0.76$ 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 $\lesssim E_c - 0.6$ eV. However, it should be noted that the Hall-effect donor is at $E_c - 0.75$ 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 $3 \times 10^{18}$ cm$^{-3}$ in thermal equilibrium, a lower limit for the total acceptor concentration below the Fermi level must be $3 \times 10^{18}$ 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 $7 \times 10^{-14}$ cm$^{-3}$ had been proposed;$^3$ these issues are discussed below. As a result of the expected low degree of contamination during the MBE growth process, which for $\sim 600$ °C growth temperatures gives rise to extrinsic acceptor (C, Zn) contaminations in the $10^{14}$–$10^{15}$-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 As$_{Ga}^{0/+}$ level; their thermal ionization energy can be roughly estimated from the thermal annealing stages to $\sim 100$ meV. The previous attribution$^4,6$ of the photoionization process to the valence-band–As$_{Ga}^{2+}$ 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 300–600 °C temperature range. From the optical-absorption studies$^7$ as well
as the Hall-effect results\(^5\) 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\(^+_\text{Ga}\) defect—concentration and EPR parameters—are unchanged. The additional 400°C anneal increases the As\(^+_\text{Ga}\) concentration by \(\sim 10\%\); but now the hyperfine interaction constant of the totality of the As\(^+_\text{Ga}\) ions has changed to \(877 \times 10^{-4}\) cm\(^{-1}\).

Nevertheless, a low-temperature photoexcitation shows still no metastability of this defect. The anneal at 500°C then reduces the As\(^+_\text{Ga}\) 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 [As\(^+\text{Ga}\)] \(\cong N_A\), it follows that \(N_A\) decreases from \(3 \times 10^{18}\) to \(1.5 \times 10^{17}\) cm\(^{-3}\) after a 600°C anneal. However, the Hall-effect\(^4\) and absorption\(^1\) results show that [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\(^+\text{Ga}\) defect has been reported before,\(^18\) but only for the near-surface regions (a few \(\mu\)m).

We now return to the apparent discrepancy between the EPR results reported here, which are consistent with an acceptor concentration of \(N_A\) of \(3 \times 10^{18}\) cm\(^{-3}\) in unannealed material, and the temperature-dependent Hall-effect results,\(^5\) which are best fitted with temperature, then \(N_D \sim 2 \times 10^{21}\) cm\(^{-3}\), which is clearly impossible and also disagrees strongly with the \(N_D\) values \((\sim 3 \times 10^{18}\) cm\(^{-3}\)) measured by both absorption\(^7\) and Hall effect\(^5\) 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 \(V_{\text{Ga}}\)) close to the valence band, and thus induce a charge transfer (As\(^0\text{Ga}\) + \(V_{\text{Ga}}\) \(\rightarrow\) As\(^+\text{Ga}\) + \(V_{\text{Ga}}\)) for As\(^+\text{Ga}\) centers in the vicinity of the pyramidal defects. The EPR results could be explained if about 10% of the total As\(^+\text{Ga}\) \((3 \times 10^{19}\) 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$_{Ga}$ defect in melt-grown GaAs—leads to the previously reported modification of the electrical and optical properties of this material after thermal annealing in this temperature range.