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Identification of an isolated arsenic antsit defect in GaAsBi

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Optically detected magnetic resonance and photoluminescence spectroscopy are employed to study grown-in defects in GaAs0.985Bi0.015 epilayers grown by molecular beam epitaxy. The dominant paramagnetic defect is identified as an isolated arsenic antsit, AsGa, with an electron g-factor of 2.03 ± 0.01 and an isotropic hyperfine interaction constant A = (900 ± 20) × 10^{-2} cm^{-1}. The defect is found to be preferably incorporated during the growth at the lowest growth temperature of 270°C, but its formation can be suppressed upon increasing growth temperature to 315°C. The AsGa concentration is also reduced after post-growth rapid thermal annealing at 600°C.

Incorporation of bismuth (Bi) in dilute quantities in GaAs has been shown to lead to several intriguing, potentially desirable changes in the fundamental properties of GaAs. The most articulated modifications stem from the interaction of Bi 6p bonding orbitals with the valence band (VB) maximum of GaAs, resulting in a large bowing effect of the decreased bandgap energy and the increased manipulation by an electric field. Furthermore, the combined orbital angular momentum of electrons could enable spin effects on optical and electrical properties should be very strongly manifested. Indeed, recent DLTS measurements have revealed the presence of a number of carrier traps in GaAsBi alloys. BiGa antisite defects were also reported in GaAs lightly doped with Bi. An improved understanding of the microscopic structure of major grown-in defects and impurities along with their influence on physical properties of the GaAsBi alloy is critically needed in order to control them and to fully explore the potential of dilute bismides for device applications.

The aims of the present work are (a) to closely examine and unambiguously identify important grown-in defects in GaAs1-xBix, (b) to obtain information about the role of defects in carrier recombination processes, and finally, (c) to evaluate the effects of growth temperature and post-growth thermal annealing on the defect formation. PL, PL excitation

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annealing on the PL spectra of the GaAs$_{0.985}$Bi$_{0.015}$ alloy

Two GaAs$_{0.985}$Bi$_{0.015}$ epilayers used in this study were grown at two different growth temperatures (270°C and 315°C) on a semi-insulating GaAs (001) substrate by solid-source MBE. The growth started with a 120-nm-thick GaAs buffer layer grown at normal conditions (580°C and a high As overpressure), and was followed by a GaAsBi epilayer (230–250 nm in thickness) grown at a lower temperature with an As/Ga flux ratio close to one as required for efficient Bi incorporation. Additionally, a reference GaAs epilayer was grown under similar conditions as described above but without Bi incorporation and with an As/Ga flux ratio about twice as high as for the GaAsBi samples. The Bi concentration was 1.5% in both GaAsBi samples, as determined by high resolution x-ray diffraction measurements, using the literature value of 6.33 Å for the GaBi lattice constant.

We should note, however, that in addition to Bi incorporation, AsGa antisite defects can contribute to the expansion of the lattice constant thus causing overestimation in the Bi composition by X-ray diffraction (XRD). Representative XRD spectra for the as-grown GaAsBi samples are shown in Fig. 1, measured with a triple-axis X-ray diffractometer from (004) planes using the Cu-Kα radiation. The appearance of the well-defined thickness fringes is indicative of good crystal quality and well-defined interfaces. Detailed study of structural properties of similar (but not identical) GaAsBi layers is reported in Ref. 28.

One piece from each GaAsBi sample was then treated by rapid thermal annealing (RTA) at 600°C for 60 s in a N$_2$ ambient. PL and ODMR measurements were performed at 5 K using either the 915-nm line of a solid state laser or the 751-nm line of a Ti:Sapphire laser as an excitation source. The PL signals were dispersed by a 1-m double grating monochromator and were detected by a liquid nitrogen-cooled Ge detector. ODMR signals were measured at both X-band (9.213 GHz) and Q-band (33.87 GHz) as spin-resonance-induced changes of the PL intensity (detected by a Ge detector) utilizing the lock-in technique in phase with an amplitude-modulated microwave field at a frequency of ~3 kHz.

Figure 2(a) shows the effects of growth temperature and annealing on the PL spectra of the GaAs$_{0.985}$Bi$_{0.015}$ alloy measured at 5 K. In the spectral region of 1.0–1.28 eV, GaAsBi exhibits a strong, broad PL band centered at ~1.15 eV, which is not present in the Bi-free reference structure. This PL emission is tentatively ascribed to recombination of localized excitons. This conclusion is supported by following experimental observations: (i) a blueshift of the PL peak position with increasing optical excitation power, see Fig. 3(a); (ii) an increase of a temperature-induced red-shift of the PL peak position with lower excitation powers (Fig. 3(b)); and (iii) a large Stokes shift of 0.3 eV, indicative of strong localization. The origin of the localized excitons could be excitons either localized at defect states or bound to the band tail states extending from the band edge due to a strong fluctuation of the bandgap as a result of local variations in the alloy composition. The alloy band gap value deduced from the PLE cut-off is 1.28 eV.

Typical ODMR spectra obtained by monitoring the 1.15 eV emission are presented in Fig. 2(b). For the epilayer grown at 270°C, a strong ODMR signal is observed and contains four equidistant lines. The intensity of this signal is dramatically reduced in the sample grown at 315°C, which indicates a significantly lower defect concentration in the alloy grown at the higher temperature. As the same substrate material was used and the GaAs buffer layers were grown under identical conditions in both samples, we can rule out the possibility that the observed ODMR signal originates from the substrate or the buffer layers. Otherwise the same ODMR signal would have been observed in both samples regardless of the growth temperatures of the GaAsBi epilayers. We can also exclude the possibility that the ODMR signal originates from a defect at the GaAs/GaAsBi interface because a defect at an interface should exhibit a reduced symmetry giving rise to an anisotropic spin-resonance signal, such as the P$_6$ defects at Si/SiO$_2$ interface and the DD1...
defect at GaP/GaNP interface, which is in contradiction to the isotropic ODMR signal observed here. Thus, we can conclude that the ODMR signal must originate from a defect situated in the GaAsBi epilayer. The observed ODMR signal is negative, i.e., corresponding to a decrease in the monitored PL intensity upon the spin-resonant transitions. It is shown as positive in Fig. 2(b) merely for easy viewing. The observed decrease in the intensity of the monitored PL under the spin-resonance condition implies that the PL is most likely not directly related to the defect involved in the spin resonance. Instead, it is a result of competing carrier recombination via a defect of a different origin from the one giving rise to the PL. Carrier recombination via the former accelerated by the spin-resonance transitions can thus lead to a corresponding decrease in the radiative carrier recombination of the latter (i.e., the 1.15 eV PL band).

To analyze the quadruplet ODMR spectrum, the following spin Hamiltonian is used in order to calculate the energy levels of the spin system at the defect and the expected magnetic-resonance field positions: $H = \mu B \cdot S + ASI$. Here, $\mu_B$ is the Bohr magneton, $B$ is the external magnetic field, and $A$ is the central hyperfine (hf) parameter that describes the coupling of the electron spin $S$ with the nuclear spin $I$ of the defect. The electronic g-factor and the $A$ parameter are scalars here, since all observed ODMR signals are isotropic. As shown in Figs. 4(a) and 4(b), the quadruplet structure can be reproduced assuming a paramagnetic defect center with a localized electron spin $S = 1/2$ that is strongly coupled by the hf interaction to a nuclear spin of $I = 3/2$ with 100% natural abundance. The only chemical element that satisfies these requirements is arsenic. Therefore, the obtained ODMR results provide an unambiguous experimental proof that the monitored paramagnetic defect involves an As atom.

A best fit to the experimental data are obtained by using the following spin-Hamiltonian parameters: $g = 2.03 \pm 0.01$ and $A = (900 \pm 20) \times 10^{-4}$ cm$^{-1}$. The simulated ODMR curves by using these parameters are shown in Figs. 4(a) and 4(b) for the X- and Q-band, respectively. The good agreement between the simulations and the experimental results justifies the reliability of the obtained fitting parameters.

A comparison of the determined spin Hamiltonian parameters with the previously reported magnetic-resonance signatures of As-containing defects in GaAs shows that the defect in fact belongs to the most thoroughly investigated family of intrinsic defects: As antisites (AsGa). The formation of these defects in the studied GaAsBi is probably not surprising, as low growth temperatures and As overpressure during the MBE growth are known to result in the incorporation of excess As in the GaAs lattice leading to an abundance of As antisites in LT GaAs. Although the As pressure is reduced during the GaAsBi growth in order to ensure Bi incorporation, both Bi and As atoms compete for the same lattice sites which may further promote the AsGa formation. Our results also show that the defect formation is largely suppressed with increasing growth temperature from 270°C to 315°C. In addition, the AsGa-related ODMR signal is completely quenched after an RTA treatment at 600°C for 60 s. This is in agreement with the previous studies of AsGa in LT GaAs, where thermal annealing at similar temperatures has been found to reduce defect concentrations, due to clustering of As atoms.

It is difficult to exactly identify the nearest neighbors of the AsGa atom since ligand hyperfine interactions are not resolved in the measured ODMR spectra. We note, however, that the defects that belong to the AsGa family in GaAs differ in the hf interaction strength $A$, which ranges from $680 \times 10^{-4}$ to $900 \times 10^{-4}$ cm$^{-1}$. The largest value is expected for an isolated AsGa defect, whereas a reduction in $A$ has been taken as evidence for complex formation that leads to a re-distribution of the electron wavefunction from AsGa to its neighboring atoms. Thus, judging from the strength of the hf interaction, we conclude that the defect observed in the GaAsBi alloy grown at 270°C is most likely an isolated
AsGa center with four As neighbors. This defect configuration is also typical for LT GaAs.34–39 The fact that the spin Hamiltonian parameters remain unaffected by the presence of 1.5% of Bi in the GaAs lattice is a result of the strong localization of the electron wavefunction at the As antisite which is known to be a deep donor. Furthermore, the linewidth (35 mT) of the magnetic resonance lines observed here is identical to that reported previously for As antisites in GaAs.26–30

The linewidth is determined by the hyperfine interaction with the ligand atoms surrounding the AsGa, this finding is thereby indicative of identical local surrounding of AsGa in both GaAs and GaAsBi, i.e., Bi is not one of the nearest neighbors of the AsGa in GaAsBi studied here. Previous ESR studies26 of Czochralski-grown GaAs lightly doped with Bi revealed that a substantial fraction (about 10%) of Bi dopants occupied the Ga site, forming BiGa antisite defects. Despite considerable efforts, however, we found no experimental evidence for such behavior in the studied GaAsBi alloys.

In conclusion, we have conducted a detailed study of grown-in defects in MBE-grown GaAsBi epilayers. A solid experimental proof is provided that the dominant paramagnetic defect, which is formed in the GaAsBi epilayer grown at 270 °C, contains an As antisite atom at its core. Based on the comparison of the deduced spin-Hamiltonian parameters for AsGa in GaAsBi with those known for AsGa-related defects in GaAs, the defect configuration is concluded to be an isolated AsGa+ center surrounded by four As neighbors. The defect acts as a competing recombination center (judging from the negative ODMR signal) and could, therefore, be harmful to the performance of optoelectronic devices based on the GaAsBi alloy. It is shown to be preferably incorporated during the growth at the lowest growth temperature, and its formation is suppressed upon increasing growth temperature from 270 to 315 °C. Post growth rapid thermal annealing at 600 °C was found to completely quench the AsGa ODMR signal. The dependence of the defect formation on growth temperature and post-growth thermal annealing is in line with the previously reported properties of AsGa in LT-GaAs.

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