Identification of the Ga Interstitial in $Al_xGa_{1-x}As$ by Optically Detected Magnetic Resonance

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A new optically detected magnetic resonance spectrum in $Al_xGa_{1-x}As$ is reported and assigned to native Ga interstitials. Luminescence-quenching signals were observed over the energy region from 0.75 to 1.1 eV. The optically detected magnetic resonance is nearly isotropic with spin-Hamiltonian parameters $g = 2.025 \pm 0.006$, central hyperfine splitting $A(^{69}Ga) = 0.050 \pm 0.001$ cm^{-1}, and $A(^{71}Ga) = 0.064 \pm 0.001$ cm^{-1} for H near [001]. The strong hyperfine coupling denotes an electronic state of A_1 symmetry, which current theories predict for the Ga interstitial but not the Ga antisite. The slight anisotropy probably indicates that the Ga_i is paired with a second, unknown defect.

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The zinc-blende lattice common to nearly all III-V semiconductors can have three types of intrinsic lattice defects: vacancies, interstitials, and antisites. Because they do not match the usual tetrahedral coordination of the perfect lattice, intrinsic defects produce deep levels in the forbidden gap and alter the electrical and optical properties of the material. Since they are formed from only the lattice elements, these defects are particularly difficult to identify and study. Success has been achieved for vacancies[1,2] and antisites[3-5] in III-V semiconductors by magnetic resonance techniques, which are the most powerful means for the study of intrinsic defects. However, very little is known about the atomic configuration or electronic structure of self-interstitials in III-V materials. Furthermore, only inferential information is available for self-interstitials in any semiconductor.[6,7]

In this Letter, a new optically detected magnetic resonance (ODMR) spectrum in $Al_xGa_{1-x}As$ is reported and assigned to the Ga interstitial.[8] Partially resolved ^{69}Ga-^{71}Ga hyperfine splitting denotes the presence of Ga at the center of the defect and the magnitude of the splitting, taken with current theoretical predictions, completes the assignment to the self-interstitial. The observations were made in $Al_xGa_{1-x}As$ grown by molecular-beam epitaxy (MBE) and provide information on MBE growth kinetics. The experiments further establish ODMR as a powerful tool for the study of defects in epitaxially grown semiconductors. Most importantly, the results reveal direct information on the structure and deep donor character of a self-interstitial in a semiconductor.

The experiments were performed with a 24-GHz, Voigt configuration ODMR spectrometer on samples grown in a Varian Associates Model GEN 1.5 MBE machine. The microwave part of the spectrometer consists of a 50-mW Gunn oscillator whose power was switched on and off at 570 Hz by a *p-i-n* modulator and sent to a TE_{011} cylindrical cavity with slots for optical access. The cavity was immersed in liquid He at 1.6 K in a stainless steel Dewar with optical tail. A 9-in. electromagnet produced the magnetic fields. Optical excitation at 530.9 nm was provided by a Kr^+ laser with about 20 mW incident on the sample. Luminescence was detected with a North Coast 817S Ge detector. The signal-to-noise ratio was enhanced by signal averaging with a Tracor Northern TN-1550. 1-μm-thick $Al_xGa_{1-x}As$ layers were grown with varying Al concentration, substrate temperature, and doping. The ODMR spectrum which is the focus of this paper was observed in different samples covering a range of these parameters. Optimal growth temperature for the production of high-quality $Al_xGa_{1-x}As$ is around 680–700 °C for a growth rate of 1 μm/h. Lower than optimal substrate temperatures favor the production of the defect. The new ODMR spectrum was not seen in samples grown at 680 °C. The sample, designated as M88, which exhibited the strongest hyperfine-split spectrum was grown with $x = 0.26$ at 620 °C and doped with Si to about 3×10^{16} cm^{-3}. Electrical measurements indicated that M88 was of high resistivity.

The photoluminescence at 1.6 K of the $Al_xGa_{1-x}As$ samples grown at lower than optimal temperatures exhibit weaker band-edge emission and stronger deep emission. Sample M88 exhibits only a very weak feature at 1.79 eV in the near band-edge spectrum. Its deep luminescence obtained with a Si filter (see Fig. 1) is rather strong and nearly featureless, and covers most of the long-wavelength range of the Ge detector.

ODMR was observed in these samples by detection of the change in the total deep photoluminescence when the microwaves are on from when they are off. In sample

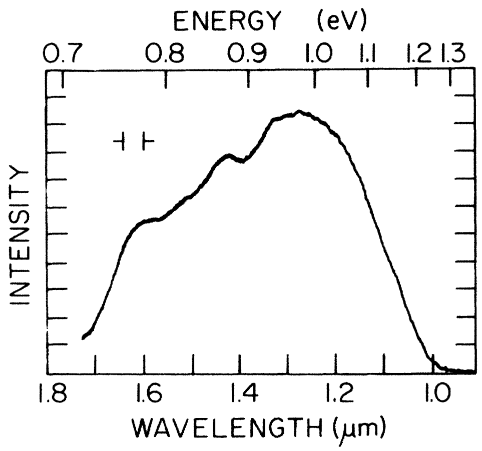

FIG. 1. Deep luminescence at 1.6 K. Data were taken with a Ge detector and Si filter. Negative ODMR signals occur for all energies of these deep emissions.

M88, negative (quenching) signals are obtained with a maximum amplitude of 0.1% (see Fig. 2). Data are shown for three directions of magnetic field relative to the crystal axes. Angles near the [001] are difficult to study for the (001) wafers in the Voigt geometry because the luminescence from the $Al_xGa_{1-x}As$ becomes weak and substrate luminescence is also detected. The spectra consist of a nearly isotropic set of 4 lines with a large, nearly equal splitting of 56 mT. These gross spectral features indicate that the electronic spin experiences a strong, central hyperfine coupling with a nucleus of spin $\frac{3}{2}$. However, the outer lines are weaker and broader than the inner lines, an indication that the hyperfine interaction involves an element with two spin-$\frac{3}{2}$ isotopes having different nuclear moments. Gallium, the only constituent of the $Al_xGa_{1-x}As$:Si which has two spin-$\frac{3}{2}$ nuclei, is the prime candidate to explain the spectrum.

To confirm the assignment to Ga, the data are compared to calculated line positions and a spectral simulation. ^{69}Ga is 60.2% abundant with a nuclear g factor of 2.0108 and ^{71}Ga is 39.8% abundant with g_N equal to 2.5549. If we neglect the slight anisotropy, the spin Hamiltonian for a particular center is

$$^{i}\mathcal{H} = g\mu_B \mathbf{H}\cdot\mathbf{S} + {}^{i}A\,\mathbf{I}\cdot\mathbf{S}, \qquad (1)$$

where the first term describes the electronic Zeeman interaction, and the second the hyperfine coupling for the particular isotope of Ga. Since the ^{71}Ga and ^{69}Ga nuclear moments have the ratio 1.29, their hyperfine constants must be in that ratio. Line positions calculated from an exact diagonalization of Eq. (1) with parameters $g = 2.025$, $^{69}A = 0.050$ cm^{-1}, and $^{71}A = 0.064$ cm^{-1} are shown near the bottom of Fig. 2. These correspond well with the data for **H** 10° from [001]. To test the fit further, a line shape was simulated by adding Gaussian

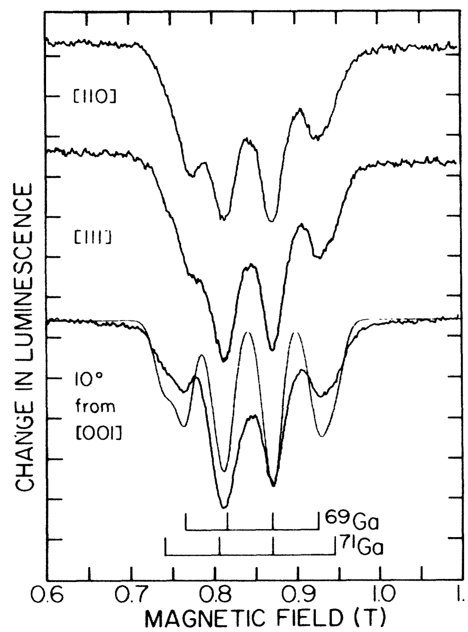

FIG. 2. ODMR at 24.14 GHz and 1.6 K for three field directions. The spectra are nearly, but not completely, isotropic. The field positions at the bottom were calculated for a Ga central hyperfine interaction with the spin Hamiltonian given in the text. The simulation (smooth line) was done by placing Gaussian lines of width 22 mT at the field positions shown with strengths proportional to the ^{69}Ga/^{71}Ga isotopic abundances. Note the correspondence in shape between the outer lines of the simulated and experimental spectra.

lines at the ^{69}Ga and ^{71}Ga positions with the proper isotopic abundances. As in previous ODMR studies,[9,10] the amplitudes of the lines for different m_I are not well fitted. However, the outer lines correspond to the data both in the revelation of a partial splitting and in a proper reflection of the isotopic abundance. Other elements (e.g., Cu) do not have the proper abundances and nuclear moments to fit the data. Thus the spectrum is assigned to a defect which has Ga at its center with a wave function which leads to a strong hyperfine interaction.

Further study is required in order to understand fully the discrepancy between the experimental and simulated spectra for **H** 10° from [001] and the slight angular dependence. Fitting of the [110] data yields hyperfine constants which are 12% smaller than those for **H** 10° from [001]. Thus the defect may be paired with a nearby defect and not have full cubic symmetry. With the symmetry lower than cubic, quadrupole interactions are possible. Where observed, these have proved to be much smaller than the magnetic hyperfine interactions observed here.[11] Partial thermalization and dynamic nuclear polarization can also affect the strengths of hyperfine lines in ODMR. Since the discrepancies and angular dependence are small for the present spectra, the causes can be regarded as small perturbations.

Since the defect consists of a Ga not at the usual group-III position in the lattice, it could be either an antisite (Ga_{As}) or an interstitial (Ga_i).[12] Comparison with recent theoretical calculations of the energy position and state symmetry for antisites and interstitials in III-V semiconductors leads to the assignment to the Ga interstitial. Large cluster recursion calculations[13] with tight-binding Hamiltonians find no states in the gap for cation antisites in AlAs and GaAs. Self-consistent Green's-function calculations[14] do find a state in the gap for Ga_{As} in GaAs, but with T_2 symmetry. Neither of these results is consistent with the experimental results since the large hyperfine coupling indicates a Fermi contact interaction with a state in the gap of A_1 symmetry. Tight-binding calculations[15] for Ga interstitials in GaP and Green's-function studies[14] of Ga interstitials in GaAs do find states of A_1 symmetry in the forbidden gap. With use of these predictions, the spectrum is assigned to the Ga interstitial.

There are three interstitial sites with high symmetry in the III-V lattice. Two have tetrahedral (T_d) symmetry and are fourfold coordinated. The first of these is surrounded by four As atoms. The second is surrounded by Al,Ga and is particularly sensitive to the alloy disorder of the mixed crystal. The third interstitial site has hexagonal symmetry (D_{3d}) with near neighbors from both sublattices. With use of the Green's-function results,[14] it is possible to infer the particular site for Ga_i from its charge state. The paramagnetic spin-$\frac{1}{2}$ state is Ga_i^{++}, which is in the gap for Ga_i-As_4 but not for the Ga_i-(Al,Ga) site. The insensitivity of the spectrum to changing alloy concentration from $x=0.2$ to 0.5 also suggests that the Ga_i is not very near to the Al,Ga sublattice.

The spin-Hamiltonian parameters reveal a wave function with deep-donor character for the Ga interstitial. Although the central hyperfine splitting of 0.050 ± 0.001 cm^{-1} for ^{69}Ga is strong, it is only about 12% of the contact hyperfine interaction of the 4s state of the free ion. This is a smaller fraction than the donor antisites exhibit, and implies that the interstitial donor is less localized than the antisite. The g value of 2.025 ± 0.006 contains a substantial positive shift from the free-electron value (2.002), but is less shifted than the g of 2.04 for As_{Ga} in GaAs.[4] These positive g shifts have been attributed to spin-orbit interaction on the nearest-neighbor ligands.[4,16] The Ga_i g value is intermediate between those of the As-As_4 antisite and the free electron and supports the model of the Ga_i-As_4 interstitial with somewhat greater delocalization than As_{Ga}.

The spectral dependence of the Ga_i ODMR shows negative signals over the entire range of the deep luminescence as seen by the Ge detector. Thus it is likely that the Ga_i is not directly involved in the emission process but is coupled to it (see Fig. 3). The shallow donor is probably Si which was intentionally doped. A weak exchange interaction between a Si donor and nearby defects produces spin-dependent selection rules and recombination rates.[17] The spin-dependent recombination with the Ga_i competes with the donor–to–deep-level process and thus produces a decrease in emission at resonance. The donor-to-Ga_i process itself may either be nonradiative or emit at a longer (not detected) wavelength. Longer wavelength studies are planned since the process, if found, would provide a measurement of the energy level for the defect.

The occurrence of Ga interstitials in these Al_x-$Ga_{1-x}As$ samples is attributed to particular features of growth by molecular-beam epitaxy. Samples grown under thermal equilibrium conditions are not expected to have a high concentration of interstitials.[14,18] Interstitials are produced in particular irradiation processes, including ion implantation. In Si, self-interstitials produced by electron irradiation diffuse readily and replace acceptors leaving them in interstitial sites.[6] Information on the self-interstitials which are part of the vacancy-interstitial (Frenkel) pairs has been inferred in studies of irradiated II-VI materials.[7] In the present case, the interstitials occur because of the differences in surface mobilities of the Al, Ga, and As atoms. Because of its low surface mobility, the Al may take an interstitial site initially and then exchange sites with the Ga atom via the reaction

$$Al_i + Ga_{Ga} \rightarrow Ga_i + Al_{Ga}. \quad (2)$$

Such a reaction is favored because of the higher bond strength of AlAs over GaAs. The effects of different growth parameters on interstitial production are being studied and the results will be presented in a separate publication.

Possibilities for further work abound. The production by ion implantation will be explored and correlations with transport studies completed. Optically detected electron-nuclear double resonance could determine more

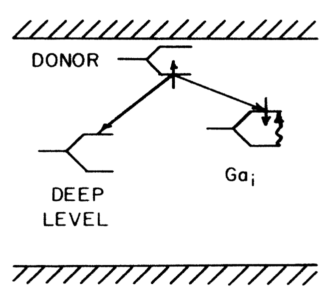

FIG. 3. Spin-dependent portion of the recombination cycle. The Zeeman splitting of each level is exaggerated. Donor–to–deep-level recombination is observed in the 0.75- to 1.1-eV range. Spin resonance (wavy line) of the Ga interstitial increases the donor-to-Ga_i recombination and thus causes a decrease of the luminescence being observed. Hence, a negative ODMR is detected.

definitely what the near-neighbor structure is. Similar ODMR signals have been observed from samples grown by organo-metallic chemical-vapor deposition.[19] Further study of these samples should help to clarify the interstitial production process. There is a clear need for a deeper theoretical understanding of the Ga_i spin Hamiltonian and other properties.

In summary, a new ODMR spectrum in $Al_xGa_{1-x}As$ is reported and assigned to the Ga interstitial primarily from an analysis of the hyperfine interaction. The direct, microscopic observations confirm the expectation of deep-donor character for the tetrahedrally coordinated self-interstitial in a semiconductor.

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