PHYSICAL REVIEW B VOLUME 43, NUMBER 3 15 JANUARY 1991-II

Gallium interstitials in GaAs/AlAs superlattices

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(Received 3 October 1990)

Optically detected magnetic resonance of point defects in a GaAs/AlAs superlattice is reported. The spectrum is characterized by $g=2.007$ and hyperfine coupling, $^{69}A=0.054$ cm^{-1} and $^{71}A=0.069$ cm^{-1}, due to Ga. The electronic state has A_1 symmetry, consistent with theoretical predictions for the interstitial Ga atom but not for the Ga_{As} antisite. Recombination via these defects reduces the intrinsic excitonic emission of the superlattice. The wave function shows no axial perturbation from the nearby potential barriers, demonstrating its localized character.

The study of the high-quality GaAs/AlAs superlattices grown by the molecular-beam-epitaxy (MBE) technique has resulted in great progress in the understanding of quantum phenomena and band structure.[1] There remain many important questions, however, regarding such aspects as the mechanisms of the optical recombination and the atomic-scale structure of the heterointerfaces. These issues are especially significant for type-II structures in which the conduction band is derived from AlAs X-point states, while the valence band is derived from the GaAs Γ states. The spatial separation of the electrons and holes in these structures has been demonstrated through the use of the optically detected magnetic-resonance (ODMR) technique.[2]

ODMR is well known as a powerful tool for studying the atomic structure of recombination centers in bulk[3] and epitaxial[4] semiconductors. Such centers in superlattices are predicted to experience a reduction in symmetry if located near an interface and their optical transitions may depend on the band structure.[5] In this paper we report magnetic-resonance observation of defects in a III-V superlattice. ODMR studies of type-II GaAs/AlAs structures reveal the presence of Ga self-interstitial recombination centers which compete with the intrinsic excitonic process. This result demonstrates the power of the ODMR technique as an atomic-scale probe of such defects in microscopically structured environments.

The superlattices used in this study were deposited by molecular-beam epitaxy on (001)-oriented semi-insulating GaAs substrates after a 5000-Å undoped GaAs buffer layer. With a GaAs growth rate of 1 μm/hr, 360 periods having five monolayers of GaAs and five monolayers of AlAs were grown at 580 °C and capped with 200 Å of GaAs. Two such samples were grown and both showed all of the ODMR features described below. The periodicities were checked with x-ray-diffraction measurements and found to be near 28 Å, consistent with the intended structure. The photoluminescence measurements were performed using 514.5-nm Ar^+ laser excitation at 5 K and with a spectral resolution of 0.3 meV. The ODMR measurements were carried out in 24- and 35-GHz spectrometers at a temperature of 1.6 K. A Kr^+ laser provided optical excitation at 530.9 nm with an incident intensity of about 10 mW/cm^2. The superlattice exciton emission at 1.956 eV (634 nm) was selectively collected by using a 0.25-m Bausch and Lomb monochrometer with a resolution of 35 nm. Alternatively, the band-edge emission from the buffer layer and substrate was selected by using a 780-nm (Schott RG780) long-pass filter. In both cases the luminescence was detected with a Si photodiode. The ODMR signals were lock-in detected as changes in the intensity of the emission in phase with the 170-Hz on-off modulation of the microwaves.

A photoluminescence spectrum in the energy region of the superlattice emission is shown in Fig. 1. An incident excitation intensity of about 10 mW/cm^2 was used to reproduce the conditions used in the ODMR measurements. The spectrum consists of an intense line at 1.956 eV labeled ($e1x$-hh1) and two weaker lines 30 and 52 meV below this. These features have been previously identified by Moore, Dawson, and Foxon[6] as the zero-phonon emission and phonon replicas of the type-II exciton. The energy is in agreement with measurements previously obtained on $(GaAs)_m/(AlAs)_m$ superlattices.[7]

ODMR spectra obtained with a microwave frequency of 34.840 GHz and a magnetic field along the [001] superlattice axis, z, are presented in Fig. 2. Several of the features in this spectrum have been observed previously by van Kesteren and co-workers[2,8] by monitoring the circular polarization of the exciton emission. The two resonances

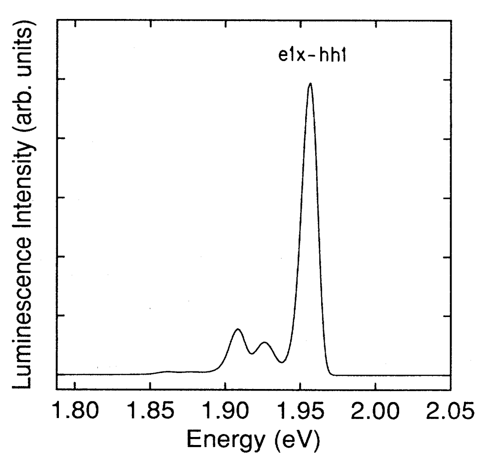

FIG. 1. Photoluminescence spectrum of the type-II superlattice observed at $T=5$ K.

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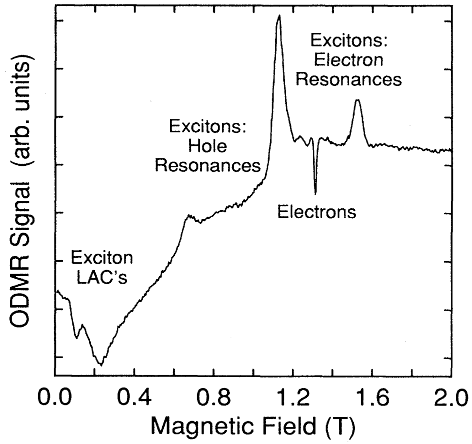

FIG. 2. ODMR spectrum of the electron and hole transitions and the level anticrossings (LAC's) of the exciton with a microwave frequency of 34.840 GHz and the magnetic field along the [001] direction. An electron resonance at 1.31 T is also observed.

at 1.12 and 1.52 T were identified by these authors as electron-spin transitions of the exciton, split by an exchange interaction with the hole.[8] The narrow line at 1.31 T was assigned to electrons not bound to holes. The two features at 0.11 and 0.23 T are due to hole- and electron-level anticrossings (exciton LAC's), respectively, of the exciton.[2] The measured electron g value, $g_{e,z}=1.910$

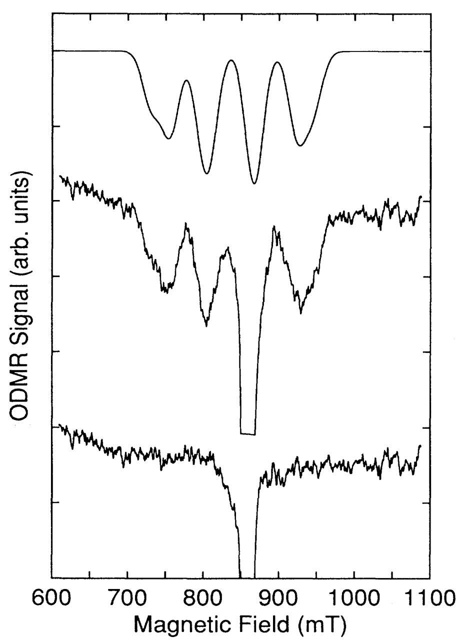

FIG. 3. ODMR spectrum and simulation of the interstitial Ga center with a microwave frequency of 23.750 GHz and the magnetic field along the [110] direction. The central trace is the raw data. The strong decreasing line at 859 mT is due to the electron resonance. The top trace is a computer simulation of the Ga_i spectrum with parameters given in the text. The bottom trace is a subtraction of the simulation from the data.

± 0.005, and exchange coupling, $c_z=21.4\pm 0.5$ μeV, are consistent with the assignments by van Kesteren *et al.*[8] Thus, the detailed ODMR observations confirm that the luminescence feature at 1.956 eV is indeed the type-II superlattice exciton emission. The resonances in the region of 0.8 T are hole-spin transitions of the exciton from which we determine the value $g_{h,z}=3.23\pm 0.03$.[9]

An expanded spectrum for the $g=2$ region was obtained with a microwave frequency of 23.750 GHz and the magnetic field along the [110] direction (see Fig. 3). The strong luminescence-quenching line at 859 mT is the electron resonance already discussed, with a g value of $g_{e,xy}=1.972\pm 0.005$. Along this direction, the exchange coupling of the exciton is much smaller[8] and as a result the electron-spin transitions of the exciton are not resolved from the unsplit electron line. The remaining four resonances are nearly isotropic with splittings close to 59 mT. The third resonance is not resolved from the electron line in Fig. 3, but can be observed at 1.27 T in the 35-GHz data of Fig. 2. A four-line spectrum indicates a large central hyperfine interaction of a spin-$\frac{3}{2}$ nucleus with an electronic spin-$\frac{1}{2}$ state. The outer lines, however, are broader than the inner lines, revealing that more than one type of spin-$\frac{3}{2}$ nucleus experiences the strong central hyperfine interaction. Gallium is an obvious candidate, with spin-$\frac{3}{2}$ isotopes ^{69}Ga (60.2% abundant) and ^{71}Ga (39.8% abundant).

The spin Hamiltonian for an isotropic spin-$\frac{1}{2}$ center with a magnetic nucleus, i, is given by

$$^{i}H=g\mu_B\mathbf{B}\cdot\mathbf{S}+{}^{i}A\mathbf{I}\cdot\mathbf{S}\,, \tag{1}$$

where the first term describes the electronic Zeeman interaction and the second the hyperfine interaction due to nucleus i. A Ga hyperfine interaction would result in a superposition of two spectra with relative intensities reflecting the isotopic abundances and a ratio of hyperfine splittings $^{71}A/^{69}A=1.27$, reflecting the known ratio of the nuclear magnetic moments. The line positions for these two spectra were calculated from an analytic diagonalization of the spin Hamiltonian with the parameters $g=2.007\pm 0.005$, $^{69}A=0.054\pm 0.002$ cm^{-1}, and $^{71}A=0.069\pm 0.002$ cm^{-1}. To simulate the spectrum, 30-mT-wide Gaussian lines with relative intensities of 60.2:39.8 for ^{69}Ga and ^{71}Ga were superposed. The resulting curve is shown at the top of Fig. 3. The fit is quite good, as is evident from the lower curve in Fig. 3 which is a subtraction of the fit from the data. The data cannot be fit by assuming another element such as As or Cu.

The Ga-centered point defects expected to have nearly tetrahedral symmetry in a GaAs/AlAs superlattice include antisites, Ga_{As}, and interstitials, Ga_i. A previous theoretical study using a self-consistent Green's-function technique has predicted a deep level for the Ga_{As} antisite in GaAs having a T_2-symmetric electronic state.[10] Other calculations involving a large-cluster recursion approach have suggested that no gap states exist for these centers.[11] These predictions are both inconsistent with the large, nearly isotropic central hyperfine interaction observed here, indicating a state of A_1 symmetry. An A_1-symmetric state is predicted for the Ga_i centers in GaAs, however, with a paramagnetic Ga_i^{2+} charge state.[10] Calculations based on a tight-binding Hamiltonian have found a similar A_1-symmetric state for Ga interstitials in GaP.[12] Therefore, based upon the comparison of the data with these theoretical predictions, we assign the ODMR spectrum to Ga interstitials.

The magnetic resonance due to the Ga_i results in a decrease in the intensity of the type-II exciton emission at 634 nm (1.956 eV). It is observed strongly with the monochromator set to this wavelength, and not observed when set more than 30 nm away. It also cannot be observed on the strong GaAs band-edge emission from the substrate and buffer layer in the region of 1.51 eV. The ODMR signal originates from the spin dependence of a recombination process involving the interstitials. Such a process reduces the intrinsic recombination through the competition for electrons or holes. There is no mechanism by which recombination in the GaAs buffer layer or substrate can be envisioned to induce such decreases in the superlattice excitonic emission. It must be concluded, therefore, that these defects are located within the superlattice.

Interstitial Ga centers have been observed previously via ODMR in MBE-grown $Al_xGa_{1-x}As$ ranging in the Al mole fraction from 0.1 to 0.45.[4,13] The spectrum was described by the spin-Hamiltonian parameters $g=2.025$, ${}^{69}A=0.050$ cm^{-1}, and ${}^{71}A=0.064$ cm^{-1}, which are similar to those determined here for the defect in the superlattice. The superlattice and alloys in question were grown under similar conditions.[4] Further, if the Ga and Al interdiffuse, the superlattice interface region will tend to resemble $Al_xGa_{1-x}As$ on an atomic scale. Thus, it is reasonable that a point defect existing in the alloy can also exist in the superlattice.

The present observation provides the opportunity to study the detailed structure of a point defect in a microscopically structured environment. The GaAs and AlAs layer thicknesses in our samples are about five monolayers each. It is clear, therefore, that the interstitials can be no more than three monolayers from an interface. The wave function of a shallow center would be expected to suffer a considerable axial eccentricity due to quantum confinement if it were located within a Bohr radius from the barrier layer.[14] If located within the barrier layer, it would induce shallow states in the well layer which would also experience these strong perturbations. Deep-level centers can experience level shifts and changes in symmetry if located a few monolayers away from an interface.[5] The precise behavior will depend upon the defect wave function and the case of the interstitial gallium atom near such an interface has not yet been treated theoretically. The g value of the gallium interstitial shifts upon placement in the superlattice environment, reflecting the changes in the electronic structure of its host material. The defect displays a nearly isotropic central hyperfine interaction, however, indicating that despite the proximity of the interfaces, there is no appreciable axial perturbation due to confinement. This lack of interaction with the potential barriers is an independent confirmation of the strong localization of the wave function.

It cannot yet be determined whether both the GaAs and the AlAs superlattice layers contain Ga_i defects which are active in the ODMR process. Since electrons and holes are spatially separated in these structures, it is possible that location in one of the two layers favors the participation in recombination. It has been suggested that the spin-dependent recombination involving Ga_i centers in $Al_xGa_{1-x}As$ is a Ga_i-shallow-acceptor pair process.[4] Such a process would tend to favor those Ga_i centers in the GaAs layers due to the higher overlap with the acceptor states. On the other hand, recombination via the capture of free holes and electrons by the Ga_i might be expected to favor the centers located at the interfaces. Experimental means of pursuing this information include a search for ODMR from shallow acceptors in such samples. In connection with this ODMR signal, the technique of optically detected electron nuclear double resonance (ODENDOR) can potentially be used to identify the lattice atoms in the immediate environment of the interstitial.

In summary, we have observed Ga interstitial defects in a GaAs/AlAs type-II superlattice directly using ODMR. A strong hyperfine splitting shows that the electron is highly localized on a central Ga nucleus as is observed for interstitials in $Al_xGa_{1-x}As$. The defect has a lower g value when placed in the superlattice environment. The central hyperfine interaction, however, does not show an axial perturbation from the nearby interfaces, reflecting the highly localized character.

We would like to thank S. M. Prokes for providing the x-ray-diffraction measurements, E. Glaser and B. V. Shanabrook for stimulating discussions, and J. C. Culbertson for aiding in the computer simulation. This work was supported in part by the U.S. Office of Naval Research. J.M.T. acknowledges support from the National Research Council and NRL.

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