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Arsenic antisite defects in $Al_xGa_{1-x}As$ observed by luminescence-detected electron-spin resonance

M. Fockele, B. K. Meyer, and J. M. Spaeth
Fachbereich Physik, University of Paderborn, Warburger Strasse 100 A, D-4790 Paderborn, Federal Republic of Germany

M. Heuken and K. Heime
Fachbereich Elektrotechnik, University of Duisburg, Kommandantenstrasse 60, D-4100 Duisburg, Federal Republic of Germany

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We report on luminescence and optically detected electron-spin-resonance investigations in $Al_xGa_{1-x}As$. The luminescence band found for $0.17 \leq x \leq 0.65$ is caused by a deep donor-acceptor recombination involving an arsenic antisite defect with an energy-level position at $E_{VB}+0.97 \pm 0.02$ eV. Neither the energy-level position nor the electron-spin-resonance spectrum vary with the alloy composition.

Intrinsic defects in the technologically important III-V semiconductors GaAs, InP, and GaP have become the subject of intense research over the last several years. Much experimental work focused on the structure identification of anion antisite defects, i.e., defects having a group-V element on a group-III site. The role of these deep-level donors as trapping and recombination centers is well established in all three semiconductors. The structure identification was achieved by electron-spin resonance (ESR) (Refs. 1-3) and in some cases by optically detected ESR (ODESR) (Refs. 4-6). Particular interest has emerged for the ternary alloys $Al_xGa_{1-x}As$ as important materials for optoelectronic applications. In this material the properties of deep-level defects such as energy-level positions, structure, and localization of the wave function can be studied as a function of the alloy composition. The formation of intrinsic defects can be widely varied by changing the growth temperature and the stoichiometry conditions when using epitaxial growth methods such as molecular-beam epitaxy (MBE) and metalorganic chemical-vapor deposition technique (MOCVD). So far, not many deep-level defects are well understood in $Al_xGa_{1-x}As$.[7] For example, the structure of *DX* centers in $Al_xGa_{1-x}As$ and GaAs is currently a much debated issue.[8]

In this Rapid Communication we report on luminescence and ODESR measurements of $Al_xGa_{1-x}As$. The luminescence band found is caused by a deep donor-acceptor recombination involving an arsenic antisite defect as the deep donor, as established by the ODESR measurements. Its energy-level position could be followed for the alloy compositions $0.17 \leq x \leq 0.65$. The unexpected result is that its position relative to the valence band does not vary with the alloy composition.

The $Al_xGa_{1-x}As$ layers were grown by MOCVD in a radio-frequency-heated reactor at low pressures of 20 mbar. Growth at 20 mbar with high-gas velocities of 1.8 m/s results in mirrorlike surfaces and a homogeneity of the Al content of 1% across a 2 in. wafer. Trimethylgallium (TMG), trimethylaluminum (TMA), and 100% arsine (AsH3) were used as source materials, palladium-diffused H_2 as the carrier gas. All undoped $Al_xGa_{1-x}As$ layers showed *p*-type conduction. The dominant shallow acceptor is carbon identified by low-temperature photoluminescence. The Al content in the layers increases linearly with the group-III partial pressure ratio *p*(TMA)/*p*(TMG) in the range $0.1 < x < 0.8$. All samples used here were grown at 700 °C on semi-insulating substrate material, the Al content was varied between 8 and 65% and was determined by x-ray double refractometry.

Luminescence measurements at 5 K were performed between 1.0 and 2.1 μm, luminescence excitation spectra in the range from 0.5 to 1.4 μm, both corrected for the spectrometer response. As excitation light sources, an Ar^+ ion laser was used for above band-gap excitation and a Xe high-pressure or tungsten lamp in combination with a monochromator for efficient sub-band-gap excitation. The ODESR was measured as microwave-induced change of the luminescence intensity. The microwave frequency was 24 GHz. Microwave power up to 1 W was provided by a traveling-wave tube. The modulation frequency of the chopped microwaves was varied from 200 Hz to 20 kHz.

The infrared luminescence measured at 5 K (Fig. 1, curve *a*) consists of a single Gaussian band centered at 0.80 eV (half-width 0.17 eV). It is observed in all samples with $0.17 \leq x \leq 0.65$, but not for $x < 0.17$, nor for pure GaAs. It can be excited with light-of-energy above and below the band gap. For above-band-gap excitation an emission band at higher photon energy of about 1.1 eV is sometimes superimposed in addition. The excitation spectrum starts at 1.05 eV and shows two prominent bands at 1.25 and 1.34 eV (Fig. 1, curve *b*). At higher energies the excitation spectrum smoothly increases up to the band-gap energy of the respective alloy composition and thus proves that the emission originates from the $Al_xGa_{1-x}As$ epilayer and is not due to the semi-insulating GaAs substrate. The excitation spectrum in the range from 1.1–1.4 eV with the double-hump structure remains at the same

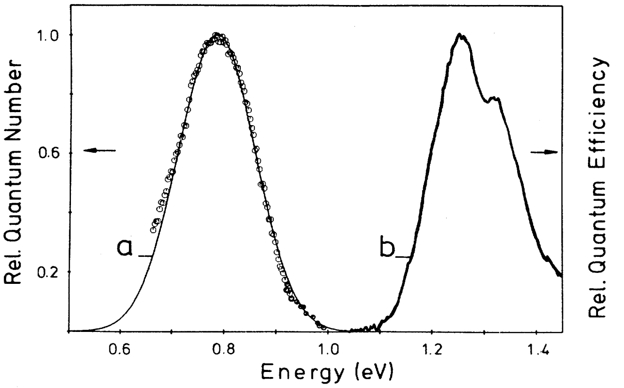

FIG. 1. Luminescence spectrum (open circles), a fitted Gaussian line (curve *a*), and the luminescence excitation spectrum (curve *b*) measured at 5 K in undoped *p*-type $Al_{0.17}Ga_{0.83}As$ grown at 700 °C on semi-insulating GaAs substrate.

energy position irrespective of the alloy composition investigated (from $x=0.17$ to $x=0.65$). Also the energy of the emission band at 0.8 eV does not vary with the Al content. These experiments indicate a deep level to acceptor- or valence-band recombination as origin of the 0.8-eV emission band.

The lifetime measurements on the 0.8 eV band showed a single exponential decay time of 1.05 ± 0.1 μsec independent of the light intensity used, consistent with the assignment of a deep-level donor-acceptor recombination (DA), where the acceptor has a fixed distance to the donor. The recombination time would be different for donor-acceptor pairs with random distribution. The DA mechanism is supported by measuring the emission intensity as a function of the light intensity. With above- and below-band-gap excitation it depends linearly on the excitation intensity, only one electron-hole pair is excited, the electron being trapped at the deep level (for *p*-type conducting samples the midgap center should be unoccupied), the hole being captured at the acceptor. C is probably involved in the recombination, which is the dominant residual acceptor impurity present in the samples.

The independence of the peak energies of the emission and excitation spectra from the Al content would imply that the deep level remains fixed to the valence band. The binding energy is estimated by assuming an equal Stokes shift in the ground and excited states. From the maximum of the emission band and the maximum of the excitation, i.e., absorption spectrum, the relaxation energy E_{SS} can be calculated

$$E_{SS}=2S\hbar\omega=E_{\rm exc}({\rm max})-E_{\rm em}({\rm max})-E_{\rm sh.acc.}\,, \qquad (1)$$

taking into account the acceptor binding energy for C of 32 meV. It results in $S\hbar\omega=0.26$ eV, where S is the Huang-Rhys factor and $\hbar\omega$ is the effective phonon frequency. The binding energy is estimated to be

$$E_T=E_{\rm CB}-E_{\rm gap}+\tfrac{1}{2}\,[E_{\rm exc}({\rm max})+E_{\rm em}({\rm max})+E_{\rm sh.acc.}]\,. \qquad (2)$$

Given the values for $x_{\rm Al}=0.17$: $E_{\rm gap}=1.72$ eV, $E_{\rm exc}=1.3$ eV, $E_{\rm em}=0.8$ eV, $E_{\rm sh.acc}=0.032$ eV, one obtains

$$E_T=E_{\rm CB}-0.66\ {\rm eV}\quad\text{or}\quad E_T=E_{\rm VB}+1.06\ {\rm eV}\,.$$

A more exact evaluation of the trap depth can be achieved by the measurement of the temperature dependencies of the emission and excitation spectra. The electron-phonon coupling is treated within a configuration coordinate model, and ground and excited states of the deep-level defect are assumed to be parabolas with different effective phonon frequencies. The temperature dependence of the second moment m_2 for the emission and excitation spectra, respectively, are given by[9]

$$m_2(T)=S(\hbar\omega)^2\coth(\hbar\omega/2kT)\,. \qquad (3)$$

The temperature dependencies of the emission and excitation bands of Fig. 1 are shown in Fig. 2 (curves *a* and *b*) for $x_{\rm Al}=0.51$. The circles mark the experimental values, the drawn lines are the fitted curves according to Eq. (3). For the ground state, the Huang Rhys factor is $S=7.5\pm1$ and $\hbar\omega=19\pm0.5$ meV, resulting in a total Stokes shift of 138 ± 8 meV. The excited state has a larger Stokes shift with 390 ± 8 meV, for which one obtains $S=30\pm1$ and $\hbar\omega=13\pm0.5$ meV. The estimate of the binding energy can now be derived from the emission energy and the respective Stokes shift. One gets $E_T=0.8+0.138+0.032=0.97\pm0.02$ eV above the valence band. Tracing the level to the pure binary system GaAs, its location should be 0.55 eV below the conduction band (see Fig. 3). The independence of the alloy composition is a very unexpected result. From deep-level transient spectroscopy (DLTS) experiments on many deep-level defects in $Al_xGa_{1-x}As$, it was found that the level position, with respect to the valence band, shifts with increasing Al content, similar to the *L*-conduction-band minimum (a shift of about 5–6 meV/% Al content).[10,11] According to this experience the excitation spectrum of the luminescence band, as well as the luminescence itself, should have moved to higher photon energies with increasing Al content, as shown in Fig. 3. Within the experimental error of ±0.02 eV, no shift is observed. The energy of the recombination luminescence is independent of the alloy composition (this refers also to the respective values of the Stokes shift). The binding energy of the deep-level defect is therefore constant. The *X*-conduction-band minimum E_X (see Fig. 3) does not vary much with x. According to Ref. 12, $E_X=1.984+0.26x-0.16x(1-x)$. However, the level position varies less strongly with x than E_X (Fig. 3). Therefore, the level must be fixed to the valence band.

The ODESR spectrum measured in the 0.80-eV luminescence band is shown in Fig. 4. The four-line spectrum is isotropic upon rotation of the crystal. Neither the line positions nor the separation of the four lines change. The spectrum is described by a Hamiltonian for $S=\frac{1}{2}$ with an isotropic g value and an isotropic hyperfine (hf) interaction with one nucleus with $I=\frac{3}{2}$.

$$\mathbf{H}=\tilde{g}\mu_B\mathbf{H}\cdot\mathbf{S}+\mathbf{I}\cdot\overleftrightarrow{A}\cdot\mathbf{S}\,. \qquad (4)$$

An exact diagonalization yields $g=(2.02\pm0.01)$ and a hf constant $A=(64\pm1)$ mT. The half-width of a single

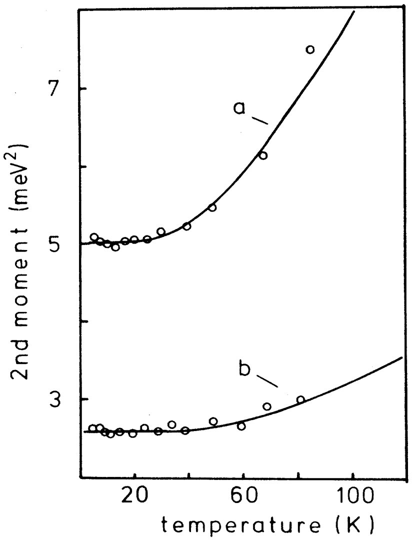

FIG. 2. Temperature dependencies of the second moment m_2 of the As-antisite emission (curve *a*) and low-energy excitation (curve *b*). The open circles are the measured values, the solid lines are fitted with Eq. (3) (see text).

ESR line is (48 ± 1) mT. A four-line ESR spectrum could originate from an ^{75}As nucleus with $I = \frac{3}{2}$ and 100% isotope abundance, or from ^{69}Ga and ^{71}Ga nuclei, which also have $I = \frac{3}{2}$ each and 60% and 40% isotope abundances, respectively. The nuclear *g* values of the two Ga isotopes differ significantly. Therefore, for Ga one expects two sets of four-line spectra, as was observed in the ODESR investigations of the Ga interstitial in $Al_xGa_{1-x}As$.[13] The two sets should have been seen for the size of the hf splitting of 64 mT. The spectrum cannot be explained assuming a Ga hf structure. There are three other aspects which rule out the Ga interstitial: In Ref. 13 it is shown that the presence of Ga_i is favored by growing the crystals at low substrate temperatures (620 °C); it is not detected in material grown at 700 °C, which was used in this investigation. The ODESR of Ga_i is detected as a negative signal in the luminescence bands down to 0.7 eV, whereas we observe the ODESR signal of the deep donor as an intensity enhancement in the 0.8 eV emission. Also, the energy-level positions are different. The line positions and single line shapes are explained by a single nucleus with $I = \frac{3}{2}$. From the similarity of the spectra with other As antisite defects and the absence of a major impurity with $I = \frac{3}{2}$ and 100% isotope abundance, we conclude that the spectrum is due to an As hf interaction. (The same spectrum was probably also observed in heavily Be-doped MBE samples in Ref. 13.) For this, one would expect a quartet spectrum with equal line intensities. The two low-field lines are somewhat less intense than the two high-field lines. The intensity of the lines partly depends on the microwave power applied, probably as the selective saturation of the nuclear Zeeman state occurs, which was also observed elsewhere.[14] In some cases, a strong nonresonant background signal was also superimposed.

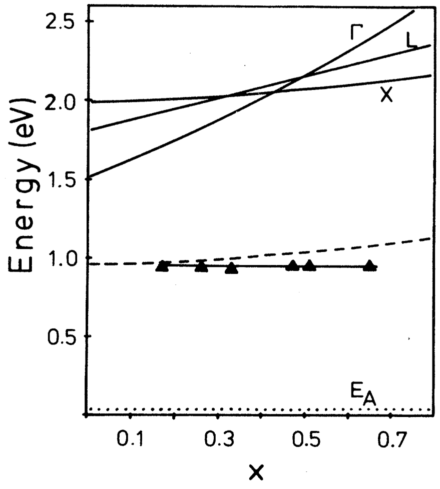

FIG. 3. Energy-level position of the deep anion antisite donor in $Al_xGa_{1-x}As$ for different alloy compositions as determined from the luminescence and luminescence excitation spectra (triangles), the solid line is a guide for the eye. The variation of the Γ, *X*, and *L* conduction-band minima with increasing Al content was taken from Ref. 12. The expected shift of the energy level following the *X*-conduction-band minimum is shown as the dashed line. The dotted line shows the carbon-acceptor energy level E_A.

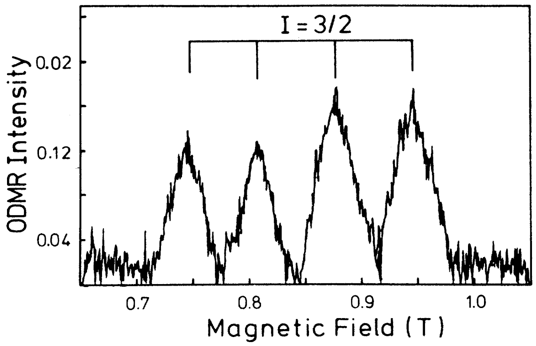

FIG. 4. ODESR detected in the deep luminescence band at 0.80 eV, 24 GHz, and 1.6 K showing the isotropic four-line spectrum due to an arsenic antisite defect. The hyperfine interaction with $I(^{75}As) = \frac{3}{2}$ is indicated by a stick diagram.

For an As atom on an interstitial site, theory claims a T_2 ground state,[15] which would not have a large isotropic hf interaction. Irrespective of the Al content, the same ESR spectrum is measured, neither *A* nor the linewidth change. With respect to the central As_{Ga}, which is surrounded by four nearest As ligands, Al is in a second-nearest-neighbor Ga shell. The independence of the ESR linewidth of the Al content can be understood for a defect structure $AsAs_4$ if only a low spin density is located on the second-nearest cation shell.

Anion antisite defects were observed to be double donors in III-V semiconductors. The singly ionized charge state D^+ is paramagnetic with $S = \frac{1}{2}$. We assign the level at $E_{VB}+0.97$ eV to the +/2+ charge state of an anion antisite As_{Ga}. The luminescence intensity varies linearly with the intensity of the exciting light, i.e., only one electron-hole pair is excited. The luminescence process is thus very similar to what was found for the P antisite defect in GaP.[5,6] There the Fermi level was below the $D^{+/2+}$ level. Upon creation of an electron-hole pair, the electron was captured by D^{2+} to form D^{+}, while the hole was captured by the residual ionized Zn acceptors. The shallow effective-mass acceptor Zn does not show up in the ODESR spectrum, unless uniaxial stress is applied.[5] Also, here we find no acceptor-related signal in the magnetic field range corresponding to the g values of $g=0.6$–0.7 reported for the shallow acceptor carbon.[16] From our investigations we cannot determine the charge state of the donor. We can only say that it changes its charge state to a paramagnetic one after electron capture.

Quite recently a DLTS investigation appeared on MBE $Al_xGa_{1-x}As$ which showed striking similarities.[17] For a variation of the Al from 0.08 to 0.4, a deep trap is found with its binding energy fixed with respect to the valence band. For $x=0.17$ it is 0.61 eV below the conduction band, whereas our value determined from the optical data is roughly 100 meV lower. The growth conditions were very similar with respect to the growth temperature and the V/III flux ratio. In electron-irradiated $Al_xGa_{1-x}As$ (Ref. 18), a trap with a binding energy of $E_C-0.33$ eV ($E3$) for $x=0$ has been observed which exhibits the same phenomenon being fixed to the valence band. It was concluded to be due to a gallium vacancy.[18]

In the material with low Al content ($x=0.08$ and $x=0$), we could not observe the defect since the emission band was no longer present. A defect with very similar hf interaction, g value, and linewidth (within experimental error) was also found in n-type GaAs upon electron irradiation at low doses by conventional ESR (Ref. 19) and optically detected ESR using the MCD (magnetic circular dichroism) technique.[20] For this defect, the energy level $D^{2+/+}$ was found to be in the upper half of the band gap at around 0.5 eV below E_{CB},[21] which is close to the value of $E_{VB}+0.97$ eV we have found here. At present we cannot say more about the precise structure model of this arsenic antisite defect.

In conclusion, the luminescence and ODESR measurements revealed a donor-acceptor recombination luminescence in $Al_xGa_{1-x}As$. It involves a donor arsenic antisite defect, the energy-level position of which, relative to the valence band, is constant for the alloy compositions $0.17 \leq x \leq 0.65$. It is this fundamental aspect of the behavior of an intrinsic defect which is new and unexpected. According to theoretical predictions, deep anion donors should not only originate from one part of the Brillouin zone, but should be made up from Γ, X, and L bands.[22] Our results clearly demonstrate that the deep anion donor found here is fixed to the valence band. One last comment refers to the relaxation energies determined from the temperature dependencies. The Stokes shift of 0.39 eV with a Huang Rhys factor of 30 ($\hbar\omega=13$ meV) shows the large lattice coupling in the excited state [it is above the value of the PP_4 antisite in GaP ($S=17$, $\hbar\omega=17$ meV) for which similar experiments have been undertaken[23]]. It could arise from a symmetric breathing mode relaxation, since no deviation from T_d symmetry is observed in the spin-Hamilton parameters. However, the phonon frequency found is considerably smaller than that of the optical phonons (35 meV) expected to be coupled to the breathing mode relaxation. It is closer to the values of the TA phonons; they are expected for symmetry lowering distortions, perhaps an indication of a near perturbation.

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