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Electron-paramagnetic-resonance study of the Sn *DX* center in direct-gap $Ga_{0.69}Al_{0.31}As$

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An electron-paramagnetic-resonance study of the Sn-related *DX* center in direct-gap $Ga_{0.69}Al_{0.31}As$ shows that the *DX* center can be transformed by photoexcitation into an excited paramagnetic state, which is metastable at 4 K. This excited state has the characteristics of a strain-split T_2 state; its asymmetric line can be decomposed into two Gaussians with the parameters $g_1=1.92, \Delta B_1=500$ G and $g_2=1.95, \Delta B_2=200$ G. The photoexcitation spectrum of this paramagnetic state, which is of the Lucovsky type with a threshold at 0.8 eV, is interpreted as an internal A_1-T_2 transition. No paramagnetic spectrum associated with the ground state of *DX* has been observed.

The group-IV and group-VI donors (Si, Sn, Se, Te), which in GaAs introduce a shallow effective-mass level, give rise in the ternary compound $Ga_{1-x}Al_xAs$ to a deep donor level *DX*.[1,2] This defect belongs to a particular class of donor defects in III-V compounds, which are characterized by a repulsive barrier for both electron emission and capture leading to persisting photoconductivity at low temperatures. The origin of the repulsive barrier and its relation to a specific atomic configuration have been the subject of numerous studies, which have been reviewed recently.[3] But there is little direct experimental information of the atomic structure of the *DX* center.[4-6] The main information stems from the application of electrical techniques, by which the optical and thermal electron emission and electron-capture cross sections have been determined.[3]

For Al compositions $x \leq 0.2$ the ground state of *DX* is resonant with the conduction band and the hydrogenic level associated with the Γ conduction band is the lowest donor level. For $x \gtrsim 0.25$ the *DX* level with an emission energy of ~ 200 meV moves into the band gap and becomes on its turn the lowest donor level. In spite of the fact that the conduction-band structure of $Ga_{1-x}Al_xAs$ changes from direct to indirect at $x \approx 0.35$, the electronic structure as well as a photoionization spectra of *DX* change very little, surprisingly.

The microscopic structure of the *DX* center is still a matter of debate. Three types of atomic models have been proposed for the *DX* center: large-lattice-relaxation (LLR), small-lattice-relaxation (SLR), and mixed (LLR-SLR) models. Lang and co-workers[1,2] originally proposed that *DX* is a LLR complex defect composed of the substitutional donor and an arsenic vacancy. However, the recent observation of the *DX* center in GaAs under hydrostatic pressure[7] as well as its correlation with the donor doping concentration, puts strong doubts on any associated defect model. Morgan[8] proposed a displaced donor model, in which *DX* is ascribed to the simple substitutional donor related to the *L* conduction band, which due to a strong Jahn-Teller interaction is driven off center in the [111] antibonding direction. From these two LLR models a paramagnetic ground state with a point symmetry lower than T_D would be expected. A different LLR model has been put forward by Chadi and Chang;[9] in their model the donor is not stable in the neutral paramagnetic charge state D^0, but dissociates into D^+ and D^-, D^- undergoing a large lattice relaxation in the [111] direction. A particularity of this model is, contrary to the preceding models, a diamagnetic ground state of *DX*, which should thus not be electron paramagnetic resonance (EPR) observable. One basic argument for the LLR models is the observed large difference between the thermal (E_{th}) and optical (E_{opt}) ionization energy of this defect with $E_{opt} \gtrsim 2E_{th}$. Generally the tacit assumption is made that the photoionization corresponds to a transition to the lowest Γ or *X* conduction bands. This assumption is tested by our EPR study for the direct-gap material, and we present evidence that it is wrong. Small lattice relaxation models relating the *DX* center to the *L* conduction band have been put forward by Saxena[10] and Henning and Ansems[11] as well as by Resca and Resta,[12] Chand *et al.*,[13] and Bourgoin and Mauger,[14] who showed that intervalley mixing can lead to a shallow deep instability of the *L* band related donor. The SLR models are apparently at odds with the high optical thresholds E_{opt} and necessitate a different interpretation of this optical transition. The SLR models imply equally an EPR active ground state for the *DX* center. Very recently, mixed LLR-SLR models based upon the observation of metastable optical absorption spectra have been proposed.[15-17] These authors ascribe both a deep relaxed and a shallow configuration to these donors. However, the experimental evidence for a metastable shallow donor state is not complete, in particular as no quantitative one-to-one relationship with the deep *DX* center has been established.

Magnetic resonance techniques are well adapted to

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study the microscopic structure of a defect and both EPR and optically detected magnetic resonance (ODMR) studies of *DX* have been reported.[16,18-20] In indirect-gap material a donor-related resonance has been observed by both techniques. It has been attributed to the hydrogenic donor level associated with the *X* conduction band.[18-20] In direct-gap material only ODMR has been applied up to now but no donor-related resonance has been observed at all.[18] No resonance associated with the *DX* ground state has been reported in these studies. This last result is, however, not yet a proof for a diamagnetic ground state. As bulk samples of mm dimensions are not available, these studies had to be performed on epitaxial layers of some μm thickness. In this case large linewidths of $\sim$1 kG would be sufficient for the *DX*, even at doping concentration of $\sim 10^{18}$ cm^{-3}, to escape EPR detection. The disappearance of the *X*-band donor resonance, when changing from indirect- to direct-gap material, seems to be simply related to the change in the conduction-band structure. In the direct-gap material with the lowest Γ conduction band, optical excitation at low temperature is expected to populate only the hydrogenic donor level associated with Γ, whose *g* value differs strongly from the *X*-band donors. We verified this simple picture by this first EPR study in direct-gap material and found it to be wrong.

All preceding magnetic-resonance studies had been performed on Si-doped samples. Our EPR study gives first results on a different *DX* center, the one induced by Sn doping.

We have studied by EPR highly doped, thick epitaxial layers of $Ga_{0.69}As_{0.31}As$ doped with tin ([Sn]) $= 2\times10^{18}$ cm^{-3}, layer thickness 32 μm). They were grown in a conventional atmospheric metalorganic vapor-phase epitaxy vertical reactor on semi-insulating, undoped GaAs substrates, including a 0.5-μm-thick $Ga_{0.5}Al_{0.5}As$ undoped buffer layer. The alloy composition has been determined by double x-ray diffraction. The EPR measurements were performed with a *X*-band spectrometer, which allows *in situ* excitation by monochromatic light in the 0.5 to 2.0 eV spectral range.

After having been cooled down to $T=4$ K in the dark the samples presented no paramagnetic spectrum, but only a large cyclotron resonance band indicating the presence of free carriers. This is the consequence of the electron-capture barrier of the *DX* center which is of comparable magnitude to the emission energy. In this case insufficient slow cooling from room temperature to 4 K leads to a partial occupation of the *DX* ground state only. For photoexcitation with $E<0.8$ eV no effect has been observed. Under photoexcitation with energies $E\gtrsim0.9$ eV both the cyclotron-resonance band changes and a paramagnetic spectrum is created [Figs. 1(a) and 1(b)]. The cyclotron resonance, which is extending over several kG in this case, first decreases after a short-time excitation and then increased under further photoexcitation to a stationary value. The EPR spectrum consists of an asymmetric line, the shape, width, and *g* factor of which vary with the excitation condition.

The EPR line observed for photoexcitation with $E\gtrsim1.0$ eV and $B\parallel$ [001] is broadened in the wings and can be approximated by a Lorentzian shape [Fig. 1(b)].

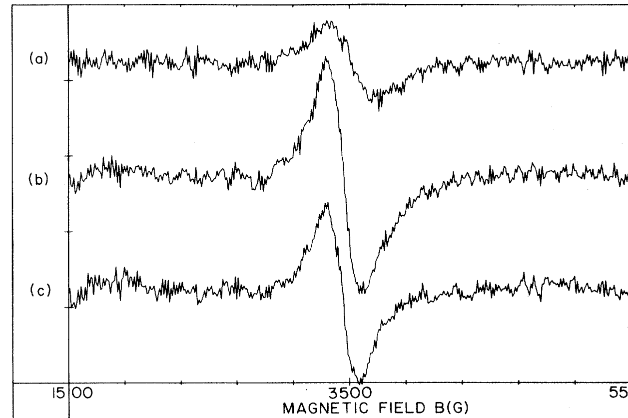

FIG. 1. EPR spectrum of $Ga_{0.69}Al_{0.31}As$:Sn, $T=4$ K, $\mathbf{B}\parallel$ [001]; (a) under photoexcitation with $E=0.90$ eV; (b) under photoexcitation with $E=1.03$ eV; (c) difference spectrum (b) − (a).

However, the asymmetry has no simple explanation. From a careful study of the spectral dependence of the line shape and confirmed by line shape simulations, we propose a different interpretation. We ascribe this spectrum to a superposition of two Gaussian single-line spectra. In fact, excitation with the lowest photon energy of 0.90 eV leads to the formation of a first symmetric EPR spectrum characterized by a *g* value of 1.92 and a line width of $\sim$500 G [Fig. 1(a)]. When the photon energy is increased to $E\gtrsim1.03$ eV the total line shape becomes asymmetric and the center of gravity shifts to higher *g* values [Fig. 1(b)]. Difference spectra show that an additional narrower line of $\Delta G\approx200$ G at $g=1.95$ is now superposed on the first spectrum [Fig. 1(c)]. Both spectra are isotropic. The integrated intensity ratio of the two spectra I_1/I_2 is $\approx$2:1. The asymmetric line shape is constant for all excitations with energies 1.03 eV $\le E \le$ 2.0 eV. Assuming a spin $S=\frac{1}{2}$, the total defect concentration is estimated to 10^{18} cm^{-3}, i.e., close to the donor doping concentration. When the photoexcitation is cut off, the total EPR spectrum decreases at $T=4$ K with two different time constants; the sharper spectrum 2 decreases first within minutes whereas spectrum 1 decrease with a time constant of $\sim$1 h. For a constant photoexcitation the integrated intensity of the sum of the two spectra varies with temperature as $1/T$ as expected for localized spins (Fig. 2). If the photoexcitation is performed at temperature $T\gtrsim25$ K the spectra are no longer observable even at $T=4$ K.

We have determined the spectral dependence of the photoexcitation spectrum in the 0.5–2.0 eV range. It is characterized by a threshold at 0.9 eV and a broad flat region up to the band gap at 1.9 eV (Fig. 3). The initial rise method normally used for the determination of the photoionization spectrum could not be applied to our samples as strong nonmonotonic and nonlinear baseline variations, reflecting the change in the cyclotron resonance, were superposed on the EPR signal. However, in this particular case, the two methods are expected to give similar results.

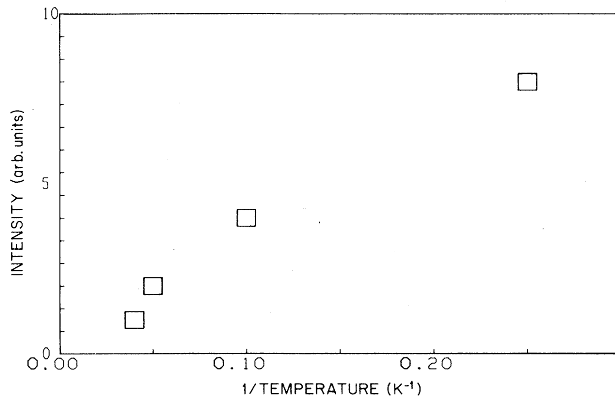

FIG. 2. Stationary spin concentration inverse temperature for a constant photoexcitation $E = 1.03$ eV.

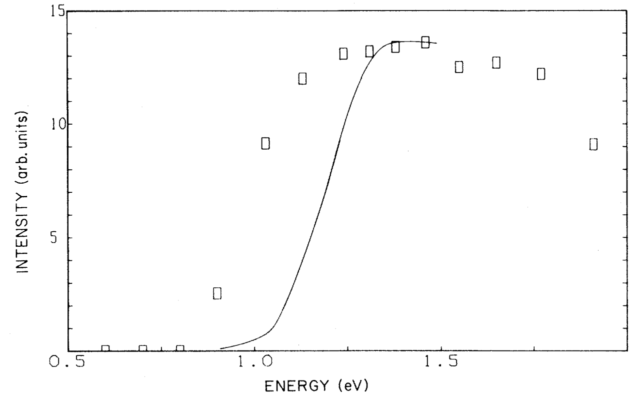

FIG. 3. EPR photoexcitation spectrum of the metastable *DX* state $T = 4$ K; (line) photoionization spectrum of the *DX* center ($x = 0.40$, $T = 80$ K after Ref. 20).

Our EPR results on the Sn related *DX* center provides two important pieces of information:

First, the *DX* center has a metastable excited paramagnetic state. Since in EPR, contrary to the photoluminescence and optical absorption measurements, absolute defect concentrations can be determined, our results show that the photoexcited paramagnetic state is a different configuration of the *DX* center and not due to the presence of another low-concentration defect. The multiplicity, intensity ratio, and *g* values of the two spectra are characteristic of a T_2 state, the degeneracy of which has been reduced by strain into a singlet and a doublet state; the hydrogenic ground state associated with the *X* conduction band is a T_2 state for the Sn dopant. Its splitting under uniaxial stress has been studied in the case GaP:Sn.[21] The biaxial strain inherent in the lattice mismatched $Ga_{1-x}Al_xAs$/GaAs heterostructures[22] induces such a splitting, however, the actual strain distribution in these samples is not known. From an analysis of the decline of the two spectra between 4 and 20 K thermal barriers of 5 and 1 meV have been determined for the doublet and singlet state, respectively.

Second, a comparison of the photoexcitation spectrum, which we have determined with the photoionization spectrum of the *DX* center measured by photocapacitance spectroscopy,[23] shows them to be very similar. Unfortunately, a photoionization spectrum of the Sn-related *DX* center for an alloy composition of $x = 0.31$ is not available. Thus the results obtained by Lang and Logan[23] for an alloy composition $x = 0.40$ at a temperature of 80 K are superposed on Fig. 3. The shape of the spectra is the same, but the threshold is shifted by 0.2 eV to higher energies. We attribute this shift to the different techniques used (initial rise, photocapacitance/saturation, EPR method). Our results in the direct-gap material demonstrate that the origin of the optical absorption band at $E > 0.8$ eV is not photoionization of *DX* into the lowest Γ conduction band. For in this case it would lead to a population of the hydrogenic states related with the Γ conduction band contrary to our observation. The photoionization spectra have recently been studied in detail as a function of the alloy composition for the Si *DX* center.[24,25] Their independence of *x*, in spite of a changing band structure at $x = 0.35$, as well as a shift of the *DX* ground state relative to the conduction-band minimum, are in favor of an interpretation as an internal A_1-T_2 transition; such a transition is expected to occur for deep substitutional donor defects in $Ga_{1-x}Al_xAs$ in the 1-eV range[26] as has, for example, been found for the As_{Ga}^0 defect in GaAs. In fact, as the photoexcitation below the threshold of 0.8 eV did not create the paramagnetic state nor did it significantly change the cyclotron resonance spectrum the probability for a direct optically induced transfer of electrons from the *DX* center to the lowest conduction band is low. This raises the problem how the photoexcitation can nevertheless give rise to photoconductivity and photocapacitance effects, which have, however, always been studied at higher temperatures ($T \gtrsim 40$ K). We have equally measured the temperature dependence of the photoexcitation spectrum; the results show that the metastable state can only be populated at temperatures $T \leq 25$ K. A simple explanation is that for higher temperatures thermal ionization of the electrons to a conduction band and subsequent scattering into Γ occur.

In conclusion, we have observed for the Sn-related *DX* center in $Ga_{0.69}Al_{0.31}As$ an excited metastable state which is very similar to the ground state observed previously for the Si *DX* center in indirect-gap material without any photoexcitation. The optical absorption spectrum with a threshold at ~0.8 eV, cannot be ascribed to a photoionization to be the lowest conduction band.

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