Nitrogen-related electron traps in Ga(As,N) layers (≤3% N)

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Capacitance spectroscopy is used to examine the compositional dependence of deep levels in Si-doped Ga(As,N) layers grown on GaAs. We find two predominant electron traps at about 0.80 and 1.1 eV above the valence band edge E_V, which do not depend on composition. For N contents above 0.1% N, the concentration of the acceptor-like gap level at $E_V+1.1$ eV strongly increases and leads to a distinct reduction of the donor doping efficiency in Ga(As,N) layers. Based on theoretical prediction, this electron trap is tentatively associated with a split interstitial defect containing a nitrogen and an arsenic atom on the same As lattice site $[(\mathrm{AsN})_{\mathrm{As}}]$. The trap at $E_V+0.80$ eV likely corresponds to nitrogen dimers, i.e., two N atoms on a single As site $[(\mathrm{NN})_{\mathrm{As}}]$. When approaching the critical layer thickness, this electron trap is increasingly generated during growth. The dimer defect can be removed by rapid thermal annealing at 720 °C after growth, in contrast to the stable bulk level at $E_V+1.1$ eV. By the formation of both N-related defects, the tensile strain in Ga(As,N) is reduced. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1568523]

I. INTRODUCTION

Nitrogen-containing III–V alloys, such as Ga(As,N) and (In,Ga)(As,N), have recently attracted considerable interest due to their unique physical properties and wide range of possible device applications. However, epitaxial growth of these alloys still remains a problem, because the crystal quality is found to deteriorate for higher concentrations of incorporated nitrogen leading to a remarkable degradation of the optical and electrical characteristics.[1–5] Since the properties of as-grown Ga(As,N) and (In,Ga)(As,N) layers can be improved by postgrowth heat treatment,[1–4] the degradation is, at least in part, due to native point defects with deep electronic levels in the band gap, which may act as compensating, life-time killing, or nonradiative recombination centers.

For some compositions of Ga(As,N)[6–9] and (In,Ga)(As,N),[10–13] deep electron and hole traps as well as their annealing behavior have been studied by deep-level transient spectroscopy.[14,15] Whereas most of the hole traps in Ga(As,N) could be identified,[7] the origin of the dominant electron traps is not clear yet. In particular, the compositional dependence of the major gap levels has not been examined until now. Deep-level spectra of *strained* Ga(As,N) layers exhibit several well-defined peaks in temperature scans,[6–9] in contrast to the rather broad signals observed for *lattice-matched* (In,Ga)(As,N) alloys.[10–12] The reason for this remarkable difference is not understood. However, level broadening in (In,Ga)(As,N) makes the analysis of deep levels difficult.

In the present study, we therefore concentrate on *strained* Ga(As,N) layers with compositions from the dilute limit (≤0.1% N) to the alloy (3% N) in order to investigate the compositional variation of the major electron traps. We find two predominant energy levels at about 0.80 and 1.1 eV above the valence band edge E_V. The first level is concentrated close to the Ga(As,N) surface reaching densities above $10^{18}\,\mathrm{cm}^{-3}$, which can be strongly reduced by rapid thermal annealing (RTA). The second trap at $E_V+1.1$ eV is a bulk level in the Ga(As,N) layer, the concentration of which strongly increases with larger N contents. Because it cannot be removed by RTA, the doping efficiency in *n*-type layers is strongly affected by this defect level in Ga(As,N) alloys.

II. EXPERIMENTAL DETAILS

Rectifying metal-semiconductor (MS) contacts on Si-doped Ga(As,N) layers grown on GaAs substrates by molecular-beam epitaxy were investigated by admittance[15] and deep-level transient Fourier spectroscopy (DLTFS).[16] Details of epitaxial growth and contact preparation have been previously published.[17] To avoid strain relaxation, the Ga(As,N) layer thickness was reduced from 500 nm for ≤0.5% N to 50 nm for 3% N. RTA was performed after growth for 120 s at 720 °C with a GaAs proximity cap under N_2 atmosphere. The electron concentration *n* in the Ga(As,N) layers was determined by capacitance versus voltage measurements ($C-V$ method).[15]

Deep-level spectra were obtained with a computer-controlled Bio-Rad DL8000 system. For temperature scans, the capacitance-time transients were digitized, and the discrete Fourier coefficients were calculated at each temperature by a numerical Fourier transformation.[16] The thermal activation energy E_t of electron traps was determined from the

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temperature dependence of the emission rate e_n for electrons from the corresponding level into the conduction band (Arrhenius plot) according to[14]

$$e_n = \sigma_n v_{\text{th}} N_C \exp\left(-\frac{E_t}{kT}\right), \tag{1}$$

where σ_n denotes the capture cross section for electrons, v_{th} the thermal velocity of electrons in the conduction band, N_C the effective density of states of the conduction band, k the Boltzmann constant, and T the temperature. The emission rate e_n was found by analyzing the peak positions in temperature scans for different Fourier coefficients.[16]

The deep-level concentration N_t was determined from the DLTFS peak height $\Delta C_{\text{m}}/C$ according to the correction given in Ref. 18:

$$\frac{\Delta C_m}{C} = \frac{N_t}{2n}\frac{(W_R-\lambda)^2-(W_P-\lambda)^2}{W_R^2}, \tag{2}$$

where W_R and W_P denote the thicknesses of the depletion layer at the quiescent reverse bias and at the pulse voltage, respectively, and

$$\lambda = \sqrt{\frac{2\varepsilon\varepsilon_0(E_F-E_t)}{q^2 n}}. \tag{3}$$

The point $(W-\lambda)$ below the MS contact indicates the position, where the Fermi level E_F crosses the trap level E_t. The deep-level response therefore originates from a depth around $1/2(W_R+W_P)-\lambda$, which can be varied by the applied bias voltage. In order to evaluate fully corrected concentration versus depth profiles for a certain electron trap, W_R, W_P, and λ were determined at the temperature of the related DLTFS peak.

III. RESULTS AND DISCUSSION

A. Compositional dependence of the deep levels in Ga(As,N)

For three compositions, typical DLTFS signals of the dominant electron traps are plotted in Fig. 1. Surface- and bulk-related deep-level spectra of as-grown Ga(As,N) layers (labeled s and b, respectively) as well as those of annealed Ga(As,N) surfaces (labeled sa) are depicted. It should be noted that, despite its perfect surface smoothness, the as-grown layer with 0.5% N could be examined only after recess-etch of at least 50 nm. The bulk of the layer with 3% N could not be inspected (see Sec. III D). For the compositions studied, the peaks A5, B3, and C1 with capacitance changes of up to 10% are confined close to the as-grown surface (compare spectra s and b in Fig. 1). They are completely removed by RTA at 720 °C for 120 s (see spectra sa). Based on these similar features, we believe that the traps A5, B3, and C1 are due to the same lattice defect near the surface of all investigated Ga(As,N) layers (see the dotted line in Fig. 1).

The electron traps A2 and B1 exhibit in bulk- as well as in surface-related spectra of Ga(As,N) the same peak heights, i.e., they are not confined to the Ga(As,N) surface. Both levels are resistant to annealing (see spectra sa). Concerning

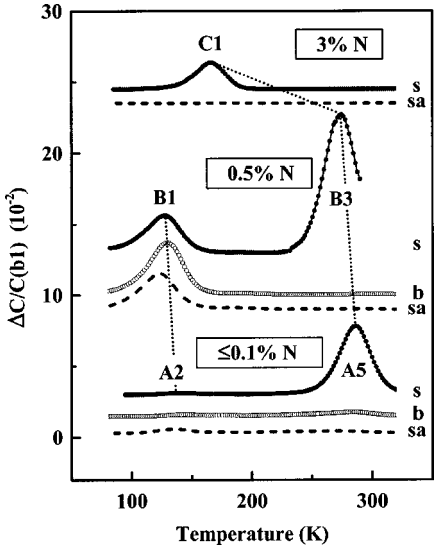

FIG. 1. Temperature scans of the DLTFS signal $\Delta C/C$ (Fourier coefficient $b1$) for three Ga(As,N) compositions as indicated (0.47 s time constant, 100 ms pulse width). The deep-level spectra labeled s and sa were measured close to the surface of as-grown and annealed layers, respectively. The b scans originate from the Ga(As,N) bulk. The dominant peaks are indicated. Dotted lines connect the peaks of electron traps with similar features. Spectra are vertically shifted for clarity.

the common properties, we assume that the deep levels A2 and B1 originate from the same bulk defect in Ga(As,N). The peak height, i.e., the concentration of the underlying defect, increases by a factor of more than 30 from the dilute N limit to the sample with 0.5% N. Although an even higher level concentration is expected for the 3% N sample, a trap with comparable features could not be found in the range between 10 and 350 K.

The compositional dependence of the dominant deep levels in the Ga(As,N) band gap is compiled in Fig. 2. The GaAs-related band offsets for 3% N content have recently been determined independently for the conduction and valence band to be $+400$ and -11 meV, respectively.[17,19] For Ga(As,N) in the dilute N limit, we have previously shown[9] that the levels A2 and A5 are linked with the intrinsic defects E3 and E4, respectively, which are known from electron-

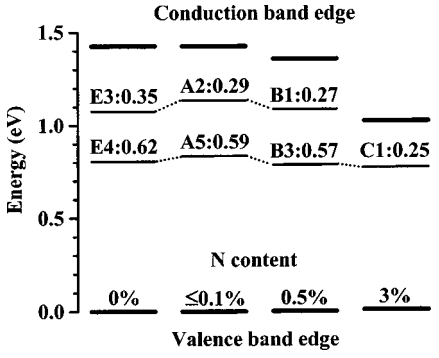

FIG. 2. Compositional dependence of dominant deep levels in the Ga(As,N) band gap. The top of the GaAs valence band is set to zero. All trap energies are given in electron volts with respect to the conduction band edge. Dotted lines connect levels of the same origin. For the traps E3 and E4, the level energies are taken from Ref. 20.

irradiated GaAs.[20] Since E3 and E4 are due to displacements in the As sublattice,[21] it is suggested that the dominant electron traps in Ga(As,N) are associated with defects on As sites. For Ga(As,N) in the dilute N limit, the apparent level energies in Fig. 2 are shifted toward the conduction band edge, because the electron traps A2 and A5 are detected only in regions with larger composition than the nominal one.[9]

The common origins of A5, B3, and C1 as well as of A2 and B1 are indicated in Fig. 2 by dotted lines. It is apparent that the E3- and E4-related levels at different compositions are energetically fixed with respect to the top of the valence band at about $E_V+1.1$ and $E_V+0.80$ eV, respectively. In accordance with these findings, the E4-related level has also been observed at the gradual Ga(As,N)-on-GaAs interface to remain at $E_V+0.80$ eV, irrespective of the compositional change from 3 to about 0.2% N.[8] From Fig. 2, it follows that for more than about 2.5% N the E3-related electron trap is resonant with the conduction band and therefore no longer detectable, in agreement with the experiment.

B. Origin of the dominant electron traps in Ga(As,N)

It is known that the tensile strain in Ga(As,N) layers grown on GaAs is partially compensated by the formation of N complexes, such as As–N and N–N split interstitial defects on single As sites.[4,22] Whereas the formation of $(AsN)_{As}$ complexes leads to compressive strain, $(NN)_{As}$ defects cause less tensile strain as compared with the substitutional N_{As} atom.[22] The formation of $(AsN)_{As}$ defects is therefore more efficient to minimize the strain in Ga(As,N), but its formation energy is higher than for the $(NN)_{As}$ defects.[23,24] In the dilute N limit, deep gap levels are predicted especially for $(AsN)_{As}$ and $(NN)_{As}$ defects at 0.42 and 0.66 eV below the conduction band edge E_C, respectively,[23] in reasonable agreement with the experimental values for the E3- and E4-related electron traps in Fig. 2. We therefore identify the dominant bulk levels A2 and B1 in Ga(As,N) as being due to $(AsN)_{As}$ complexes.

The traps A5, B3, and C1 are tentatively associated with the $(NN)_{As}$ defect. Since the electron density at the surface is drastically enhanced after removal of this level by annealing, the acceptor-like character of the $(NN)_{As}$ -related trap is confirmed. It should be noted that a similar defect consisting of two N atoms on a phosphorous site $[(NN)_P]$ has been identified in N-doped GaP.[25] The related electron trap at $E_C-0.45$ eV could also be removed by annealing and led to a higher photoluminescence intensity of epitaxial GaP layers.

C. Spatial distribution of deep-level defects in Ga(As,N)

For the dominant electron traps in Ga(As,N) layers, depth profiles of the concentration are displayed in Fig. 3. The concentration of other levels is below $5\times10^{15}\,cm^{-3}$. In contrast to recent publications on Ga(As,N) and (In,Ga)(As,N),[6,10–13] we apply the full correction for the DLTFS signal according to Ref. 18 in order to obtain reliable deep-level concentrations. The depth profiles of the Si dopant concentration n_{Si} as determined from $C-V$ measurements are also plotted in Fig. 3.

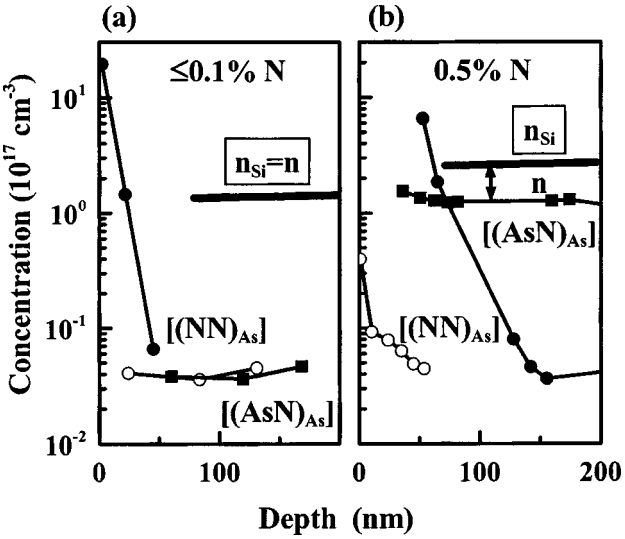

FIG. 3. Depth profiles of Si and deep level concentrations in Ga(As,N) measured in (a) for the dilute N limit and (b) for 0.5% N. The distribution of the $(NN)_{As}$ dimer defect, i.e., of level A5 in (a) and level B3 in (b), is plotted for the as-grown and annealed layers by dots and circles, respectively. The distribution of the $(AsN)_{As}$ defect, i.e., of level A2 in (a) and level B1 in (b), is plotted by squares. In (a), the electron density n in the bulk is given by the concentration n_{Si} of Si dopants as measured by the $C-V$ method. In (b), n is determined by the difference between n_{Si} (measured by the $C_{hf}-V$ method) and the concentration of the $(AsN)_{As}$ defect as indicated by an arrow.

For each composition, the concentration of the $(NN)_{As}$-related level in as-grown layers (dots in Fig. 3) rises exponentially toward the surface and reaches values above $10^{18}\,cm^{-3}$, i.e., it becomes higher than the dopant level n_{Si}. After annealing, the surface density of the $(NN)_{As}$ defect is decreased by more than two orders of magnitude (circles in Fig. 3). The annealing mechanism at the surface is either related to the outdiffusion of nitrogen or to reactions with As vacancies, which may lead to the dissociation of $(NN)_{As}$ defects accompanied by the generation of two substitutional N_{As} sites. With increasing N content, the formation of this defect is apparently enhanced at earlier growth stages of the 500-nm-thick layers. The strong accumulation of this native defect at the Ga(As,N) surface is probably linked to increasing strain during growth. Approaching the critical layer thickness, increasing strain may be reduced by the additional formation of a larger number of $(NN)_{As}$ defects.[22]

The concentration of the $(AsN)_{As}$ -related bulk level is homogeneously distributed. It increases drastically from about $4\times10^{15}\,cm^{-3}$ in the dilute limit [squares in Fig. 3(a)] to about $1.3\times10^{17}\,cm^{-3}$ for 0.5% N [squares in Fig. 3(b)]. In contrast to the $(NN)_{As}$ complex, the $(AsN)_{As}$ defect is stable against annealing at 720 °C, probably due to its higher formation energy.[23] This intrinsic level therefore controls the electrical properties of annealed Ga(As,N) alloys.

D. Doping efficiency in annealed Ga(As,N)

To demonstrate the impact of the $(AsN)_{As}$ defect on the electrical properties of Ga(As,N) after annealing, capacitance C and conductance G of a MS contact on an annealed sample with 0.5% N are shown in Fig. 4. Both quantities strongly

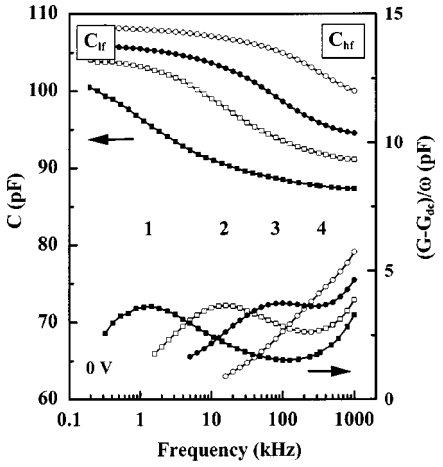

FIG. 4. Frequency dependence of the capacitance C and the conductance G (divided by $\omega=2\pi f$) for a MS contact on annealed Ga(As,N) with 0.5% N measured at 0 V and temperatures of 218 (1), 250 (2), 274 (3), and 308 K (4). At low and high frequencies, the respective capacitances C_{lf} and C_{hf} of the admittance dispersion are indicated. The ac behavior of the conductance is clearly seen, when the dc conductance G_{dc}, which can be determined at low frequencies, is subtracted from the measured G value at higher frequencies.

depend on the measuring frequency f and temperature. C decreases from a low-frequency value C_{lf} to a high-frequency value C_{hf}, whereas the conductance G divided by $\omega=2\pi f$ exhibits peaks at f_m (admittance dispersion).[15] The time constant τ of a trap-related dispersion correlates via $\tau^{-1}=2\pi f_m \approx 2e_n$ with the thermal emission rate e_n for electrons into the conduction band.[15]

In Fig. 5, the emission rate e_n determined from the admittance dispersion in Fig. 4 is compared with e_n values deduced for the dominant traps B1 and B3 from the deep-level spectra in Fig. 1. The Arrhenius plot for the trap B1 matches the temperature dependence of $\tau^{-1}/2$ for the admittance dispersion (dashed line in Fig. 5). The frequency- and temperature-dependent properties of the MS contact on the annealed Ga(As,N) layer shown in Fig. 4 are therefore controlled by the $(\mathrm{AsN})_{\mathrm{As}}$ defect. Since the corresponding level

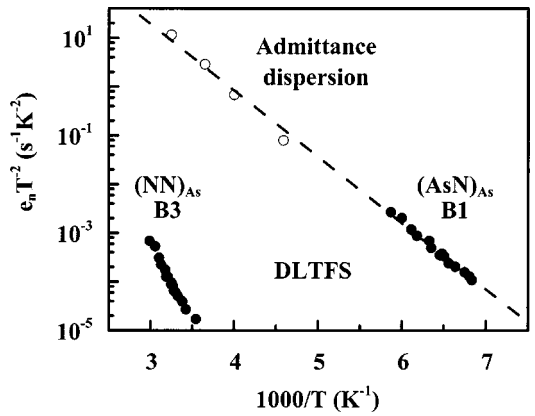

FIG. 5. Arrhenius plots of the thermal emission rate e_n for the dominant electron traps B1 [$(\mathrm{AsN})_{\mathrm{As}}$ defect] and B3 [$(\mathrm{NN})_{\mathrm{As}}$ defect] deduced from Fig. 1 for Ga(As,N) with 0.5% N (dots). The temperature dependence of $\tau^{-1}/2$ determined from the admittance dispersion in Fig. 4 (circles) correlates with the B1 characteristics (dashed line).

is acceptor-like, the $C-V$ method at high frequency ($C_{\mathrm{hf}}-V$) does not directly deliver the distribution of the free-electron concentration n, but the dopant density n_{Si}.[15] n is given by the difference between n_{Si} and the concentration of the dominant $(\mathrm{AsN})_{\mathrm{As}}$ defect [see the arrow in Fig. 3(b)]. From Fig. 3 it is apparent that the doping efficiency is further reduced by larger N contents in Ga(As,N) layers. For the layer with 3% N, it is therefore expected that free electrons are not available in the bulk, i.e., corresponding DLTFS signals cannot be obtained (see Sec. III A).

IV. CONCLUSIONS

The two dominant gap states in Ga(As,N) originate most likely from N-related point defects in the As sublattice. When the composition is changed, their electronic levels are fixed to the valence band edge E_V. Based on theoretical predictions, the level at $E_V+1.1$ eV can be associated with a bulk defect, which consists of an arsenic and a nitrogen atom on a single As site [$(\mathrm{AsN})_{\mathrm{As}}$]. This electron trap is resistant to RTA treatment at 720 °C and thus responsible for the reduced Si doping efficiency even in annealed Ga(As,N) alloys. For more than 2.5% N, the related state is resonant with the conduction band. It should be noted that this defect may be a candidate for efficient nonradiative recombination, since its capture cross section for electrons is $10^{-15}-10^{-14}\,\mathrm{cm}^2$. The other dominant level at $E_V+0.80$ eV probably originates from nitrogen dimers, i.e., two N atoms on a single As site [$(\mathrm{NN})_{\mathrm{As}}$]. When the critical layer thickness is approached, the corresponding electron trap is increasingly generated during growth. It leads to a strong carrier depletion at the as-grown surface, which can be, however, strongly reduced by annealing. The $(\mathrm{AsN})_{\mathrm{As}}$ and $(\mathrm{NN})_{\mathrm{As}}$ defects are apparently formed during growth in order to reduce the tensile strain in the Ga(As,N) layer.

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