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Nitrogen-induced increase of the maximum electron concentration in group III-N-V alloys

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The maximum free-electron concentration is observed to increase dramatically with the nitrogen content x in heavily Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ $(0 \leqslant x < 0.033)$ films. For example, an electron concentration of 7×10^{19} cm^{-3} was observed at $x = 0.033$; a value more than 20 times larger than that observed in GaAs films grown under similar conditions. It is shown that the increase is caused by a combination of two effects: (1) a downward shift of the conduction band and (2) an increase of the electron effective mass caused by flattening of the conduction-band minimum. Both these effects are due to modifications to the conduction-band structure caused by an anticrossing interaction of a localized N state and the conduction band of the III-V host.

The limitation on the maximum attainable free-electron and/or hole concentrations by doping is an important issue for the physics of semiconductors and the functionality of their devices. Consequently, the fundamental mechanisms that lead to the practical doping limits in semiconductors continue to be a subject of current interest.[1–4] Despite years of extensive studies there is still no consensus on the mechanism responsible for the limitations of free carriers in semiconductors.

The amphoteric native defect model has been shown to provide qualitative predictions of the maximum free-carrier concentration achievable by doping in a wide variety of semiconductors including III-V (Refs. 5 and 6) and, most recently, II-VI (Ref. 7) materials. The model relates the type and concentrations of native defects responsible for dopant compensation to the location of the Fermi level with respect to an internal energy reference, the Fermi-level stabilization energy E_{FS}. The E_{FS} was found to be located at ≈4.9 eV below the vacuum level and is constant for all III-V and II-VI semiconductors. Semiconductor materials with the conduction (valence) band located close to E_{FS} can be easily doped n type (p type). In III-V semiconductors, it is found that the maximum (minimum) energy location of the Fermi energy, measured relative to E_{FS}, is very similar (roughly 1 eV from E_{FS}).

GaAs has its conduction band at $E_{FS} + 0.9$ eV and its valence band at $E_{FS} - 0.5$ eV and thus is predicted to exhibit limitations on the maximum free-electron concentration but no significant limitation on the maximum hole concentration. Experimentally, the maximum free-electron concentration n_{max} in GaAs achievable under equilibrium growth conditions is limited to the mid 10^{18} cm^{-3} range, corresponding to the Fermi energy E_F located approximately at 0.1 eV above the conduction-band edge or at 1 eV above E_{FS}.[8] We note that nonequilibrium techniques such as Se+Ga co-implantation[9] and pulse electron beam irradiation techniques[10] have been used to achieve n_{max} values in GaAs up to 2×10^{19} cm^{-3} corresponding to a maximum Fermi level at $E_{FS} + 1.3$ eV.

In this paper we report the observation that the maximum free-electron concentration in heavily Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ alloys increases rapidly with the N concentration. The maximum value attained 7×10^{19} cm^{-3} at $x = 0.033$ is larger than that attained in GaAs by any doping method. We use the amphoteric native defect model to show that the increase is caused by N-induced modifications of the conduction-band structure.

Se-doped $Ga_{1-3x}In_{3x}As_{1-x}N_x$ films (1–3 μm thick) with x ranging from 0 to 0.033 were grown on GaAs substrates by metalorganic vapor-phase epitaxy (OMVPE).[11] The growth temperatures ranged from 550 °C and 580 °C and H_2Se was used as the Se source. The In content in the films was measured by Rutherford backscattering spectrometry (RBS). The atomic fraction of N atoms incorporated into the As sublattice (x) was determined by reflection (004) double-crystal x-ray diffraction (XRD) measurements using the method discussed in Ref. 11.[12] The RBS-measured In contents in the films were equal to $3x$ to within 20%; this ratio produces films that are lattice matched to the GaAs substrate. Secondary ion mass spectroscopy (SIMS) using a Cs^+ beam was used to measure the concentration of the Se dopant. The net sheet density and mobility of the free carriers were determined from Hall effect measurements in the Van der Pauw geometry. The net donor concentration profiles were obtained by electrochemical capacitance-voltage (ECV) profiling using 0.2 M NaOH:EDTA as the electrolyte.

Figure 1 shows the atomic profiles of In, N, H, and Se for a $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ film ($x = 0.024$) measured by SIMS. A uniform concentration of Se (3×10^{20} cm^{-3}) is observed in the film. Similarly uniform atomic profiles with Se concentrations in the range $2-7 \times 10^{20}$ cm^{-3} were measured in all of the samples. We note that the dimethylhydrazine used as a N source in the OMVPE growth caused hydrogen to be present in the range $10^{19}-10^{20}$ cm^{-3} for all films with $x > 0$.[13]

Profiles of the net donors for the $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ films with $x = 0$ to 0.033 measured by ECV are shown in Fig. 2. It should be noted that the ECV-measured net donor concentrations for the Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ films agree

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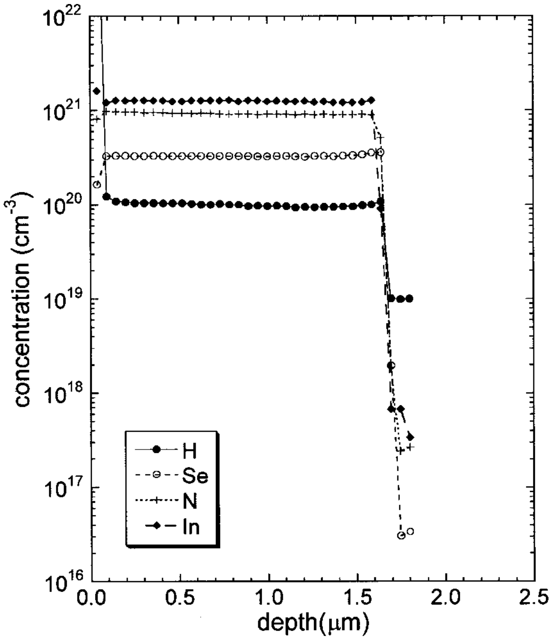

FIG. 1. SIMS profiles of H, In, N, and Se in a 1.5-μm-thick Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ film with $x=0.024$ grown on GaAs.

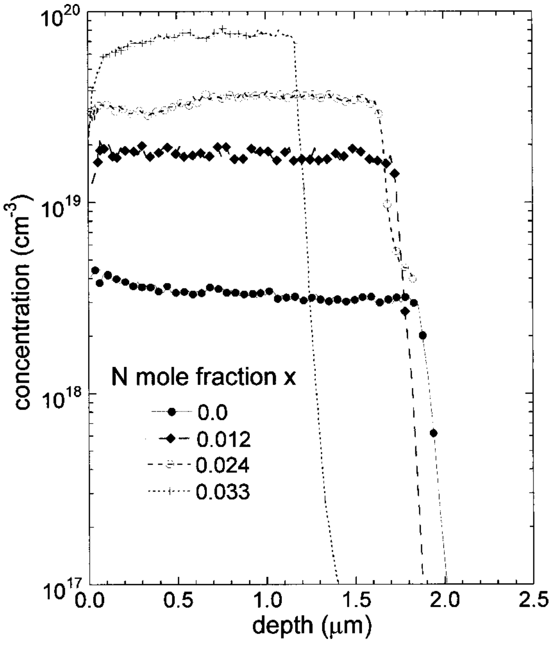

FIG. 2. Free-electron concentration profiles for the $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ alloys films with $x=0-0.033$ measured by the electrochemical capacitance-voltage technique.

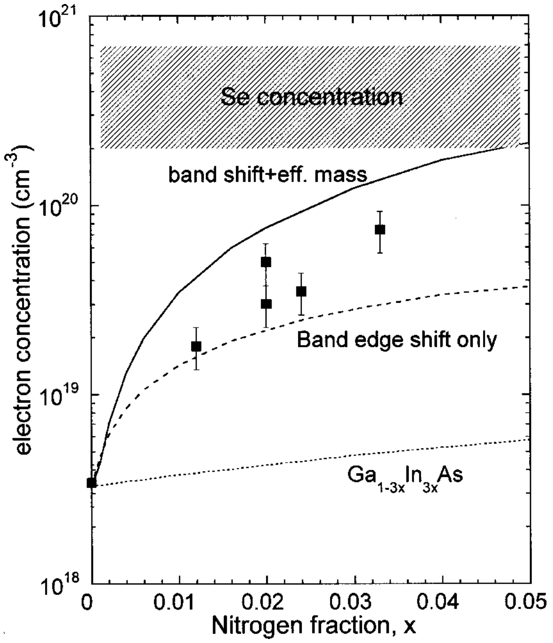

FIG. 3. A comparison of the measured maximum electron concentration with the calculated values as a function of N fractions in $Ga_{1-3x}In_{3x}N_xAs_{1-x}$. Two different cases of the calculated $n_{\max}$ are shown: one included effects of downward shift of the conduction band only (dashed curve) and the other included both the band shift and the enhancement of the density of states effective mass (solid curve). The calculated $n_{\max}$ for samples with no N (i.e., the effects from the band gap lowering produced by In incorporation only are considered) are also shown in the figure (dotted curve). The shaded area indicates the range of Se concentration in these samples.

well (within 20%) with the free-electron concentrations obtained by Hall effect measurements. For simplicity, hereafter, we refer to both the Hall and ECV measured concentrations as the free-electron concentration. Since the Se atomic concentrations in these films are at least an order of magnitude higher than the free-electron concentration,[14] the measured free-electron concentration shown in Fig. 3 can be considered to be the maximum achievable free-electron concentration $n_{\max}$ for the specific growth conditions. Figure 3 graphs $n_{\max}$ vs x; $n_{\max}$ increases strongly with x with a maximum observed value of 7×10^{19} cm^{-3} for $x=0.033$. This value is ca. 20× that observed for a GaAs film (3.5×10^{18} cm^{-3}) grown under the same conditions.

It has recently been shown that incorporating small amounts of nitrogen leads to a dramatic reduction of the fundamental band gap in group III-V semiconductors.[15–20] In $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ it is known that the band-gap reduction exceeds 180 meV per atomic percent N. Within the amphoteric defect model, this band-gap reduction would lower the conduction-band edge with respect to E_{FS} and an increase in $n_{\max}$ would be predicted. Recently, Shan *et al.*[21] have shown that the band-gap reduction in III-N-V alloys is caused by a splitting of the conduction band into two nonparabolic subbands induced by an anticrossing interaction between a narrow band of localized N states and the extended conduction-band states of the host semiconductor matrix.[21,22] Application of that model here enables us to make quantitative predictions of the x dependence of $n_{\max}$ in $Ga_{1-3x}In_{3x}N_xAs_{1-x}$.

The anticrossing model has been described in detail elsewhere;[21,22] we only show here the points essential to the modeling of $n_{\max}$. Due to its size mismatch with the host lattice, N forms a localized state whose repulsive interaction with the conduction-band states splits the conduction band of a III-N-V alloy into two subbands. Application of simple perturbation theory yields the dispersion relations for the upper and lower conduction subbands, E_+ and E_-:

$$E_{\pm}(k)=\frac{1}{2}\left[E_N+E_M(k)\pm\sqrt{[E_N-E_M(k)]^2+4C_{NM}^2x}\right], \tag{1}$$

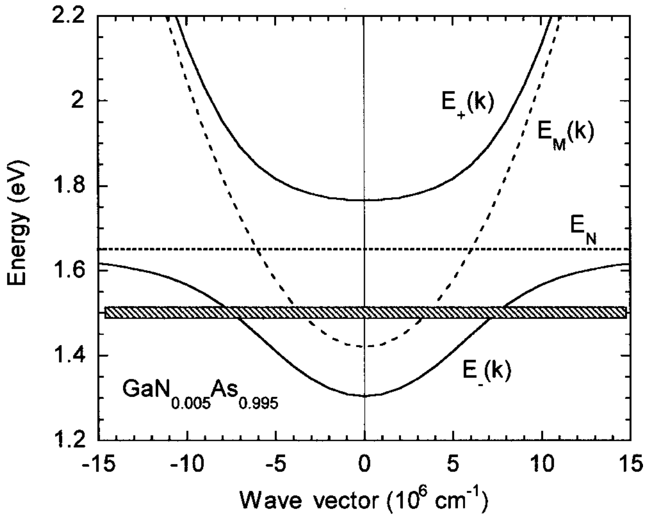

FIG. 4. The band structure of a $GaN_{0.005}As_{0.995}$ alloy calculated using the band anticrossing model showing the splitting of the conduction band into two nonparabolic subbands $E_+(k)$ and $E_-(k)$. The dashed and dotted lines represent the unperturbed conduction band of the host semiconductor matrix $E_M(k)$ and the dispersionless, highly localized E_N level. The shaded area represents the approximate maximum energy location of the Fermi energy, $E_{F\max}$.

where E_N is the energy of the N level, $E_M(k)=E_0+k^2/(2m_M)$ is the standard parabolic dispersion relation for the host semiconductor matrix with the electron effective mass m_M, and C_{NM} is the matrix element describing the coupling between N states and the extended states.[21,22] It has been found previously that E_N lies 1.65 eV above the valence-band maximum and $C_{NM}=2.7$ eV in $Ga_{1-y}In_yN_xAs_{1-x}$ at small values of y.[22] The dispersion relation calculated with Eq. (1) is shown in Fig. 4, demonstrating that the incorporation of N leads to a significant distortion of the conduction-band structure. Two aspects of this distortion are important here: (1) the formation of the lower subband that causes the band-gap energy reduction and (2) the considerable flattening of the lower subband near its minimum leading to a large enhancement of the electron effective mass.[23] We have also indicated the approximate maximum energy location of the Fermi energy ($\approx E_{FS}+1$ eV) corresponding to the $n_{\max}$ measured in the GaAs sample without N in Fig. 4 (shaded area).

We examine initially the effect of the band-gap reduction only. Within the amphoteric defect model, we would expect that the band-gap reduction with increasing x should lower the conduction-band edge with respect to E_{FS}. A larger $n_{\max}$ would then be predicted. We make quantitative predictions as follows. The maximum electron concentration $n_{\max}$ is calculated from the Fermi-Dirac integral

$$n_{\max}=\int_{E\_0}^{\infty} D(E) f_o(E,E_{F\max}) dE, \tag{2}$$

where $E_-(0)$ is the conduction-band edge, *D(E)* is the conduction-band density of states, and $f_o(E,E_{F\max})$ is the Fermi-Dirac distribution function. Initially, we evaluate *D(E)* using the energy position of the conduction-band edge calculated by Eq. (1) as a function of x, an unperturbed density of states with a fixed conduction-band effective mass of $0.07m_o$ (the value in GaAs), and $E_{F\max}=E_{FS}+1.0$ eV (which reproduces $n_{\max}$ in our GaAs film). The results are shown as the dashed line in Fig. 3. Although a substantial increase in $n_{\max}$ is predicted, the curve lies well below all of the experimental points, indicating that there is an additional mechanism responsible for the increase in $n_{\max}$.[24]

We therefore consider the N-induced change in the density of states as reflected through the changes of the effective mass. Using Eq. (1) it can be shown that the energy-dependent effective mass for the N-modified conduction band is[22]

$$m^*=m_M\left[1+\frac{C_{NM}^2 x}{(E_N-E)^2}\right] \tag{3}$$

and the modified conduction-band density of states is

$$D(E)=\frac{m_M^{3/2}}{\sqrt{2}\pi^2\hbar^3}\left[\left(1+\frac{C_{NM}^2 x}{(E_N-E)^2}\right)\left(E+\frac{C_{NM}^2 x}{(E-E_N)}\right)^{1/2}\right], \tag{4}$$

where m_M is the electron effective mass in the parabolic conduction band of the semiconductor matrix. As can be seen from Eqs. (3) and (4), the effective mass and the density of states depend very strongly on the electron energy relative to the localized E_N level.

Using Eq. (4) in the Fermi-Dirac integral [Eq. (2)] we calculate $n_{\max}$ considering both the effects of band-gap reduction and the increase in the effective mass.[25] Again, we assume that the Fermi level is pinned at a maximum location of 1 eV above the Fermi level stabilization energy E_{FS} when the dopant concentration is higher than the saturated electron concentration. As is shown by the solid line in Fig. 3, a very large enhancement of the $n_{\max}$ is predicted in $Ga_{1-3x}In_{3x}N_xGa_{1-x}$ when all the modifications of the conduction-band structure are included in the calculations. The theory accounts quite well for the experimentally observed increase of the electron concentration with x. We note that the predicted value of $n_{\max}$ was not reached in our films. We attribute this difference between experimental and theoretical results to the compensation and passivation of donors by N-related defects and H present in the samples.

In addition, electron mobility in the Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ films was found to be in the range 20–60 cm^2/V s from Hall effect measurements. This can be attributed to the strong alloy disorder scattering which is almost three orders of magnitude more effective than the scattering in standard semiconductor alloys, as well as to the enhanced electron effective mass in these alloys.[22,23] These values of electron mobility in the $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ alloys are to be expected from the N modified conduction-band structure and are similar to those for holes in GaAs with similar mass.

In conclusion, we show that the N-induced modification of the conduction-band structure leads to a large increase in the maximum attainable free-electron concentration in the group III-N-V semiconductor alloys. A more than one order of magnitude enhancement of the maximum electron concentration has been found in the Se-doped $Ga_{1-3x}In_{3x}N_xAs_{1-x}$ alloy with only 3.3% of nitrogen. The results are consistent with the predictions of the amphoteric native defect model when the changes to the conduction band induced by nitrogen are described by an anticrossing between a localized N state and the extended states of the conduction band. Our finding offers an interesting opportunity to use alloying with nitrogen to overcome doping limits in *n*-type III-V semiconductors.

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[12] In all films with $x>0$, the SIMS-measured N contents were always higher than those measured by XRD. For example, the N concentration shown in Fig. 1 corresponded to a N mole fraction of $x\sim 0.042$, whereas the XRD measurement on this film yielded $x=0.024$. We infer this to mean that, in this case, 57% of the N atoms in the film reside in ''active,'' substitutional group-V sites.

[13] Hydrogen could passivate shallow donors in GaAs. However, in our samples the hydrogen concentrations are always more than three times lower than the Se dopant concentrations.

[14] Channeling particle induced x-ray emission (*c*-PIXE) angular scan measurements revealed that over 90% of the Se dopants were in substitutional positions and only less than 10% of Se atoms appeared to form random precipitates. These results support the claim that the free-electron concentration in the Se-doped samples is limited by incorporation of compensating native acceptors (as predicted by the amphoteric native defect model) rather than by the solid solubility of Se in this material.

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[23] The main findings of the band anticrossing model were recently confirmed by more rigorous calculations using sp^3s^* tight-binding approach, see A. Lindsay and E. P. O'Reilly, Solid State Commun. (to be published).

[24] Even if $E_{F\max}$ is increased to $E_{\mathrm{FS}}+1.3$ eV, corresponding to the largest $n_{\max}$ reported in GaAs, the curve will lie significantly below some of the data points.

[25] In the calculations of the electron concentration, the unphysical divergence of the density of states $D(E)$ at $E=E_N$ was removed by introducing a broadening parameter so that the total volume of electronic states is conserved. It should be noted, however, that since the maximum Fermi energy is located well below E_N, the procedure does not affect the results of the calculations.