

Mutual passivation of group IV donors and nitrogen in diluted GaN_xAs_{1-x} alloys

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We demonstrate the mutual passivation phenomenon of Ge donors and isovalent N in highly mismatched alloy GaN_xAs_{1-x} doped with Ge. Layers of this alloy were formed by the sequential implantation of Ge and N ions followed by pulsed laser melting and rapid thermal annealing. The mutual passivation effect results in the electrical deactivation of Ge_{Ga} donors (Ge on Ga sites) and suppression of the N_{As} (N on As sites) induced band gap narrowing through the formation of Ge_{Ga}-N_{As} nearest neighbor pairs. These results in combination with the analogous effect observed in Si-doped GaN_xAs_{1-x} provide clear evidence of the general nature of the mutual passivation phenomenon in highly mismatched semiconductor alloys. © 2003 American Institute of Physics. [DOI: 10.1063/1.1616980]

GaN_xAs_{1-x} (with x typically less than 0.05) belongs to the class of highly mismatched semiconductor alloys (HMAs) in which small quantities of more electronegative elements (N) replacing metallic anions (As) cause dramatic changes in the alloy's electronic properties.¹⁻⁵ The unusual properties of HMAs have been successfully described by the anticrossing interaction between localized states of the foreign electronegative element (N) and the extended states of the host semiconductor matrix.^{1,6} Such interaction gives rise to a drastic reduction of the band gap, and increases in the electron effective mass^{7,8} as well as the density of states of the conduction band.⁷ As a consequence, over an order of magnitude enhancement in the maximum achievable free electron concentration has been demonstrated in GaN_xAs_{1-x} thin films doped with group VI donors (Se and S).⁹⁻¹²

Our recent investigation of epitaxially grown GaN_xAs_{1-x} thin films doped heavily with Si revealed that the Si and N mutually passivate each other's electronic activity.¹³ The reduced electrical activity of Si_{Ga} donors (Si on Ga sites) in GaN_xAs_{1-x} alloys was attributed to the formation of nearest neighbor Si_{Ga}-N_{As} pairs. The formation of these Si_{Ga}-N_{As} pairs also affects the conduction band structure by deactivating a fraction of the N_{As} sites. In this letter we use Ge doping of GaN_xAs_{1-x} to demonstrate that the mutual passivation effect is a general phenomenon for all group IV donors in GaN_xAs_{1-x}.

Ge ions, 340 and 100 keV, were implanted into semi-insulating GaAs substrates with doses of 6.4×10^{15} and 1.7×10^{15} cm⁻², respectively. Matching N distributions were

obtained by dual energy N⁺ implantation of 80 and 33 keV with doses of 7.0×10^{15} and 2.4×10^{15} cm⁻², respectively. This Ge⁺ and N⁺ coimplantation created a ~200 nm thick layer of Ge and N codoped GaAs with ~2 mol % (~ 4.4×10^{20} cm⁻³) of both species (2%N+2%Ge). Layers produced from only N (2%N) or Ge (2%Ge) ion implantation were used as references. The implanted GaAs samples were subjected to pulsed laser melting (PLM) in air using a KrF laser ($\lambda=248$ nm) with a full width at half maximum (FWHM) pulse duration of ~38 ns and fluence of 0.45 J/cm². The samples were subsequently processed by rapid thermal annealing (RTA) at temperatures between 600 and 950 °C for 5–120 s in flowing N₂. This postimplantation treatment will be referred to as PLM-RTA. We have recently utilized this method to realize GaN_xAs_{1-x} layers with x as high as 0.016.^{14,15}

The free carrier concentration was measured by the Hall effect in the van der Pauw geometry and electrochemical capacitance-voltage (ECV) profiling techniques. The band gaps of the films were measured using photoreflectance (PR) at room temperature using a chopped HeCd laser beam ($\lambda=442$ or 325 nm) for modulation. The spectral line widths and band gaps were determined by fitting the PR spectra to the Aspnes third-derivative functional form.¹⁶

The passivation of the N activity by the Ge atoms in the 2%N+2%Ge sample after PLM-RTA is illustrated in the series of photoreflectance (PR) spectra presented in Fig. 1. A fundamental band gap transition at 1.24 eV is observed for GaAs samples implanted with 2%N alone after PLM-RTA at 950 °C for 10–120 s, corresponding to ~1 mol % incorporation of N in the substitutional As sites (N_{As}). In contrast, the

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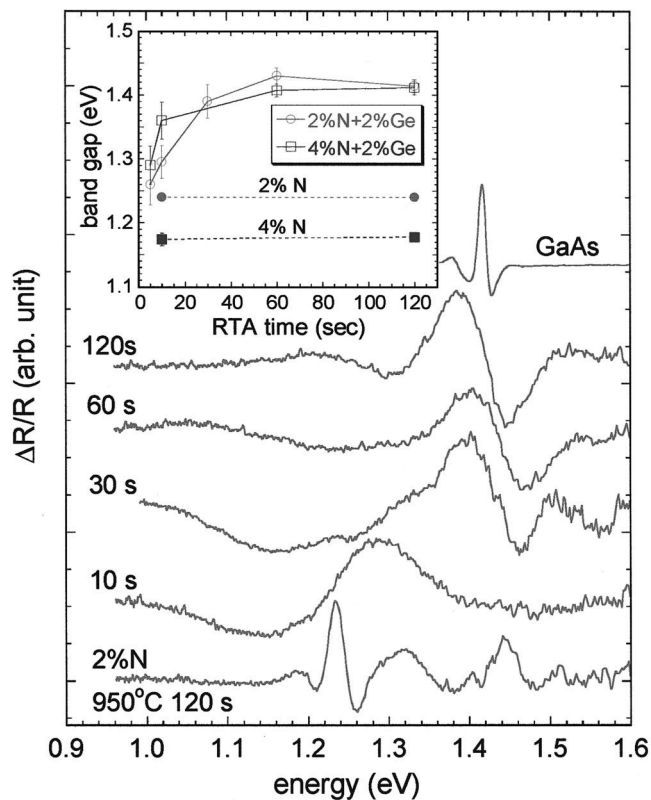


FIG. 1. Photoreflectance (PR) spectra measured from a series of GaAs samples implanted with 2%N+2%Ge followed by PLM-RTA at 950 °C for a duration of 5–120 s. PR spectra from a GaAs wafer (top spectrum) and a GaAs sample implanted with 2%N only after PLM+RTA at 950 °C for 120 s (bottom spectrum) are also shown. The inset shows the band gap energies determined from PR measurements from 2%N, 2%N+2%Ge, 4%N, and 4%N+2%Ge samples after PLM+RTA at 950 °C for durations of 5–120 s.

band gap of the 2%N+2%Ge samples increases from 1.24 to 1.42 eV (band gap of GaAs) as the RTA duration increases to 60 s, and reveals that N_{As} is passivated by Ge. We propose that the sufficiently short melt duration (~ 200 ns) during PLM leads to the incorporation of Ge and N atoms to levels far beyond equilibrium randomly in their preferential sublattice. During subsequent RTA, the temperature is sufficient to enable Ge atoms to diffuse and attain a lower-energy configuration. Since N is more electronegative than As (the Pauling electronegativities of N and As are 3.0 and 2.0, respectively) it has a tendency to bind the fourth valence electron of Ge atoms in Ga sites Ge_{Ga} , and therefore the formation of $Ge_{Ga}-N_{As}$ nearest neighbor pairs is favored energetically. The gradual increase in the band gap of the 2%N+2%Ge sample as a function of the RTA temperature and/or time duration can be attributed to the passivation of N_{As} by Ge_{Ga} through the formation of nearest neighbor $Ge_{Ga}-N_{As}$ pairs. The estimated diffusion length of Ge in GaAs at 950 °C for 10 s is $\sim 2-20$ Å.¹⁷ This is comparable to the average distance from a Ge atom to its nearest N_{As} for GaN_xAs_{1-x} with $x \sim 0.01$ (~ 10.3 Å).

The change in band gap of the GaAs samples containing both N and Ge and N alone is shown as a function of the RTA duration in the inset of Fig. 1. Results from another set of samples implanted with 4%N+2%Ge and 4%N alone are also shown. For the sample implanted with 4%N, a layer of GaN_xAs_{1-x} with $x = 0.016$ is formed with a band gap of 1.17

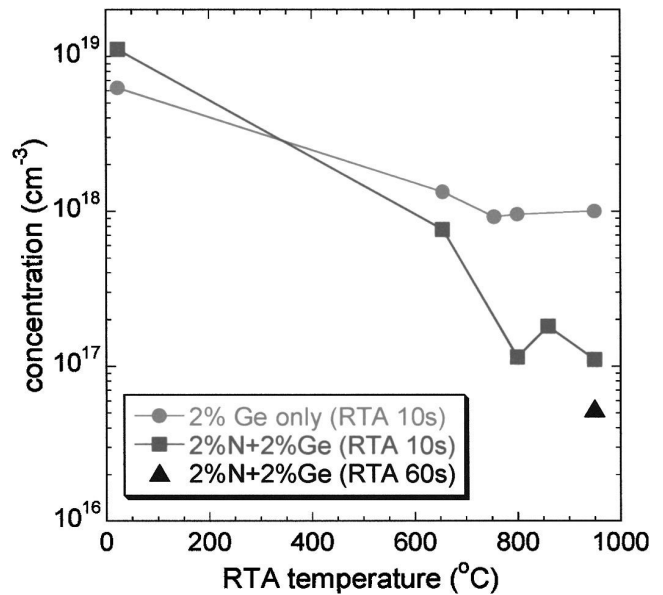


FIG. 2. Free electron concentrations of the 2%Ge and 2%N+2%Ge samples after PLM+RTA at increasing temperatures for 10 s obtained by Hall effect measurements. The electron concentration of the 2%N+2%Ge sample after PLM+RTA at 950 °C for 60 s is also shown.

eV. After PLM-RTA at 950 °C for 10 s, the band gap of the 4%N+2%Ge sample (1.36 eV) becomes closer to that of GaAs compared to the band gap of the 2%N+2%Ge sample (1.29 eV). This can be explained since the average distances from a Ge atom to its nearest N_{As} are ~ 10.3 and 8.8 Å for the 2% ($x = 0.01$) and 4%N ($x = 0.016$) implanted samples, respectively. Therefore for a given amount of Ge in GaN_xAs_{1-x} (with Ge concentration higher than x) and the same annealing conditions, a larger fraction of N_{As} is passivated by Ge_{Ga} for samples with higher x .

Since N_{As} has a tendency to bind the fourth valence electron of Ge_{Ga} donors, we expect a reduction of the concentration of electrically active Ge donors. Figure 2 shows the electron concentration of the 2%N+2%Ge and 2%Ge samples followed by PLM-RTA for 10 s in the temperature range of 650–950 °C. For both samples the electron concentration approaches 10^{19} cm^{-3} after PLM. 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.^{18,19} The electron concentration exceeding the equilibrium n_{max} results from the highly non-equilibrium PLM process.

For the 2%Ge sample, thermal annealing after PLM drives the system toward equilibrium with an electron concentration of $\sim 1 \times 10^{18}$ cm^{-3} .^{20,21} The electron concentration of the 2%N+2%Ge samples, on the other hand, drops over two orders of magnitude to lower than 10^{17} cm^{-3} after RTA at temperatures higher than 650 °C. This is consistent with the passivation of Ge_{Ga} donors via the formation of $N_{As}-Ge_{Ga}$ pairs by Ge diffusion during RTA.

It has been widely recognized that N-induced modifications of the conduction band lead to a drastic reduction of the electron mobility in GaN_xAs_{1-x} .^{9,22} During the postimplantation treatment, it is expected that some of the Ge diffused into the substrate forming a layer of Ge-doped GaAs below the GaNAs:Ge layer. Hall effect measurements may be com-

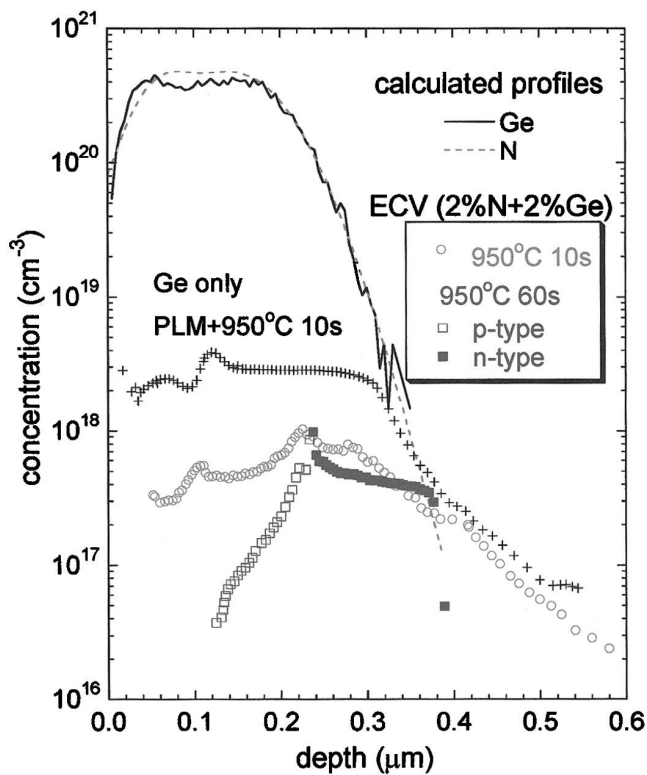


FIG. 3. Net donor (acceptor) concentration profiles obtained by electrochemical capacitance-voltage measurements of a GaAs sample implanted with 2%Ge followed by PLM-RTA at 950 °C for 10 s and the 2%N+2%Ge samples processed by PLM-RTA at 950 °C for 10 and 60 s. The calculated Ge and N atomic distributions are also shown.

plicated when such parallel layers with very different electrical behavior coexist in the sample.^{10,23}

Figure 3 shows three ECV profiles of the 2%Ge sample PLM-RTA at 950 °C for 10 s and the 2%N+2%Ge samples PLM-RTA at 950 °C for 10 and 60 s. The Ge and N atomic distributions calculated using the PROFILE code²⁴ are also shown. PLM-RTA at 950 °C for 10 s leads to a strong decrease in the donor concentration for the 2%N+2%Ge sample compared to the 2%Ge alone sample, consistent with the Hall effect measurements.

In the 2%N+2%Ge sample after RTA at 950 °C for 60 s, the top $\sim 0.25 \mu\text{m}$ layer is *p* type, followed by an *n*-type layer below. The *p*-*n* junction depth in this sample corresponds to the melt depth in GaAs for PLM using a fluence of 0.45 J/cm^2 .¹⁵ The *p*-type activity in the top layer in this sample is attributed to the complete passivation of Ge_{Ga} by N_{As} through the formation of $\text{Ge}_{\text{Ga}}-\text{N}_{\text{As}}$ nearest neighbor pairs in the laser melted region. The electrical activity of the small concentration of Ge_{As} acceptors is revealed once the Ge_{Ga} donors are passivated by N_{As} in the PLM region.

In conclusion, a comparison of the band gap and the electrical behavior in the GaAs samples implanted with Ge alone and with N+Ge followed by PLM-RTA shows that the formation of $\text{Ge}_{\text{Ga}}-\text{N}_{\text{As}}$ pairs results in *mutual passivation* of both species: it eliminates the electrical activity of Ge_{Ga} donors and deactivates N_{As} as the isovalent dopant. Consequently, Ge doping in $\text{GaN}_x\text{As}_{1-x}$ under equilibrium condi-

tions results in a highly resistive or *p*-type $\text{GaN}_x\text{As}_{1-x}$ layer with the fundamental band gap governed by a net "active" N, roughly equal to the total N content minus the Ge concentration. These results together with those in our previous report on the mutual passivation of Si and N in $\text{GaN}_x\text{As}_{1-x}$ clearly demonstrate the general nature of this phenomenon. The mutual passivation effect described here may be exploited for electrical isolation, band gap engineering, and quantum confinement.

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