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## Influence of Si–N complexes on the electronic properties of GaAsN alloys

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We have investigated the influence of Si–N complexes on the electronic properties of GaAsN alloys. The presence of Si–N complexes is suggested by a decrease in carrier concentration, n, with increasing N-composition, observed in GaAsN:Si films but not in modulation-doped heterostructures. In addition, for GaAsN:Te (GaAsN:Si), n increases substantially (minimally) with annealing-T, suggesting a competition between annealing-induced Si–N complex formation and a reduced concentration of N-related traps. Since Si-N complex formation is enhanced for GaAsN:Si growth with the  $(2 \times 4)$  reconstruction, which has limited group V sites for As–N exchange, the (Si-N)<sub>As</sub> interstitial pair is identified as the dominant Si-N complex. © 2009 American Institute of Physics. [DOI: 10.1063/1.3198207]

In GaAs, silicon can act as a donor or an acceptor, depending on its occupation of Ga or As lattice sites. Si is commonly used as an *n*-type dopant for GaAs-based materials and devices grown by molecular beam epitaxy and metalorganic chemical vapor deposition. However, (In)GaAsN alloys doped with Si often exhibit poor optical and electronic properties, with free carrier concentration, n, and electron mobility,  $\mu$ , significantly lower than those of (In)GaAs:Si.<sup>1,2</sup> On the other hand, for InGaAsN:Te alloys, the highest reported  $\mu$  is 2000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,<sup>3</sup> an order of magnitude higher than the typical  $\mu$  for (In)GaAsN:Si alloys.<sup>1</sup> Thus, the degraded electronic properties of (In)GaAsN:Si might be due to the interaction between N and Si donors, which form a Si-N complex, leading to a reduced electrical activity of Si in (In)GaAsN. However, there have been conflicting reports on the form of the Si-N complex,<sup>4,5</sup> and the influence of Si-N complexes on GaAsN electronic properties remains unknown

Rapid thermal annealing (RTA) has been reported to substantially increase the resistivity of GaAsN films doped with Si or Ge, with a negligible effect on those doped with Se.<sup>6</sup> A slight increase in the effective bandgap also was reported for GaAsN:Si, and was explained by the formation of substitutional Si-N pairs, Si<sub>Ga</sub>-N<sub>As</sub>, which inhibit the electronic activity of Si donors.<sup>6</sup> The calculations of Li et al.<sup>5</sup> predicted that Si<sub>Ga</sub>-N<sub>As</sub> binding in GaAsN is energetically favored, and that  $Si_{Ga}$ -N<sub>As</sub> formation pushes the shallow Si<sub>Ga</sub> donor levels deep into the bandgap. On the other hand, Janotti et al.<sup>4</sup> proposed a more energetically favorable interstitial pair,  $(Si-N)_{As}$ , which acts as a deep acceptor in *n*-type GaAsN. In this work, we report a N composition dependent decrease in n, which is observed in bulk-like films but not modulation-doped heterostructures. We also report an annealing-induced increase in n, whose magnitude depends on the *n*-type dopant species, suggesting a competition between annealing-induced Si-N complex formation and a reduced concentration of N-related carrier traps. The formation of Si-N complexes is enhanced for GaAsN:Si growth with the  $(2 \times 4)$  reconstruction, which has limited group V sites available for As-N exchange. Thus, we identify the interstitial Si–N pair,  $(Si-N)_{As}$ , as the dominant Si–N complex.

The  $GaAs_{1-x}N_x$  alloy films were grown on semiinsulating (001) GaAs substrates by molecular-beam epitaxy, using Ga, As<sub>2</sub>, Si or GaTe (for *n*-type doping), and an  $N_2$  rf plasma source. For bulk-like films, after an initial 250 nm thick GaAs buffer layer grown at 580 °C, 500 nm GaAsN films were grown with either Si or GaTe doping.<sup>7</sup> The Si and GaTe cell T were chosen to target equivalent n in GaAs:Te and GaAs:Si control films. Most GaAsN layers were grown at relatively low T (~400 °C), to avoid growth in the socalled "forbidden window," a specific T range where multilayer growth has been reported.<sup>8</sup> These films will be referred to as "low-T GaAsN:Si." Several GaAsN:Si layers were also grown at elevated substrate T, 580 °C, which will be referred to as "high-T GaAsN:Si." For modulation-doped heterostructures, after the buffer layer growth, a 50 nm thick GaAs(N) channel was grown at 400 °C. Next, a 5 min pause was used to ramp the substrate T to 580  $^{\circ}$ C, and layers of 1 nm GaAs, 20 nm undoped Al<sub>0.3</sub>Ga<sub>0.7</sub>As, 60 nm Si-doped Al<sub>0.3</sub>Ga<sub>0.7</sub>As, and 10 nm GaAs were then grown in succession. Since a two-dimensional electron gas (2DEG) forms at the channel-spacer interface, modulation-doped heterostructures with GaAs (GaAsN) as the channel layer will be referred to as "control 2DEG" ("nitride 2DEG").

For select samples, RTA was performed for 60s in the temperature range of 650-800 °C, using a GaAs proximity cap in N<sub>2</sub> ambient to prevent As out-diffusion. Highresolution x-ray rocking curves (XRC) were measured with a Bede D1 x-ray diffractometer using Cu  $K\alpha$ 1 radiation. Analysis of a series of (004) and (224) XRCs indicates that the average N composition in the GaAsN films remains unchanged after annealing up to 800 °C. Photoluminescence (PL) spectra were collected with a 488 nm Ar laser and an HR320 spectrometer equipped with a liquid nitrogen cooled InGaAs detector. Electron transport measurements were

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FIG. 1. (Color online) (a) Free carrier fraction as a function of N composition for GaAsN:Si bulk films. The free carrier fraction is defined as the ratio of free carrier concentration in the GaAsN film to that of the GaAs film doped with equivalent target doping concentration. The free carrier fractions of GaAsN:Si films are significantly lower than unity and decrease with increasing N composition. (b) The sheet carrier density,  $n_s$ , for several control and nitride 2DEGs, where  $n_s$  are similar for the control and dilute nitride 2DEGs at all three measurement-Ts.

implemented in both the Van der Pauw and Hall bar geometries, as described in Ref. 1. n and  $\mu$  were determined using resistivity and Hall measurements at room T and low T(1.6 and 4 K).

Figure 1 presents the free carrier fraction, defined as the ratio of  $n_{\text{GaAsN}}$  to that of  $n_{\text{GaAs}}$  with equivalent targeted doping concentration, for Si-doped bulk-like GaAsN films. As shown in Fig. 1(a), the free carrier fraction is significantly lower than unity, and decreases with increasing N composition, suggesting the presence of N-related charge trapping centers in the GaAsN:Si films. Figure 1(b) shows the sheet free carrier density,  $n_s$ , versus measurement-T for several control and nitride 2DEGs with equivalent targeted Si doping concentrations in the AlGaAs doping supply layer. In contrast to the bulk-like films,  $n_s$  are similar for the control and dilute nitride 2DEGs at all three measurement-Ts. In the bulk-like films, Si and N reside in the same layer; in 2DEGs, Si donors are spatially separated from the GaAsN channel layer, reducing the likelihood for formation of N-Si nearest neighbors. Since the electron trapping is observed in bulklike films but not in 2DEGs, the electron trapping is likely related to the presence of Si dopants in the vicinity of N atoms, presumably due to the formation of Si-N complexes.

The charge trapping effects of Si-N complexes are further investigated through a comparison of the electronic



FIG. 2. (Color online) Free carrier concentration, n, and electron mobility,  $\mu$ , for GaAs(N):Si and GaAs(N):Te as a function of annealing-T. With increasing annealing-T,  $\mu$  increases for both films, while n increases substantially (minimally) for GaAsN:Te (GaAsN:Si) films.

properties of Si and Te-doped GaAsN bulk-like films. Figure 2 shows n and  $\mu$  as a function of annealing-T for GaAsN:Si and GaAsN:Te bulk films, in comparison with GaAs:Si and GaAs:Te control films. As-grown GaAsN films exhibit significantly lower *n* and  $\mu$  than the GaAs control films, and GaAsN:Te films have slightly higher *n* than GaAsN:Si films. After annealing, minimal changes in n and  $\mu$  are observed for the GaAs control films. In GaAsN:Te, a substantial increase in both n and  $\mu$  with increasing annealing-T is observed. However, in GaAsN:Si films, we observed a similar increase of  $\mu$  as in the GaAsN:Te films, but only minimal increase of *n*. The charge trapping effect of Si–N complexes in GaAsN:Si is also evident in the optical properties. Figure 3 presents PL spectra for as-grown and annealed GaAsN:Te and GaAsN:Si films with equivalent N compositions. For the as-grown films, the near-bandedge PL peak emission intensity of GaAsN:Te is 1.5 times higher than that of the GaAsN:Si film. For both films, the full width at half maximum (FWHM) is similar and reduced by  $\sim 15\%$  following annealing. However, the near bandedge PL emission intensity exhibits 20-fold (6-fold) increases for GaAsN:Te (GaAsN:Si). Thus, the annealing-induced increase in PL efficiency is remarkably larger for GaAsN:Te in comparison with that of GaAsN:Si.

The insignificant annealing-induced increase in *n* and PL emission intensity of GaAsN:Si provides additional evidence for the charge trapping effect of Si–N complexes. For GaAsN:Te, annealing leads to higher *n* and  $\mu$ , presumably due to the reduction in N-related free carrier traps, such as N interstitials.<sup>9–13</sup> In case of GaAsN:Si, the annealing-induced reduction in electron trapping is presumably balanced by the



FIG. 3. (Color online) PL spectra for as grown and annealed GaAsN:Si and GaAsN:Te films. For the as-grown films, the near-bandedge PL peak emission intensity of GaAsN:Te is 1.5 times higher than that of the GaAsN:Si film. For both films, the FWHM are similar and are reduced  $\sim 15\%$  following annealing. However, the PL emission intensity exhibits 20-fold (6-fold) increases for GaAsN:Te (GaAsN:Si) after annealing.

enhanced formation of Si–N pairs. Calculations suggest that Si–N complex formation is energetically favorable in the GaAsN:Si system.<sup>4,5</sup> In addition, the diffusion length of Si in GaAs at 750 °C for 60 s is estimated to be 1.5 nm,<sup>14</sup> comparable to the average distance between N atoms in GaAsN with 1%–2% N (1.3–1.6 nm, assuming random distribution). Thus, annealing induces Si diffusion to N atoms, and the consequent formation of Si–N complexes. Similar effects have not been predicted or reported for group VI-N complexes.

Table I compares *n* and  $\mu$  for low and high-*T* GaAs<sub>1-x</sub>N<sub>x</sub>:Si films with *x*=0.005–0.02. The low-*T* GaAsN:Si films are *n*-type with *n*~2 to 5×10<sup>17</sup> cm<sup>-3</sup> and  $\mu$ ~200 cm<sup>2</sup>/V s, consistent with literature reports.<sup>1,2</sup> However, for high-*T* GaAsN films, the degenerately Si-doped GaAsN films are observed to be slightly *p*-type, with hole concentrations ~1×10<sup>15</sup> cm<sup>-3</sup>. Although Si is amphoteric in GaAs, within the high-*T* GaAsN:Si films, Si is expected to predominantly occupy Ga sites, acting as a donor.<sup>15</sup> Indeed, for the high-*T* GaAs:Si films, *n*-type conductivity is observed, as shown in Table I. For high-*T* GaAsN:Si, most Si are presumably electrically inactive due to the formation of Si–N complexes in either Si<sub>Ga</sub>–N<sub>As</sub> or (Si–N)<sub>As</sub> form, while a negligible fraction of Si atoms replacing As sites act as acceptors, leading to *p*-type conductivity.

During the growth of the GaAsN at 400 and 580 °C, the surface reconstructions are  $(2 \times 1)$  and  $(2 \times 4)$ ,

TABLE I. Free carrier concentration, n, and electron mobility,  $\mu$ , for asgrown low-*T* GaAsN:Si and high-*T* GaAsN:Si films with various N compositions N%.

Low-T GaAsN:Si			High-T GaAs(N):Si		
N (%)	<i>n</i> (cm <sup>-3</sup> )	$\mu$ (cm <sup>2</sup> /V s)	N (%)	<i>n</i> (cm <sup>-3</sup> )	$\mu$ (cm <sup>2</sup> /V s)
1.0	$3.1 \times 10^{17} (n)$	230	0	$1.3 \times 10^{18} (n)$	2000
1.3	$2.7 \times 10^{17} (n)$	192	0.6	$3.0 \times 10^{15} (p)$	130
1.9	$1.5 \times 10^{17} (n)$	161	1.0	$6.5 \times 10^{15} (p)$	246

respectively.<sup>16,17</sup> It has been reported that the  $(2 \times 4)$  reconstruction leads to a greater fraction of N incorporated interstitially, since it has fewer group V sites per unit area than  $(2 \times 1)$  surfaces.<sup>18</sup> Similarly,  $(N-Si)_{As}$  are more likely to form on the  $(2 \times 4)$  reconstructed surface. On the other hand, for the  $(2 \times 1)$  surface, due to the high areal density of group V sites, N and Si atoms may more effectively incorporate substitutionally and form Si<sub>Ga</sub>–N<sub>As</sub> bonds. Thus, the enhanced formation of Si–N pairs for high-*T* GaAsN:Si grown with a  $(2 \times 4)$  reconstruction suggests that  $(Si–N)_{As}$  is the most likely form of Si–N complexes in GaAsN:Si.

In summary, we have investigated the influence of Si–N complexes on the electronic properties of GaAsN alloys. The presence of Si–N complexes is suggested by a N-composition dependent decrease in n, which is observed in bulk-like films but not modulation-doped heterostructures. In addition, for GaAsN:Te (GaAsN:Si), n increases substantially (minimally) with annealing-T, suggesting a competition between annealing-induced Si–N complex formation and a reduced concentration of N-related traps. Since the formation of Si–N complexes is enhanced for GaAsN:Si growth with (2×4) reconstruction, which has limited group V sites available for As–N exchange, the interstitial Si–N pair, (Si–N)<sub>As</sub>, is identified as the dominant Si–N complex.

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