

## Scaling of band-gap reduction in heavily nitrogen doped GaAs

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The band-gap reduction caused by heavy impurity doping in a semiconductor can be written as  $\delta E_g(x) \propto x^\alpha$ , where  $x$  is the mole fraction of the impurities, and  $\alpha$  is the scaling exponent. It is well known that  $\alpha = 1/3$  for  $n$ - or  $p$ -type (i.e., charged) doping, where the isolated impurity center forms bound states. In contrast, the incorporation of isoelectronic impurities into a semiconductor commonly results in alloy formation. In this case, the impurities do not form any bound states (with small cluster sizes), and one finds that  $\alpha = 1$ . However, for the case of nitrogen doping in GaAs, although isolated nitrogen impurities do not form bound states, nitrogen impurity pairs do, and we find  $\alpha = 2/3$ . The scaling rule revealed here demonstrates that the dominant mechanism for the large band-gap reduction observed in  $\text{GaAs}_{1-x}\text{N}_x$  is the formation of an impurity band associated with nitrogen pair bound states.

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It is well known that heavy doping of  $n$ -type or  $p$ -type impurities in semiconductors causes a band-gap reduction, as a consequence of impurity band formation.<sup>1,2</sup> A similar effect is expected to occur for the doping of isoelectronic impurities in semiconductors, when the isoelectronic impurity is capable of introducing bound states in the dilute limit. However, the band-gap reduction induced by heavy isoelectronic doping has received much less attention until recently. Although, the band-gap reduction was reported in heavily Te-doped CdS at least 35 years ago,<sup>3</sup> it only started to attract a great deal of experimental and theoretical attention in the past few years, after the large band-gap reduction was observed in heavily nitrogen doped GaAs.<sup>4</sup>

For  $n$ - or  $p$ -type doped semiconductors, the band-gap reduction,  $\delta E_g$ , has been found to have an approximate  $n^{1/3}$  or  $x^{1/3}$  dependence both experimentally and theoretically,<sup>2,5</sup> where  $n$  is the impurity concentration and  $x$  is the mole fraction of the impurities. The underlying physics for the  $x^{1/3}$  scaling rule is simply that the bandwidth of the impurity band or the band-gap reduction is proportional to the electron-electron interaction, and this interaction is inversely proportional to the average impurity separation.<sup>2</sup>

The band-gap reduction in heavy nitrogen doped GaAs or  $\text{GaAs}_{1-x}\text{N}_x$  with  $x < 5\%$  has been measured by various techniques: photoluminescence and absorption,<sup>4</sup> electroreflectance,<sup>6</sup> photoreflectance.<sup>7</sup> Considerable scatters exist among a large number of experimental data from different research groups, due to the inconsistency in the determination of the nitrogen concentration, sample growth conditions, as well as experimental techniques. The functional form of  $\delta E_g(x)$  was not specifically given for most published results. Only in limited cases, the data were empirically fit to either a quadratic function of a  $x - bx^2$  with  $a$  and  $b > 0$ ,<sup>6</sup> or a “two-level-repulsion” model<sup>8</sup> that in fact has the same type of dependence (when expanded to the quadratic term).<sup>9</sup> The significance of these experimental data lies in the fact that  $\delta E_g(x)$  has a sublinear  $x$  dependence. Theoretical calculations have been able to give numerical results for  $\delta E_g(x)$  to

the correct order of magnitude, but the values have been changing during the years<sup>10,11</sup> and differ from one method to the other.<sup>11,12</sup> Other phenomenological models have also been developed to explain the band-gap reduction as well as the behavior of a nitrogen related resonant level. These include a modified two-level-repulsion model,<sup>13</sup> and a multi-valley coupling model.<sup>14</sup> It is not at all a surprise that these models were able to fit the relatively simple trend of experimental data reasonably well, considering the number of fitting parameters included. We have recently used the impurity band model to explain the  $x$  dependence of the conduction band effective mass of  $\text{GaAs}_{1-x}\text{N}_x$ .<sup>15</sup> The question we would like to pose is: does the isoelectronic impurity system share any similarity with charged doping systems in terms of the scaling rule for  $\delta E_g(x)$ ? Besides the obvious difference between charged and isoelectronic doping, a major difference is that the isolated nitrogen impurity does not have a bound state,<sup>16,17</sup> and only nitrogen pairs give rise to bound states.<sup>18,19</sup>

A relevant situation arises when the incorporation of isoelectronic impurities is viewed as forming an alloy. As an example, for  $\text{Ga}_{1-x}\text{In}_x\text{As}$ , neither an isolated In nor a pair of In has been found to form any bound states,<sup>20</sup> and the band-gap reduction has been shown to have a linear dependence at least in the region of  $0.03\% < x < 14\%$ .<sup>20,21</sup> Only a fairly large cluster of InAs, usually referred to as a quantum dot, is able to form bound states in GaAs.<sup>22</sup> For the alloys belonging to this category, the density of the large clusters is diminishingly small in the dilute alloy region, and so they can only contribute to the density of states around the tail of the alloy band gap.

The aim of this work is to investigate the scaling rule for the band-gap reduction for a heavily isoelectronic impurity doped semiconductor in which the isoelectronic impurities are able to form bound states with a very small cluster size, making it inappropriate to be viewed as an alloy. GaAs:N is taken as an example, where the dominant nitrogen pair bound state is found to be 7 meV below the GaAs band

gap.<sup>18</sup> We will compare our experimental results with a few theoretical calculations,<sup>10–12</sup> emphasizing the scaling rule rather than the numerical values.

All the  $\text{GaAs}_{1-x}\text{N}_x$  samples used in this study were grown by gas-source molecular beam epitaxy (MBE), using a radio frequency nitrogen radical beam source, on semi-insulating GaAs substrates. For samples with  $x < 1\%$ , the epilayer thickness is 4000 Å with a 2000 Å GaAs buffer; for samples with  $x > 1\%$ , the epilayer thickness is 1000 Å with a 2500 Å GaAs buffer and 250 Å cap. The N concentrations were determined by high-resolution x-ray rocking curve (XRC) measurement and theoretical dynamical simulations.  $\text{GaAs}_{1-x}\text{N}_x$  epilayers were confirmed as being coherently strained to the substrates, by asymmetric {511} XRC measurements.<sup>23,24</sup> Electroreflectance spectra were measured at room temperature in contactless mode.<sup>25</sup>

Figure 1 shows electro-reflectance spectra of typical  $\text{GaAs}_{1-x}\text{N}_x$  samples. For a few low nitrogen concentration samples, broadened Franz-Keldysh oscillations (FKOs) can be observed.<sup>6</sup> Thus, the data were fit to a FKO lineshape function with a broadening parameter.<sup>6,25</sup> For the other samples with relatively high nitrogen concentrations, the data were fit to a third order derivative lineshape function.<sup>26</sup> The epitaxial strain induced valence-band splitting can be seen for samples with  $x = 2.3\%$  and 3.3% at room temperature, with the light hole like state being the lower energy state. However, at 80 K, the splitting has been observed for all the samples with  $x \geq 1.1\%$ .<sup>24</sup> Thus, we have fit the room temperature data for  $x \geq 1.1\%$  samples with a lineshape function for two critical points.

Figure 2 shows the log-log plots of the band-gap reduction as a function of doping level for three typical systems: GaAs:Si,<sup>27</sup> GaAs:N, and GaAs:In.<sup>20</sup> For high concentration samples, the results for both the light hole and heavy hole are shown. Although the band-gap reduction in GaAs:N is found to be much larger than that for GaAs:In for the same doping level, which has led to the popular view of  $\text{GaAs}_{1-x}\text{N}_x$  being an abnormal alloy with a giant band-gap reduction or giant bowing, it is in fact significantly smaller than that for GaAs:Si. This qualitative difference can be easily understood from the perspective of impurity band formation in terms of two major factors:<sup>15</sup> the long-range Coulomb interaction for the donor versus the short-range potential for the isoelectronic center, and the bound states density being proportional to  $x$  for the donor versus  $x^2$  for the nitrogen pair. It thus appears unnatural to describe the behavior of heavily nitrogen doped GaAs within the framework of conventional alloys. From simple reasoning, the fact that the band-gap reduction or intercenter interaction for an impurity band is inversely proportional to the average separation of the impurity centers leads one to expect that the band-gap reduction in GaAs:N should have a scaling rule like  $\delta E_g(x) \propto x^{2/3}$ . Indeed, as shown in Fig. 2, the line drawn through the data with a slope of 2/3 agrees very well with the data. In fact, a fit to the  $\delta E_g(x) = \beta x^\alpha$  dependence yields  $\alpha = 0.667 \pm 0.02$  and  $\beta = 4.1 \pm 0.3$ , where  $x$  is in mole fraction and  $\delta E_g(x)$  in eV. Although this result agrees perfectly with simple physical intuition, it actually has included an additional effect: the modification of band gap caused by epitaxial strain. The con-

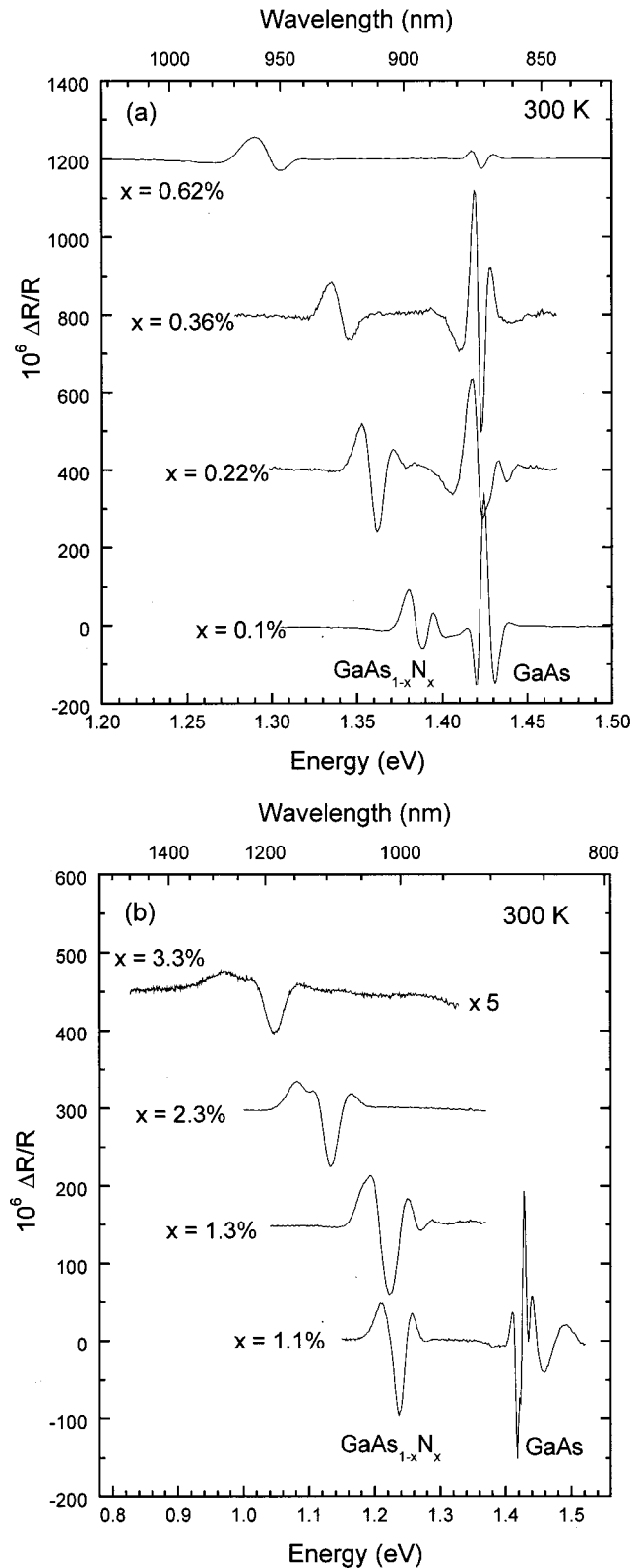


FIG. 1. Electroreflectance spectra of  $\text{GaAs}_{1-x}\text{N}_x$ : (a) for  $x < 1\%$  and (b) for  $x > 1\%$ .

tribution of this effect can be estimated with the known typical deformation potential for the nitrogen pair state ( $a_{\text{NN}} \sim 2.6$  eV)<sup>18</sup> and valence band shear deformation potential ( $b \sim 2$  eV). With the contribution of the strain removed, we

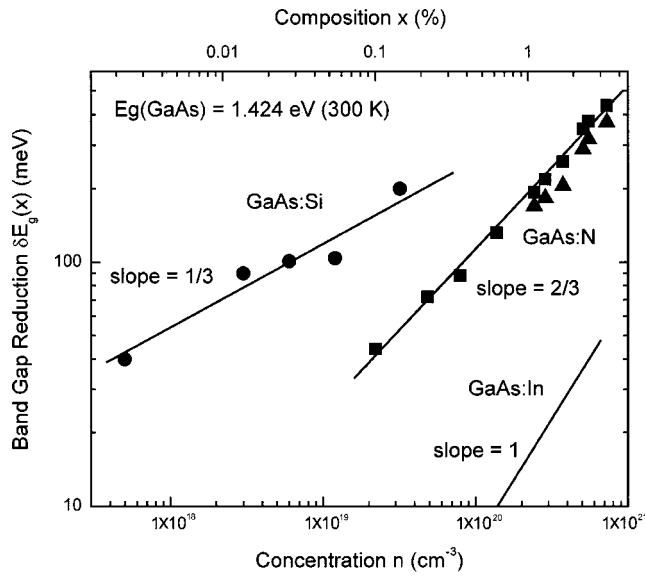


FIG. 2. A comparison of the band-gap reduction as a function of impurity concentration or composition for three typical systems. Data for GaAs Si ( $n$ -type doping) are from Yao and Compaan's paper (Ref. 27), data for GaAs:In (alloy) are Laurenti *et al.*'s (Ref. 20), and data for GaAs:N (isoelectronic doping) are the results of this work. Symbol  $\blacksquare$  indicates the band edge or light-hole band edge, symbol  $\blacktriangle$  indicates the heavy-hole band edge.

get  $\alpha = 0.645$ .

Figure 3 shows the comparison of our data with another set of experimental data that were obtained from a set of MBE samples which appear to have similar sample quality as ours.<sup>23</sup> As one can see, the two sets of data agree quite well in general. Since the band gaps in Ref. 23 were determined by fitting the linear transmission data near the band edge, a larger uncertainty would be expected. Also, the valence-band splitting was not resolved in Ref. 23. A fitting

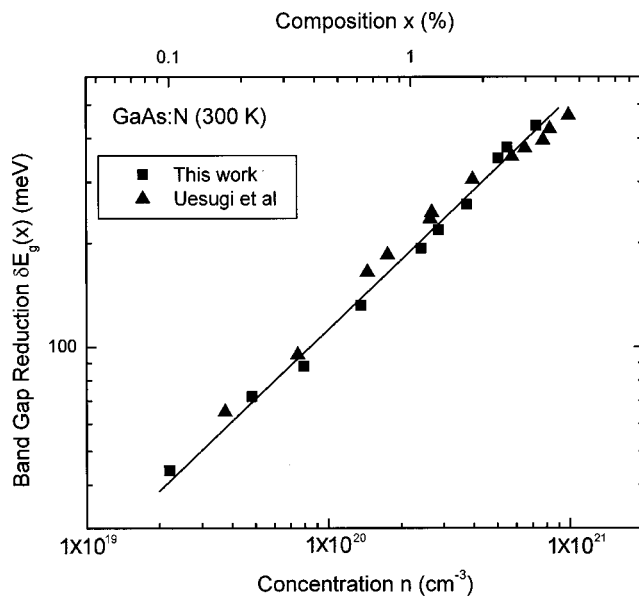


FIG. 3. A comparison of our data with those of Uesugi *et al.* (Ref. 23).

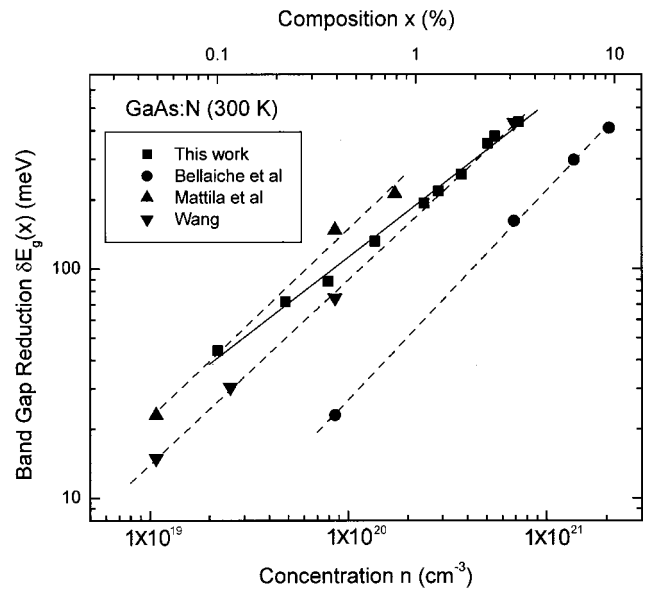


FIG. 4. A comparison of our experimental data with those of theoretical calculations of Bellaiche *et al.* (Ref. 10), Mattila *et al.* (Ref. 11) and Wang (Ref. 12). Solid and dashed lines are fitting curves.

to  $\Delta E_g(x) \propto x^\alpha$  gives  $\alpha = 0.60$ , which agrees reasonably well with our result. This comparison indicates that the scaling rule we have observed is indeed intrinsic to this system.

Figure 4 shows the comparison of our data with a few theoretical calculations which either used the same technique (the empirical pseudopotential method) but with different pseudopotentials,<sup>10,11</sup> or a different technique (a modified local density approximation method).<sup>12</sup> As shown in Fig. 4, despite the fairly large deviation in the absolute values of the band-gap reduction, being either larger or smaller than that of the experimental result, the slopes,  $\alpha = d \log[\Delta E_g(x)]/d \log[x]$ , of the three theoretical results appear to be quite similar, and are always significantly larger than that of the experimental result. The values obtained are  $\alpha = 0.914, 0.824,$  and  $0.806$  for Ref. 10, Ref. 12, and Ref. 11, respectively. In both Ref. 11 and Ref. 12, nitrogen atoms were assumed to be regularly distributed in GaAs, i.e., an ordered structure which excluded any pairing or clustering that would be expected for a random structure. It is thus understandable that these  $\alpha$  values are quite close to 1, since only the interaction of the isolated nitrogen centers, which form resonant states in the conduction band, was taken into account. When one weakens the perturbation of nitrogen impurities to the host band structure, then just as for the case of conventional isovalent substitution, the scaling exponent is expected to be closer to that of a conventional alloy ( $\alpha = 1$ ), which is evidenced by the trend of the three calculations: the smaller the band-gap reduction or the weaker the effective nitrogen perturbation, the larger the value of  $\alpha$  obtained.

A relevant situation occurs in GaP:N, where the nitrogen doping in GaP introduces a series of bound states with a spread of  $\sim 140$  meV below the indirect band gap.<sup>28</sup> As has been demonstrated recently, the formation of the nitrogen

impurity band follows the sequence of increasing binding energy: from the isolated N center to the deepest  $NN_1$  center.<sup>29</sup> Thus, the scaling rule for the band-gap reduction will not be as simple as  $x^{2/3}$  or  $x^{1/3}$  in general. Although an accurate determination of  $\delta E_g(x)$  is yet to be done, a fitting of the band gaps determined by the transmission measurements for  $0.9\% \leq x \leq 3.1\%$  to  $\delta E_g(x) \propto x^\alpha$  results  $\alpha = 0.55$ ,<sup>30</sup> which is comparable to the result for GaAs:N. We would like to emphasize that the GaAs:N system provides us a unique opportunity to make a comparison between a charged and an iso-electronic doping system.

To summarize, for  $GaAs_{1-x}N_x$  with dilute nitrogen, the band-gap reduction induced by the heavy nitrogen doping is

found to follow the scaling rule of  $\delta E_g(x) \propto x^\alpha$ , with  $\alpha \approx 2/3$ . A comparison of experimentally obtained values for the scaling exponent  $\alpha$  with those obtained theoretically confirms the key role played by nitrogen pair bound states in the formation of an impurity band that leads to the large band-gap reduction observed for this material.

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