



Overcoming limitations in semiconductor alloy design

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(Received 30 April 2001)

The phenomenon of giant band gap 'bowing' recently observed in several III-V dilute nitride alloys is promising for increasing the flexibility in choice of semiconductor band gaps available for specified lattice constants. However, the poor electrical transport properties that these materials exhibit seriously limit their usefulness. It is proposed that these materials behave as heavily nitrogen-doped semiconductors rather than dilute nitride alloys and that the abnormal or irregular alloy behavior is associated with impurity band formation that manifests itself in the giant bowing and poor transport properties. The potential for regularizing the alloy behavior using isoelectronic co-doping is discussed.

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Key words: isoelectronic impurity, co-doping, GaAs:N:Bi, GaP:N:Bi.

1. Introduction

Semiconductor heterostructures constitute the building blocks of several electronic and photonic devices such as solar cells, diode lasers, light emitting diodes (LEDs) and heterojunction bi-polar transistors. The heterostructure components and their stacking geometry are often utilized for tailoring features for improving device performance. Although the choice of semiconductors for synthesizing a heterostructure for a particular device application is guided by the specific electrical or optical design requirements, this choice is also guided by the ability to grow the required stack of semiconductor layers epitaxially. Thus, the semiconductor lattice size in addition to its electronic bandstructure is an important criterion for heterostructure design. The requirement of a specified bandstructure feature and lattice size is most often fulfilled by the use of substitutional alloys, thus circumventing the discrete and finite repertoire of available elemental and compound semiconductors. They have thus been the subject of extensive studies as regards their alloy thermodynamics and electronic properties. Recently, the phenomenon of giant band gap 'bowing' that has been observed in several III-V dilute nitride alloys offers the exciting promise of increasing the flexibility in choice of semiconductor band gaps available with specified lattice constants. However, the poor electrical transport properties that these materials exhibit seriously limit their usefulness. In this paper, these limitations will be discussed, with suggestions for overcoming them.

2. Background

The lattice size of a substitutional semiconductor alloy $A_{1-x}B_xC$ has experimentally been found to be well approximated by the concentration weighted average of that of its constituents AC and BC, which is usually referred to as Vegard's rule or law [1]. Also, the band gap is found to be close to, but generally lower than, the

concentration-weighted average of that of the constituent compounds and this deviation is well described in terms of a bowing coefficient which is usually quite small (about 1 eV) [2]. Thus, the band gap and lattice size of the alloy covers the range of values between those for the two end point constituent compounds provided that they are not immiscible in this range. But, in spite of the variety of band gaps and lattice sizes that are made possible by alloying semiconductors, there have been many situations encountered over the past few decades where, although it is possible to obtain an alloy having the desired lattice constant, the alloy does not have the required band gap. Such frustrations impose severe penalties in device design. An example of this is the technologically important field of vertical cavity surface emitting lasers (VCSELs) used for fiber optic communications [3]. The difficulty with Bragg mirror stacks of quaternary alloys grown on InP substrates lies in their poor thermal conductivity. Although high-reflectivity AlAs/GaAs Bragg mirror stacks can readily be grown on GaAs substrates, it is not possible to find an alloy for the active region of the VCSEL with a band gap near 0.8 or 0.95 eV and which is lattice matched to GaAs. To grow such VCSELs, it has thus been necessary to resort to complicated techniques which often involve 'lift-off' and 'fusion bonding' steps in the laser fabrication process [3]. Another alloy constraint example is the quadruple junction solar cell where the optimal heterostructure for realizing a 40% efficient solar cell would be comprised of light absorbing semiconductor active regions grown epitaxially with the sequence of band gaps 0.67/1.05/1.42/1.9 eV on a Ge substrate [4]. GaInP₂, GaAs and Ge are ideally suited lattice-matched semiconductors for the top, next to top, and bottom cells, but there existed no material lattice matched to GaAs with a band gap of 1.05 eV until quite recently [4].

3. Recent progress and new perspectives

3.1. Giant bandgap 'bowing' phenomena

About a decade ago, Weyers *et al.* [5] succeeded in incorporating almost 1% N into GaAs using OMVPE (organo-metallic vapor phase epitaxy) techniques and observed a surprising lowering of the band gap by about 140 meV, contrary to what is expected by Vegard's rule. This rekindled interest in a subject that is over three decades old: namely, the N isoelectronic trap. Research from the 1960s to the 1980s had established that N behaves as an isoelectronic trap in GaP and GaAs [6–8]. Thermodynamic calculations [9] predicted that N was insoluble in both these materials and in the early work on bulk crystals and LPE material it was only possible to achieve N doping levels less than 10¹⁹ which allowed for the identification of N-induced trap levels in these semiconductors [6–8], as shown in Fig. 1. The ability to incorporate over an order of magnitude more N (>1%) into these semiconductors is attributed to the use of non-equilibrium growth techniques such as OMVPE and MBE (molecular beam epitaxy). The experiments of Weyers *et al.* were soon repeated by several groups around the world, confirming that the band gap of GaAs was lowered by about 180 meV with just 1% of N incorporation into GaAs, and by 400 meV with just 3% N [10]. GaAs_{1-x}N_x began to be viewed as an alloy and the anomalous large lowering of its band gap to be described as a giant band gap 'bowing' (the bowing parameter varies with *x* but is ~20 eV) [11]. These results were followed by a flurry of research activity after the suggestion by Kondow *et al.* [12] about the possibility of realizing 1.3 μm lasers using GaAs_{1-x}N_x active regions grown on GaAs substrates. At around the same time it became evident that GaAs_{1-x}N_x could also be used to provide the 1.05 eV band gap material lattice matched to GaAs for realizing the 40% efficient quadruple junction solar cell and several research groups raced towards this goal [4]. It thus appeared that the anomalous and giant 'bowing' of the band gap in GaAs_{1-x}N_x offered a way out of the semiconductor alloy constraints that limited the design of some technologically important devices.

Soon it was evident, however, that the giant band gap 'bowing' in GaAs_{1-x}N_x came with a caveat. The electron mobilities in this material were severely degraded and several efforts to improve this using rapid thermal annealing resulted only in marginal improvements, thus dampening the initial excitement of using this material for both solar cells and lasers [13]. In the remainder of this paper, the exciting research during

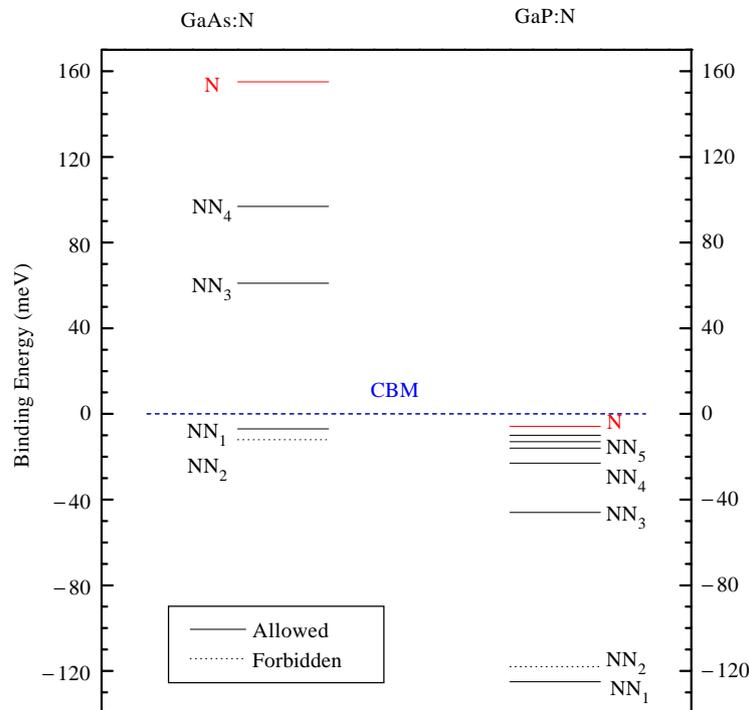


Fig. 1. Nitrogen-induced trap levels in GaAs and GaP.

the past few years on understanding the physical mechanisms underlying the phenomenon of the anomalous giant band gap ‘bowing’ will be discussed from the viewpoint of determining whether the limitations of the $\text{GaAs}_{1-x}\text{N}_x$ system can be overcome.

3.2. Heavy doping and impurity bands

Using photoluminescence studies at low temperatures and high pressures on GaAs samples doped with $<0.01\%$ N, Wolford *et al.* [7] and Liu *et al.* [8] determined that the isolated N impurity forms a resonant level 150–180 meV above the conduction band edge of GaAs. Almost a decade later, in an effort to understand the origin of the giant ‘bowing’ phenomenon, Perkins *et al.* [14] used electro-modulated reflectivity studies to investigate the giant ‘bowing’ phenomenon in heavily N-doped GaAs, and directly observed a level (denoted as E_+) above the conduction band edge whose existence was inferred by Shan *et al.* [15] using photoreflectance studies under high pressure. Employing a simple two-level repulsion model, Shan *et al.* assumed that the giant band gap ‘bowing’ in $\text{GaAs}_{1-x}\text{N}_x$ arose from level repulsion between the isolated N-resonant level and the GaAs conduction band edge. But soon thereafter, Zhang *et al.* [16] demonstrated a very unusual behavior for the conduction band effective mass in GaAs:N. Since the carrier lifetimes in GaAs:N are too short to be able to measure the effective mass with conventional techniques that involve cyclotron resonance, this was determined by fabricating GaAs/GaAs:N quantum wells with several well widths for each value of N doping, and inferring the effective mass from the confinement-induced shifts in the QW ground state transition energies. The results obtained revealed that the conduction band effective mass exhibited a very abrupt increase by almost an order of magnitude on going from 0.01% N to 1% N and then gradually decreased as the N doping approached a value of about 3%, as shown in Fig. 2. This surprising be-

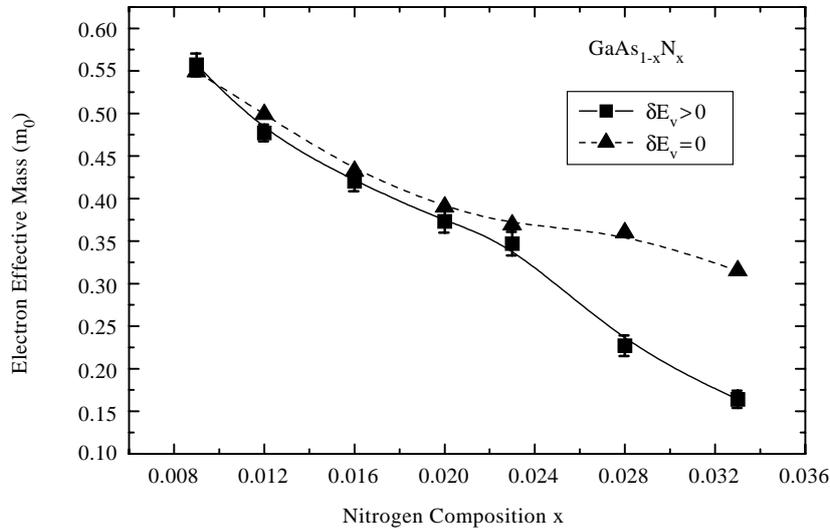


Fig. 2. Variation of conduction band effective mass in GaAs:N (from [16]).

havior was a clue to the presence of an impurity band in GaAs:N induced by the heavy N doping. Subsequent low-temperature photoluminescence and selective excitation of photoluminescence studies by Zhang *et al.* [17] showed the evolution of the discrete N trap levels in GaAs into a N-induced impurity band. Recently, peculiarities of the N-resonant levels in GaAs:N have been dramatically demonstrated in resonant Raman scattering studies by Cheong *et al.* [18].

The physics of the N isoelectronic trap in GaP and GaAs_xP_{1-x} was extensively studied in the 1960s and 1970s because of the potential for use of these materials for LEDs. However, because of the N-solubility problem analogous to that for GaAs:N, the doping levels studied were limited to <0.1%. This work has recently been reviewed by Zhang and Ge [19]. By the early 1990s it became possible to incorporate much larger amounts of N into GaP using non-equilibrium growth techniques such as MBE, and Baillargeon *et al.* [20] and Liu *et al.* [21] revealed the existence of a large redshift of the absorption edge or a band gap reduction in GaP doped with about 1% N, suggesting the formation of a N-induced impurity band in this material as well. Almost a decade later, research by Xin *et al.* [22] showed that the absorption edge in GaP:N for N concentrations exceeding 1% appeared to have the energy dependence characteristic of a direct gap semiconductor ($\sqrt{E - E_g}$ dependence), renewing interest in this material for LED technologies. The evolution of the conduction band edge in GaP:N from the merger of bands formed from the N trap levels in this material is quite apparent in Fig. 3.

As mentioned earlier, the caveat with both the N-doped GaAs and GaP was the poor carrier mobilities. Both these are a natural consequence of the peculiar nature of the conduction band minimum in GaAs:N and GaP:N. The conduction band edge in these N-doped materials evolves out of the formation of an impurity band. As the conduction band effective mass studies in GaAs have indicated, the increase in curvature (see Fig. 4) of the impurity band with increased N doping causes the effective mass to decrease from its abnormally high value in the flat impurity band that is characteristic of low N doping concentrations, and that is reminiscent of hopping transport between impurity levels that overlap only weakly. The impurity bands which evolve from the NN trap levels broaden with heavy N doping and merge with the bottom of the conduction band, thus giving rise to the phenomenon of giant band gap 'bowing'. A question that thus emerges in this unusual situation is whether one should view GaAs_{1-x}N_x as an abnormal alloy or rather as a heavily doped semiconductor GaAs:N [16, 17, 23].

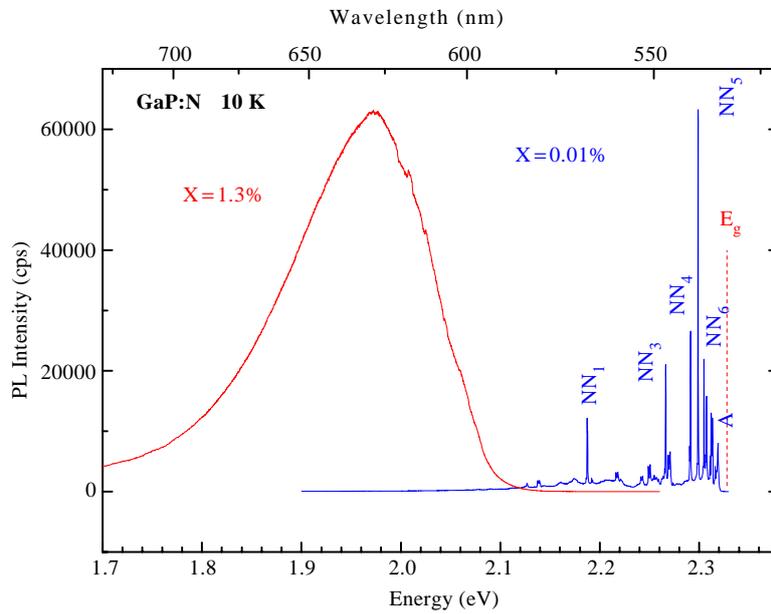


Fig. 3. Low-temperature photoluminescence spectra showing evolution of conduction band edge in GaP from nitrogen-induced trap levels. (from Yong Zhang *et al.*, Phys. Rev. **B62**, 4493 (2000)).

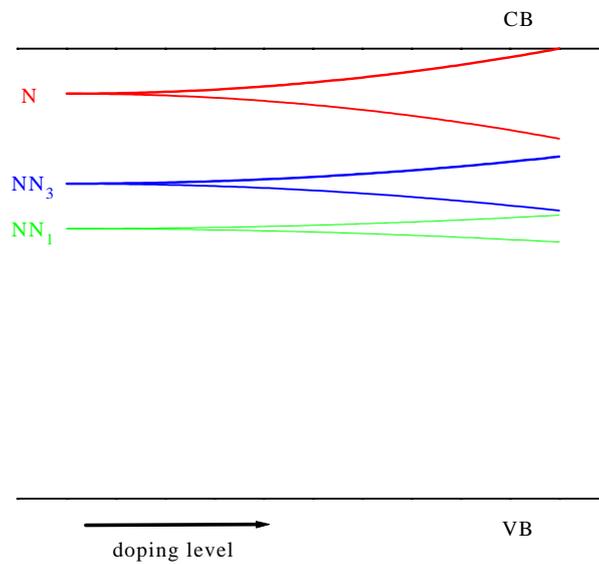


Fig. 4. Schematic illustration of the evolution of impurity bands from different N-bound states in GaP.

3.3. Irregular alloys

When two semiconductors AC and BC are mixed, this typically results in the formation of a disordered alloy $A_xB_{1-x}C$ if the physical properties of A and B do not differ greatly from each other, and in that case

the properties of the alloy change smoothly from those of BC to those of AC as x is changed from 0 to 1. Such is the case for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$, for example. The semiconductors AC and BC must, of course, be miscible for a range of x , which is mostly true when the properties of A and B do not differ greatly. This contrasts with the n- or p-type charge doping of semiconductors, where the solubility of the donor or acceptor in the host is limited (for example, as for GaAs:Si and GaAs:Zn). In some situations the differences between alloys and doped semiconductors is not so clear. Heavy n-type doping of the order of 10^{19} (or 0.1% dopant concentration) causes a nearly 200 meV band gap reduction in GaAs which results from impurity band formation [24], whereas a 0.1% N doping in GaAs results in a band gap reduction of less than 50 meV [10]. However, one does not speak of GaAs:Si as an alloy and so the question arises as to why GaAs:N is being referred to as a $\text{GaAs}_{1-x}\text{N}_x$ alloy. The reason for this is that N is an isoelectronic impurity in III–V alloys and thus does not result in charge doping. There are two types of isoelectronic impurities: those that do not give rise to bound states (such as GaAs:Al or GaAs:In) and those that do give rise to bound states in the host. If the isoelectronic impurity generates bound states located in the band gap (either through isolated centers or pairs) such as is the case for GaAs:N and GaP:N, then with heavy doping the impurity levels associated with these bound states evolve into impurity bands that broaden and merge with the conduction band edge, and this merger gets manifested as a giant band gap ‘bowing’. The formation of an impurity band in heavily n- or p-type doped semiconductors has been well studied, together with its associated Mott metal–insulator transition [25]. Although the formation of impurity bands in heavily isoelectronically doped alloys like GaAs:N and GaP:N is relatively new, the phenomenon was actually observed in the $\text{CdS}_{1-x}\text{Te}_x$ system for concentrations $x > 10^{-4}$ almost 35 years ago [26]. More insight into the common physical relationships between alloys, heavily charge-doped semiconductors and heavily isoelectronically doped semiconductors is provided by a scaling rule recently observed by Zhang *et al.* [23]. As shown in Fig. 5, the band gap reduction in a doped semiconductor is observed to follow a scaling rule:

$$\delta E_g(x) = \beta x^\alpha \quad (1)$$

where x is the mole fraction of the dopant. For alloys like $\text{In}_x\text{Ga}_{1-x}\text{As}$, the scaling exponent α is very close to 1. For heavily doped n-type semiconductors, $\alpha \approx 1/3$. The physics underlying 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 proportional to the average impurity separation. For isoelectronically doped GaAs:N the scaling exponent $\alpha \approx 2/3$. The significance of the scaling exponent α being close to $2/3$ lies in that it confirms that the band gap reduction in heavily doped GaAs:N is primarily due to the formation of an impurity band associated with nitrogen pair bound states. This is the primary reason for the irregular or abnormal behavior of these alloys, as will be discussed below.

3.4. Physics of isoelectronic traps

Because of the difference in valence between the dopant atom and the host atom that it replaces, a non-isoelectronic donor (acceptor) atom donates an electron (hole) to the conduction (valence) band of the host crystal. The Coulomb potential of the resulting ionized donor (acceptor) atom varies with distance as r^{-1} and generates a shallow donor (acceptor) bound state. In contrast, for isoelectronic traps that are generated by isoelectronic impurities such as N in GaAs or GaP, it is the difference in electronegativity, size and pseudopotential between the isoelectronic impurity and the host atom it replaces that generates the trap state [27]. Such traps are characterized by a potential that varies with distance much faster than r^{-1} [28]. The potential well created by the isoelectronic trap is therefore much steeper than that created by the non-isoelectronic donor (acceptor) and because of this an electron (hole) trapped around the isoelectronic impurity atom is localized much more tightly around it. This spatial localization of electrons (holes) by isoelectronic traps smears out the electronic eigenstates in k -space causing them to be delocalized in the Brillouin zone. This proves advantageous in allowing radiative transitions from these states to the band edges, thus enabling

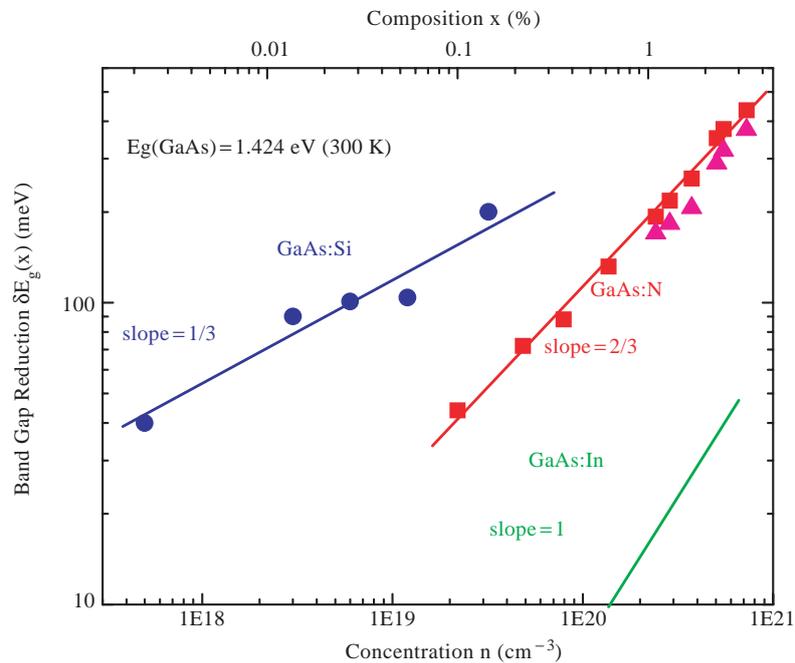


Fig. 5. Comparison of band gap reduction as a function of impurity concentration for three typical systems. Data for (a) GaAs:Si (n-type doping) are from [24], (b) GaAs:In (regular alloy) are from J. P Laurenti *et al.*, Phys. Rev. **B37**, 4155 (1998), and (c) GaAs:N are from [23].

light emission from indirect gap semiconductors like GaP. As discussed above, heavy N doping in GaP and GaAs leads to impurity band formation, redshifts in the photoluminescence, and the giant band gap ‘bowing’ phenomenon. However, the spatial localization around the isoelectronic traps that generate the impurity bands is precisely what disadvantageously affects the carrier mobility. This is the caveat with heavily isoelectronically doped semiconductors wherein the properties of the resulting alloy are irregular. Evidently, the very success in incorporating large amounts of insoluble isoelectronic dopants using non-equilibrium growth techniques is what leads to ‘irregular alloy’ behavior.

3.5. Physics of co-doping

A question thus emerges as to whether there exists a solution to the above problem. Having established the analogies between isoelectronic doping and charge (n- or p-type) doping, the simplest approach to providing an answer is to seek a solution in a manner that parallels the analogous problem that exists for charge doping. There, it is well known that the solubility of an acceptor (donor) impurity can be significantly increased by co-doping with a donor (acceptor). Using this approach, it has been possible to increase the doping concentrations of As donors and Ga acceptors in Si by almost three orders of magnitude [29]. Recent theoretical predictions indicated that co-doping of ZnO with Ga donors and N acceptors would overcome the difficulties in obtaining low-resistivity p-type ZnO and this has been experimentally verified [30, 31]. The enhancement in solubility to a level well above the solubility limit was explained in terms of the formation of ion pairs between donors and acceptor ions and a consequent reduction in the Madelung energy [30]. In GaN, Ploog and Brandt observed a significant enhancement in the solubility of Be acceptors when co-doped with O donors, and that this was accompanied by an improvement of one to two orders of magnitude in the carrier mo-

bilities despite the high doping concentrations [32]. The enhancement in mobility resulted because pairs of oppositely charged long-range Coulomb scatterers combine to behave as single short-range dipole scatterers. The above-mentioned successes motivate the use of a similar strategy for overcoming the limitations of isoelectronic doping.

3.6. Physics of isoelectronic co-doping

In GaP:N up to ten N pairs along with the isolated N center have been found to generate trap states below the conduction band edge [33]. Because of the short-range impurity potential associated with the N isoelectronic traps, they can capture an electron and result in the formation of a long-range screened Coulomb potential [34]. Thus, the nitrogen isoelectronic traps in GaP behave as deep acceptors (levels near the conduction band edge). In contrast to N, Bi is known to form isoelectronic trap levels just above the valence band edge in GaP and the isolated Bi and Bi pair levels are known to behave as hole traps [35]. Because these traps can capture holes and result in the formation of a long-range Coulomb potential, the Bi isoelectronic traps behave as deep donors in GaP [36]. Isoelectronic co-doping GaP with N and Bi should therefore yield advantages analogous to those obtained in the charge co-doping of semiconductors. The solubility of the isoelectronic dopants as well as the carrier mobility should be enhanced, leading to a more 'regular alloy'-like behavior with a concomitant improvement in photoluminescence efficiency and carrier lifetime. In fact, evidence for the enhanced solubility of N and Bi co-dopants in GaP already exists in the literature [37]. In contrast to GaP, the behavior of Bi in GaAs has only rarely been studied and it is not known whether Bi generates hole traps in GaAs. $\text{GaAs}_{1-x}\text{Bi}_x$ has recently been grown and its band gap shows a large 'bowing' [38]. However, the observed temperature insensitivity of its band gap [38] may have less to do with the explanations relating to the semimetallic behavior of GaBi [38, 39] but more to do with the fact that the valence band edge evolves out of a Bi impurity band and that, since Bi traps behave as deep donors, the temperature variation of these levels does not follow that of the band edge, which is a characteristic of deep levels. Thus, one of the benefits of using isoelectronic co-doping for the active regions of lasers will be the inherent temperature insensitivity of the devices. Bi should also prove beneficial in tuning the valence band offset for holes in the multiple quantum well active regions of lasers independently of the conduction band offset which is mainly determined by N in GaAs:N:Bi.

The ability to enhance the solubility of N and Bi in GaAs should lead to stronger overlap between the wavefunctions of neighboring N dopant atoms and similarly of neighboring Bi dopant atoms and thus to more regular transport properties as opposed to hopping-like transport properties. The small size of N substituting for As (P) on the group V sublattice can be balanced by the large size of Bi substituting on the same sublattice in GaAs (GaP), facilitating coherent epitaxial growth of the isoelectronically co-doped alloy on GaAs (GaP) substrates. In the case of GaP, the direct band gap characteristics of the heavily isoelectronically co-doped material combined with the ability to grow GaP:N:Bi epitaxially on Si substrates would introduce exciting possibilities for use of this material for fabricating photonic devices such as solar cells, LEDs and lasers. In fact, the VCSEL, solar cell and LED examples cited earlier would all benefit greatly. N and Bi co-doping could be used beneficially in InP and InGaAs₂ as well. Finally, isoelectronic co-doping could also be used advantageously in II-VI alloy systems like, for example, ZnSe, which could be isoelectronically co-doped with O deep acceptor-like traps and Te deep donor-like traps.

4. Conclusion

The 'irregular or abnormal alloy' behavior in $\text{GaAs}_{1-x}\text{N}_x$ and $\text{GaP}_{1-x}\text{N}_x$ has been discussed and it has been argued that these materials are better described as heavily doped semiconductors rather than as alloys. Isoelectronic co-doping has been proposed as a method for obtaining 'regular alloy' behavior in these systems where it leads to enhancements in (1) the solubility of isoelectronic dopants, and (2) carrier mobilities. The

arguments presented in this paper indicate that the use of isoelectronic co-doping should make it possible in several situations to overcome the limitations imposed by semiconductor alloy constraints on the design of some technologically important devices such as solar cells, lasers and LEDs. Use of the technique could expand the repertoire of available choices for semiconductor compounds and alloys having band-gap/lattice-constant paired values suited for epitaxial growth of device structures that implement design principles closest to the ideal.

Acknowledgements—This research was supported by the U.S. Department of Energy under contract No. DE-AC36-83CH10093 and by the NREL DDRD program No. 0659.0004.

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