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HEAVILY NITROGEN-DOPED III-V SEMICONDUCTORS FOR HIGH-EFFICIENCY SOLAR CELLS

Yong Zhang, A. Mascarenhas, and S. K. Deb
National Renewable Energy Laboratory (NREL), 1617 Cole Blvd. Golden, CO 80401

H. P. Xin, and C. W. Tu
Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA 92093

ABSTRACT

We demonstrate that the formation of an impurity band of the nitrogen-induced pair-bound states in GaAs_{1-x}N_x is responsible for the observed large band gap reduction, δE_g . δE_g is found to scale as $x^{2/3}$ (i.e., inversely proportional to the average separation of nitrogen pair centers). This is the same mechanism for the band gap reduction occurring in a heavily n-type or p-type doped semiconductor, where δE_g has been known to scale as $x^{1/3}$ (i.e., inversely proportional to the average separation of the isolated impurity center). The nature of the impurity band leads to the intrinsically low carrier mobility in this material. Quantum confinement for the electron belonging to the impurity band has been demonstrated in GaAsN/GaAs quantum wells. The electron effective mass is found to decrease on increasing x , as expected for an impurity band.

INTRODUCTION

Recently, new semiconductor "alloys," III-V nitrides with dilute nitrogen, have attracted a great deal of attention for potential applications in high-efficiency multi-junction photovoltaic devices. It has been demonstrated that incorporating a few percent nitrogen into conventional semiconductors (e.g., GaAs, GaInAs, and GaP) the band gaps of the host materials can dramatically change. For instance, merely 3% nitrogen doping in GaAs results in a 400 meV band gap reduction, which brings the band gap of GaAs close to 1 eV at room temperature. A 1 eV material is a critical component for a four-junction solar cell (i.e.: Ge, 1 eV material, GaAs, GaInP) that has a theoretical efficiency over 40%. However, in reality, the inclusion of the new 1 eV material GaAsN or GaInAsN has not yet met the high-efficiency expectation. Thus, it is of vital importance to understand the underlying physical origin for the nitrogen-doping induced property changes for these III-V alloys and answer questions such as: "Are there any intrinsic limits that will make these nitride compounds unsuitable for solar cell applications? And if there are, can these be eliminated by modifying these nitride compounds?"

These materials can be looked at from two different points of view: either it is an alloy or a heavily doped semiconductor. From the alloy point of view, a III-V semiconductor with a few percent or less of nitrogen is naturally considered as a dilute nitrogen alloy. However, from the point of view of impurity doping, one may consider a doping level of 10^{19} cm^{-3} as being a heavy doping. In fact, it is not at all a surprise that the incorporation of small amount of impurities can give rise to a large band gap reduction. A familiar example is heavily n-type or p-type doped semiconductors. For instance, 0.1% n-type doping in GaAs causes a nearly 200 meV band gap reduction because of the formation of an impurity band. Whereas for a 0.1% nitrogen doping in GaAs, the band gap reduction is actually less than 50 meV. The key point is that nitrogen atoms are isoelectronic impurities in these III-V semiconductors, which make them suitable for desired device applications, whereas the n-type doped materials are unsuitable even though they can have larger band gap reductions for the same doping levels.

During the past few years, heavily nitrogen doped III-V semiconductors have been viewed as dilute semiconductor alloys. Because of this, they were and had to be classified as abnormal alloys. An important fact has been ignored whilst trying to understand the mechanism of the observed large band gap reduction in the GaAsN or GaPN "alloy," which is that nitrogen doping introduces various bound states in the gap of the host material. The existence of bound states is the key factor for the large band gap reduction occurring in a heavily n-type or p-type doped semiconductor, through the formation of an impurity band[1]. We will show that the same mechanism applies to the large band gap reduction observed in heavily nitrogen-doped GaAs. Besides the band gap reduction, we have demonstrated another important effect of impurity band formation, which is that the electron effective mass in heavily nitrogen-doped GaAs is found initially to be very heavy, but to subsequently decrease on further increasing the nitrogen doping[2]. This phenomenon is expected to occur in n-type doped GaAs, but has not yet been experimentally observed due to complications (e.g., the so called Mott transition) typically observed in the case of charged doping[1]. From this point of view, III-V-N materials are ideally suited for studying physics associated

with heavy doping that proves to be difficult in conventional n-type or p-type doped systems.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The $\text{GaAs}_{1-x}\text{N}_x$ samples used in this study were grown epitaxially by gas-source molecular beam epitaxy (MBE), using a RF nitrogen radical beam source, on semi-insulating GaAs substrates. For bulk 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 range of x for the bulk samples is $0.1\% \leq x \leq 3.3\%$. All $\text{GaAs}/\text{GaAs}_{1-x}\text{N}_x/\text{GaAs}$ multiple quantum well (MQW) samples have the same GaAs barrier thickness (202 Å), the same number of wells (seven wells), and a 500 Å GaAs cap layer, with the nitrogen composition of the well layer varying from 0.9% to 4.5%, and the well width varying from 30 Å to 90 Å. More details for MQW samples can be found in Ref. [2]. The N concentrations were determined by high-resolution x-ray rocking curve (XRC) measurement. $\text{GaAs}_{1-x}\text{N}_x$ epilayers were confirmed as being coherently strained to the substrates, by asymmetric {511} XRC measurements[3,4]. Electro-reflectance spectra were measured at room temperature in contactless mode[5].

Fig. 1 shows electro-reflectance spectra of typical bulk $\text{GaAs}_{1-x}\text{N}_x$ samples. For a few low-nitrogen concentration samples, broadened Franz-Keldysh oscillations (FKOs) can be observed[6]. Thus, the data were fit to a FKO lineshape function with a broadening parameter[5]. For the other samples with relatively high nitrogen concentrations, the data were fit to a third-order derivative lineshape function[7].

Fig. 2 shows Log-Log plot of the band gap reductions as a function of doping level for three typical systems under heavy doping conditions: GaAs:Si, GaAs:N, and GaAs:In. The first and the last system are normally viewed as a heavily doped semiconductor and semiconductor alloy, respectively. We would like to point out that the remaining one is more appropriately viewed as a heavily doped semiconductor than an alloy. For both n-type and p-type doped GaAs, experimental results have revealed a scaling rule between the band gap reduction δE_g and the doping level n : $\delta E_g \propto n^{1/3}$, which is shown in Fig. 2 using GaAs:Si as an example[8]. Such a scaling rule is consistent with the assumption that the interaction energies are inversely proportional to the average carrier-carrier distance $n^{-1/3}$ [1]. For GaAs:N, since an isolated nitrogen center does not generate a bound state[9], but some nitrogen pairs do[10,11], the relevant interaction is amongst the paired nitrogen centers. Thus, the scaling rule is expected to be $\delta E_g \propto n^{2/3}$. The experimental data in fact very closely obeys this scaling rule, as shown in Fig.2. 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. As for GaAs:In, the scaling rule is found to be $\delta E_g \propto n$ [12], which is expected for a conventional alloy in the dilute region. As a matter of fact, neither an isolated In nor a pair of In has been found to generate any bound states in GaAs, although a large InAs cluster (or a

InAs quantum dot) can indeed have a bound state in the gap of GaAs[13].

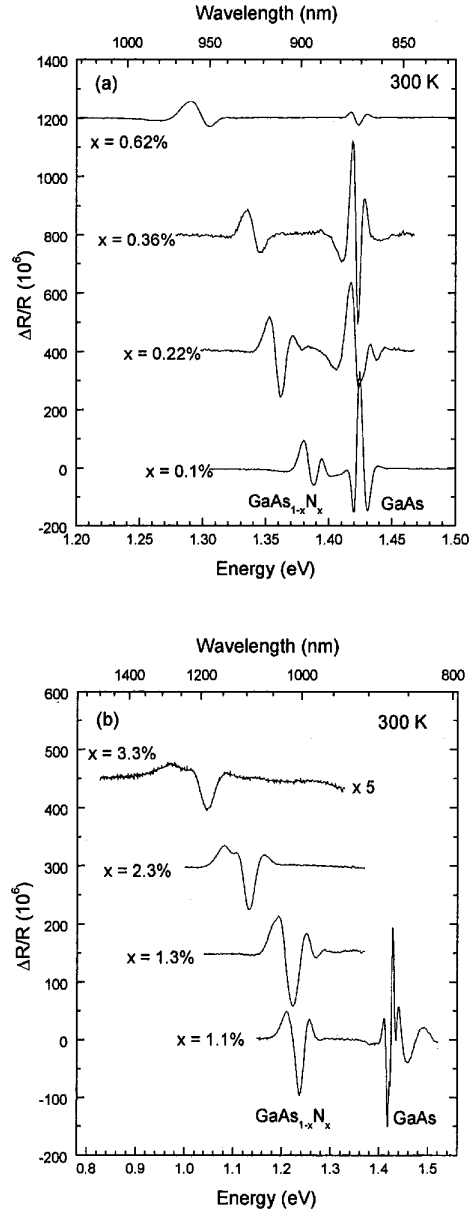


Fig. 1. Electro-reflectance spectra of bulk $\text{GaAs}_{1-x}\text{N}_x$: (a) for $x < 1\%$ and (b) for $x > 1\%$.

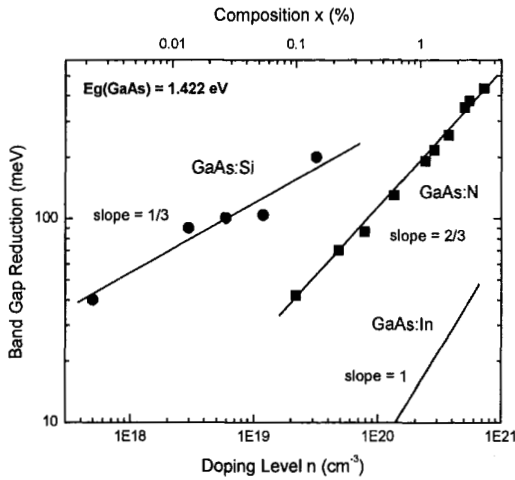


Fig. 2. A comparison of the band gap reduction as a function of impurity concentration or composition for three typical systems. Data for GaAs:Si (n-type doping) are from Yao and Compaan's paper (Ref. [8]), data for GaAs:In (alloy) are Laurenti et al's (Ref. [12]), and data for GaAs:N (isoelectronic doping) are the results of this work.

Fig. 3 shows electro-reflectance spectra of a few GaAs_{1-x}N_x MQW samples with a fixed x = 1.6% but different well width. Similar to what is well-known for the case of GaAs/AlGaAs QWs, we observe (1) the interband band transitions associated with different quantum confined sub-bands of the conduction band, and (2) the confinement energies increase with reducing the well width. These observations indicate that electrons initially localized at individual impurity centers in the dilute doping limit become de-localized upon the formation of the impurity band at high doping levels. In this sense, they behave like free electrons in a bulk semiconductor. By analyzing data similar to those of Fig. 3 for all the MQW samples using a one-dimensional quantum well mode[2], we obtain the composition dependence of the electron effective mass in GaAs_{1-x}N_x, as shown in Fig.4, which agrees with the expectation of the impurity band model that the effective mass of the impurity band decreases on increasing impurity concentration[1]. However, because of the localized nature of the bound states, even when they evolve into an impurity band at high doping levels, the properties of the impurity band are somewhat different from bands in bulk semiconductors. Upon impurity band formation, the impurity wavefunction becomes partially de-localized, but is still incapable of spreading throughout the whole crystal. In a macroscopic system with randomly distributed impurities, the density of states may be a continuous function of energy for an impurity band, but it consists of a set of discrete levels uncorrelated with each other and randomly scattered in the energy space[14]. Thus, carriers in an impurity band tend to have a lower mobility than those in bulk semiconductors, which is the intrinsic limitation for the device application of Ga(In)AsN materials. An ordered structure should in principle be able

to reduce the random fluctuations, as been demonstrated in ordered GaInP alloys[15].

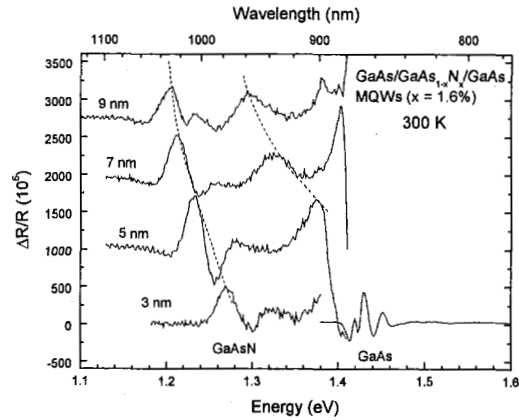


Fig. 3. Electro-reflectance spectra of GaAs/GaAs_{1-x}N_x quantum wells with different well width.

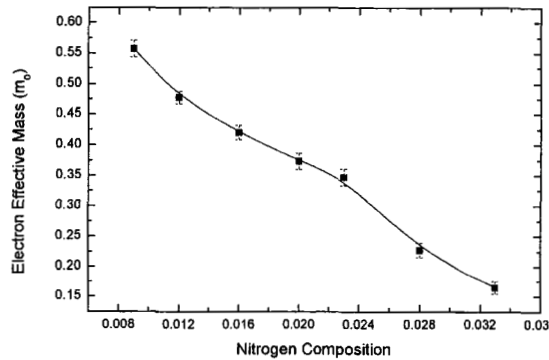


Fig. 4. Electron effective mass of GaAs_{1-x}N_x as a function of nitrogen composition x.

SUMMARY

The band gap reduction observed in heavily nitrogen-doped GaAs or GaAs_{1-x}N_x is found to scale as $\delta E_g(x) \propto x^{2/3}$, and the electron effective mass is found initially to be very heavy but to subsequently decrease on further increasing the nitrogen doping. These findings correlate with two key effects of the impurity band formation: (1) impurity-impurity interaction, which results in the band gap reduction, is inversely proportional to the average separation of the impurity centers, and (2) the dispersion of the impurity band increases with increasing the impurity concentration. Because of the localized nature of the impurity bound state and the random fluctuation of the impurity distribution, the carrier mobility is intrinsically low in these materials.

ACKNOWLEDGMENTS

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