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Effect of hydrogen on the electronic properties of $In_xGa_{1-x}As_{1-y}N_y$/GaAs quantum wells

A. Polimeni, G. Baldassarri H. v., H. M. Bissiri, and M. Capizzi
Istituto Nazionale di Fisica della Materia, Dipartimento di Fisica, Università degli Studi di Roma ''La Sapienza,'' Piazzale A. Moro 2, I-00185 Roma, Italy

M. Fischer, M. Reinhardt, and A. Forchel
Universität Würzburg, Technische Physik, Am Hubland 97074 Würzburg, Germany

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Atomic hydrogen irradiation leads to striking effects on the electronic properties of $In_xGa_{1-x}As_{1-y}N_y$/GaAs single quantum wells as measured by photoluminescence spectroscopy. The $In_xGa_{1-x}As_{1-y}N_y$ band-gap energy blueshifts with increasing hydrogen dose and finally saturates at the value of a corresponding reference sample without nitrogen. The luminescence intensity decreases upon hydrogen irradiation with a strong dependence on nitrogen content. The above results have been found in a large set of samples differing for nitrogen and indium content, and are related to the formation of bonds between hydrogen and one or more nitrogen atoms.

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Since the proposal of the $In_xGa_{1-x}As_{1-y}N_y$/GaAs system as a material for long-wavelength emitters (i.e., $\lambda=1.3$ and 1.55 μm) (Refs. 1 and 2) III–N–V based heterostructures have attracted renewed interest for both potential applications and fundamental research. A large band-gap reduction (see, e.g., Refs. 1–5) and an increase of the electron effective mass[6] upon substitution of arsenic with a few percent of nitrogen have been reported. Although there is not a general consensus on the theoretical model that best describes these observations, the above effects are usually ascribed to the modification of the energy levels of the conduction-band edge induced by N.[7–15] The puzzling effects exerted by nitrogen on the (InGa)As host lattice ought to be related to the large difference in size and electronegativity between Ga (or In) and N atoms, which gives rise to an imbalance of the electronic charge distribution toward N. In GaN, a monotonic increase in the electronic charge density on going from Ga to N has been predicted to lead to equilibrium positions of hydrogen in the lattice markedly different from those found in Si and GaAs.[16] Experimentally, the existence of N–H bonds has been suggested by far infrared spectroscopy in GaN:H.[17] In spite of the number of works on hydrogen in GaN,[18] nothing is known about hydrogen in (InGa)(AsN). Therein, H could act as a probe affecting the nature of bonds between N and its atomic neighbors in the lattice, thus providing important hints on the role played by nitrogen on the electronic properties of the (InGa)As host material.

Here, we report on the effect of atomic hydrogen irradiation on the electronic properties of $In_xGa_{1-x}As_{1-y}N_y$/GaAs single quantum wells (QW's), as investigated by photoluminescence (PL) spectroscopy. The effective band gap of the QW blueshifts upon hydrogen irradiation. By increasing hydrogen dose, it saturates at, or close to, the energy gap of a corresponding N-free reference sample. This surprising behavior is attributed to the formation of bonds between hydrogen and a single nitrogen atom. On the other hand, complexes of H with N clusters lead to a quenching of the PL emission efficiency. These effects have been observed systematically in a large set of samples differing for indium and/or nitrogen concentrations. Therefore, hydrogen strongly interacts with the localized electronic charge associated with nitrogen in III-N-V alloys and gives rise to effects not observed previously in other semiconductor compounds and alloys.

A number of $In_xGa_{1-x}As_{1-y}N_y$/GaAs single QW's grown by solid source molecular beam epitaxy (MBE) have been investigated. N_2 cracking was obtained by using a radio frequency plasma source. Indium (nitrogen) concentrations in the samples are: $x=0.32$ ($y=0.027$), $x=0.34$ ($y=0.007$), $x=0.38$ ($y=0.042$, 0.052), $x=0.41$ ($y=0.022$, 0.031). The N concentration has been determined by a combined analysis of x-ray diffraction and optical data. For each subset of quantum wells having the same indium content and well width, L, but differing for the nitrogen concentration, a reference sample without nitrogen (blank) has been grown. L ranges from 6.0 nm to 8.2 nm. All samples have a 100 nm thick GaAs capping layer. Postgrowth treatment with atomic hydrogen was obtained by ion-beam irradiation from a Kaufman source with the samples held at 300 °C. The ion energy was about 100 eV and the current density was few tens of $\mu A/cm^2$. Several hydrogen doses ($d_H=1$, 5, 50, 270, and 690×10^{16} ions/cm^2) have been used in this study. PL was excited by the 515 nm line of an Ar^+ laser, dispersed by a single 1 m monochromator and detected by a cooled Ge detector.

PL spectra of two QW's having $x=0.34$ and $L=7.0$ nm without (dashed lines) and with nitrogen ($y=0.007$, continuous lines) are shown in Fig. 1 for different hydrogen doses (d_H increases from bottom to top). Data are taken at $T=150$ K in order to avoid PL band broadening and carrier localization at room and low temperature ($T<100$ K), respectively.[19] The presence of a small amount of nitrogen markedly affects the dependence on hydrogen irradiation of the QW optical properties. In the $In_xGa_{1-x}As_{1-y}N_y$ quantum well, the PL peak energy, $h\upsilon_P$, increases steadily up to $d_H=5.0\times10^{17}$ ions/cm^2 and then it saturates at the value of the blank band gap. PL intensity slightly increases at small d_H, then strongly decreases at high H doses. PL linewidth sizably

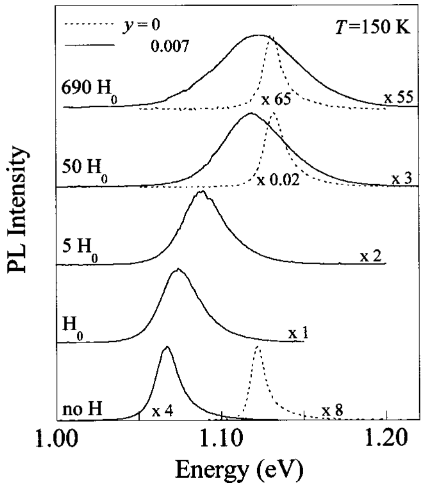

FIG. 1. Peak normalized photoluminescence spectra of N-free (dashed lines) and N-containing (y=0.007) quantum wells (continuous lines) irradiated with different H doses ($H_0 = 1.0 \times 10^{16}$ ions/cm^2). QW indium content and thickness are x=0.34 and L=7.0 nm, respectively. The spectra are taken at T=150 K and laser power density P=15 W/cm^2. Normalization factors are given for each spectrum.

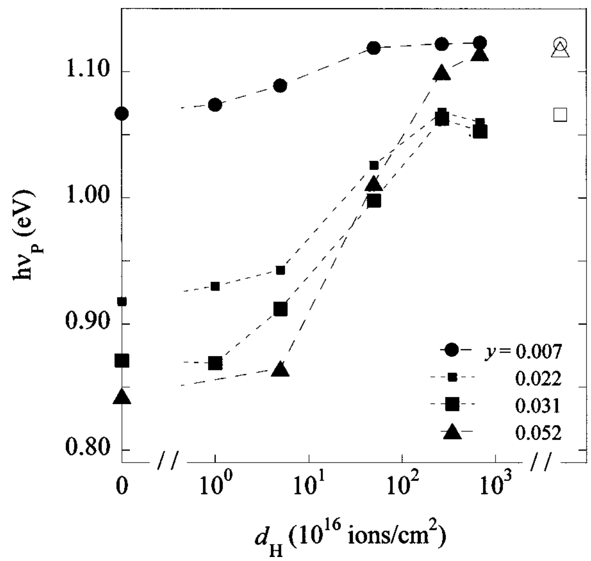

FIG. 2. PL peak energy, $h\upsilon_P$, as a function of hydrogen dose for samples having different nitrogen and indium concentrations (full symbols). Open symbols refer to reference QW's without nitrogen. All data are taken at T=150 K.

broadens upon hydrogenation indicating an increase of microscopic disorder. Similar effects are observed in all N containing samples. On the contrary, in the N-free-sample, only a slight fluctuation ($\pm$5 meV) of the PL peak energy can be noticed, most likely due to sample inhomogeneity. The PL intensity increases steadily with d_{H} and then worsens only at the highest H dose. This effect has been already reported in Ref. 20 where it has been attributed to H passivation of defects and nonradiative centers. We point out that a heat treatment like that experienced during H irradiation, but in absence of H, has no effect on the sample PL efficiency, linewidth, and peak energy.

Figure 2 shows the dependence on d_{H} of the PL peak energy for samples having different indium and nitrogen concentrations (full symbols). In the untreated samples ($d_{\mathrm{H}} = 0$), the emission energy of QW's with nitrogen decreases with y, as commonly observed.[1–5] With increasing hydrogen dose, the PL recombination energy increases and tends to saturate at a value equal, or close, to the energy of the corresponding N-free sample (open symbols). Note that the saturation energy value is reached at lower hydrogen dose the lower the nitrogen content. We now discuss in more detail this striking effect produced by H irradiation in N-containing samples. As a preliminary, we define two quantities. In the inset of Fig. 3, the blueshift of the $In_xGa_{1-x}As_{1-y}N_y$ band gap (B_{H}) induced by hydrogen and the redshift of the band gap (R_{N}) of the N-free QW due to N incorporation are shown for a typical sample. The ratio B_H/R_{N} gives the percentage of the N-induced band-gap reduction that is recovered upon H irradiation so that $B_{\mathrm{H}}/R_{\mathrm{N}} = 1$ corresponds to full electronic passivation of nitrogen atoms in the well. Figure 3 shows $B_{\mathrm{H}}/R_{\mathrm{N}}$ as a function of d_{H}/y, i.e., as a function of the hydrogen dose normalized to the N content of the well. Data for almost all samples fall on a same curve although the N content varies by almost one order of magnitude.[21] This shows that the same physical mechanism, regardless of nitrogen content, is responsible for the band-gap increase induced by hydrogen. Since $B_{\mathrm{H}}/R_{\mathrm{N}}$ scales with d_{H}/y, we attribute the band-gap reopening of

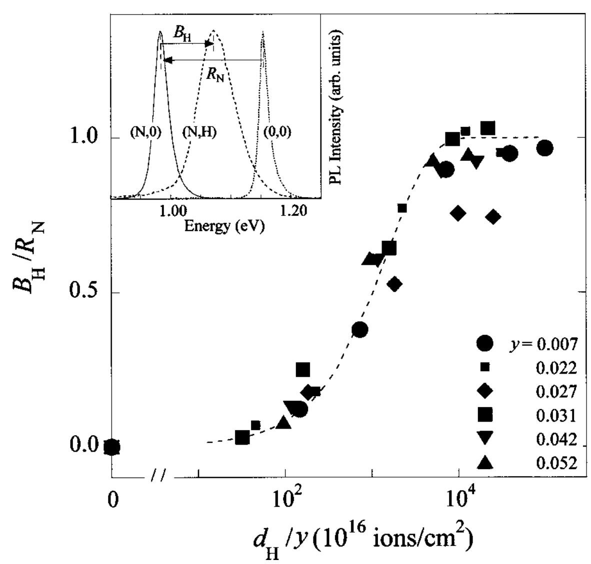

FIG. 3. Dependence on the ratio d_{H}/y of the percentage of band-gap recover, $B_{\mathrm{H}}/R_{\mathrm{N}}$, in $In_xGa_{1-x}As_{1-y}N_y$/GaAs QW's. The dashed line is a guide to the eye. B_{H} and R_{N} are defined in the inset of the figure for a typical QW structure (x=0.32, L=6.0 nm). B_{H} is the blueshift of the photoluminescence peak energy induced by hydrogen in N-containing QW's and R_{N} is the redshift of the photoluminescence peak energy due to N incorporation in the N-free reference QW. (N,0), (N,H), and (0,0) indicate the photoluminescence spectrum of a sample containing nitrogen (y=0.027) but no hydrogen, nitrogen (y=0.027) and hydrogen (dose 5.0×10^{17} ions/cm^2), and no nitrogen and no hydrogen, respectively. All data are taken at T=150 K.

$In_xGa_{1-x}As_{1-y}N_y$:H quantum wells to the interaction of a single hydrogen atom with a *single* nitrogen atom. On the same ground, one can exclude that the band-gap recover in $In_xGa_{1-x}As_yN_{1-y}$ is due to H interacting with clusters formed by *n* nitrogen atoms. In fact, the plot of B_H/R_N vs d_H/y^n is much more scattered for $n>1$ than for $n=1$. This implies that the band-gap reduction observed in the (InGa)As host lattice upon incorporation of N is caused by the interaction of the conduction-band edge states of the host matrix with an energy level introduced by a *single* N atom. Then we conclude that the formation of N clusters, which clearly occurs in (InGa)(AsN)[19,22,23] does not play a role in the large redshift of (InGa)As band gap originating from N incorporation.

It may be worth trying to account for the band-gap opening induced by H in $In_xGa_{1-x}As_{1-y}N_y$ in the framework of H bonding to point defects in semiconductors.[24] The charge transfer from the group III atoms toward the strong electronegative N atoms favors the formation of H–N bonds in (InGa)(AsN):H. This is consistent with theoretical predictions of a N antibonding equilibrium position for H^+ in GaN.[16,25] One can speculate that the formation of H–N bonds leads to the passivation of the N atoms in (InGa)(AsN), namely, to a strong energy shift of the N related level, most likely deep into the energy gap. On the theoretical side, the interaction of energy levels due to *single* N atoms with the conduction-band edge has been invoked to account for the redshift induced by N in (InGa)(AsN).[4,13,15,26] Therefore, the formation of N–H bonds increases the energy distance between the N level and the conduction-band states, setting to zero their interaction and increasing the (InGa)(AsN) energy gap.

Another peculiar effect of hydrogen irradiation regards the behavior of PL efficiency at different H doses. Figure 4 shows the dependence of the PL integrated intensity on hydrogen dose in QW's having nitrogen (indium) concentration $y=0.0$ ($x=0.34$) (open circles), 0.007 (0.34) (full dots), 0.022 (0.41) (full squares), 0.031 (0.41) (full triangles), 0.052 (0.38) (full diamonds). As already shown in Fig. 1, the luminescence efficiency in the $x=0.34$ blank monotonously increases with H dose (more than two orders of magnitude for $d_H=2.7\times10^{18}$ ions/cm^2), until it decreases at $d_H=6.9\times10^{18}$ ions/cm^2, likely because of the damage due to the H irradiation. Similar results have been obtained in the other blanks. In the case of the four N containing samples, two different regimes are noticed. At low d_H, the rate of increase in the PL integrated intensity with H dose observed in the blank sample weakens for increasing N content and becomes negative at high N concentrations. The decrease of the PL intensity with d_H observed in the blank for $d_H=2.7\times10^{18}$ ions/cm^2 starts at lower d_H values the higher the N content. In particular, at a fixed H dose the decrease of PL integrated intensity exhibits a more than quadratic dependence on N concentration. This indicates that the nonradiative centers responsible for the quenching of the PL signal are due to hydrogen binding to two or more nitrogen atoms. We point out that all QW's shown in Fig. 4 have similar PL efficiencies before hydrogenation. This excludes that the different dependences on d_H of the PL integrated intensity observed in different QW's could be ascribed to a density of nonradiative recombination centers varying from sample to sample. The PL quenching reported here is consistent with recent transport measurements in *p*-type (InGa)(AsN) samples grown by gas source MBE.[27] Therein, an increase of carrier concentration upon thermal annealing has been explained in terms of a corresponding decrease of the concentration of trapping centers due to residual hydrogen.

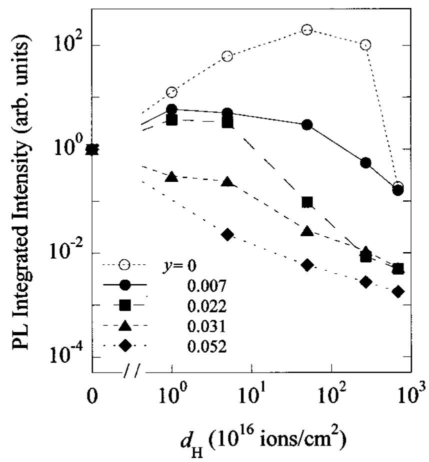

FIG. 4. Photoluminescence integrated intensity vs hydrogen dose, d_H, for samples having different nitrogen concentration, *y*. Each subset of data is normalized to the value of the PL integrated intensity at $d_H=0$. All samples exhibit a similar PL efficiency at zero hydrogen dose.

In conclusion, hydrogen irradiation markedly affects the electronic properties of $In_xGa_{1-x}As_{1-y}N_y$/GaAs quantum wells. (i) It restores the band-gap energy to the value it has in the lattice without nitrogen. (ii) It produces a sizable decrease of the PL efficiency. We attribute the former of these effects to the binding of H to a single N atom (with an ensuing electronic passivation of N), and the latter of these effects to the formation of nonradiative recombination centers for carriers caused by the interaction of H with N clusters. As a final remark, we believe that the present results should be considered (and eventually reproduced) by any theoretical model aimed to describe the role of N in III-N-V heterostructures.

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