Hydrogen-induced band gap tuning of (InGa)(AsN)/GaAs single quantum wells

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The effect of atomic hydrogen on the electronic properties of (InGa)(AsN)/GaAs single quantum wells (QWs) has been investigated by photoluminescence (PL) spectroscopy. For increasing hydrogen dose, the band gap of the material increases until it reaches the value corresponding to a N-free reference QW. The band gap variation is accompanied by an increase of the line width of the PL spectra and a decrease of the PL efficiency. Annealing at 500 °C fully recovers the band gap and PL line width the sample had before hydrogenation. These results are accounted for by the formation of N–H complexes, which lowers the effective nitrogen content in the well. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1376436]

Hydrogen is the smallest atom, with one electron in its only shell. This explains both the high diffusivity of H in intrinsic semiconductors, as well as the strong chemical activity of H. Moreover, hydrogen is present in most of the steps of semiconductor growth and device processing. Therefore, great attention has been focused on the effects of H in Si, InP, GaAs,[1] and GaN,[2] which are materials of relevance for technological applications. Not much is known, instead, about the role of H in ternary and quaternary compounds, in particular those containing nitrogen.

In $In_xGa_{1-x}As$, the substitution of a few percent of As atoms by N atoms leads to a strong reduction of the band gap energy toward values of interest for light transmission through optical fibers ($\lambda = 1.3$ and 1.55 μm).[3–6] Although an increase of carrier concentration upon annealing of (InGa)(AsN) epilayers has been attributed to H desorption from the material,[7] nothing is known about the effects, if any, of intentional H irradiation on the optical properties of this material. Moreover, the high reactivity and small size of H make this atom an ideal probe of the bonds between N and its atomic neighbors in the lattice.

In this paper, we show that the insertion of H in $In_xGa_{1-x}As_{1-y}N_y$/GaAs quantum wells (QWs) or the H removal from these QWs changes in a reproducible way the optical properties of the material. In particular, for increasing H doses the $In_xGa_{1-x}As_{1-y}N_y$ QW energy gap increases, until it reaches the value it has in a reference N-free $In_xGa_{1-x}As$/GaAs QW (or blank). Thermal annealing at 500 °C restores, instead, the optical properties the $In_xGa_{1-x}As_{1-y}N_y$/GaAs QW had before hydrogenation. These findings are explained by the formation of N–H complexes, which decreases the effective N concentration and consequently increases the band gap energy of the QW.

The investigated $In_xGa_{1-x}As_{1-y}N_y$/GaAs single QWs were grown by solid source molecular beam epitaxy. A radio frequency or an electron-cyclotron-resonance plasma source was used for N_2 cracking. Indium concentration, x, ranges from 0.25 to 0.41; nitrogen concentration, y, from 0.007 to 0.052; and well width, L, from 6 to 8 nm. All samples have a 100 nm thick GaAs capping layer. Post-growth treatment by atomic hydrogen irradiation at 300 °C was obtained by a Kaufmann source, with an ion energy of 100 eV and a current density of a few tens of μA/cm^2. Hydrogen doses, d_H, were 1, 5, 50, 270, and 690 H_0 ($H_0 = 1.0 \times 10^{16}$ ions cm^{-2}). One hour thermal annealing was performed at 10^{-6} Torr at temperatures ranging between 220 and 550 °C. Photoluminescence (PL) was excited by the 515 nm line of an Ar^+ laser, dispersed by a single 1 m monochromator and detected by a N_2 cooled Ge detector. We will focus here on the results obtained in a QW with $x = 0.34$, $y = 0.007$, and $L = 7.0$ nm and its corresponding N-free blank. These results, in fact, are qualitatively independent of the indium and nitrogen concentration of the sample, as it will be discussed in detail elsewhere.

Figure 1 shows the room temperature PL spectra of hydrogenated $In_{0.34}Ga_{0.66}As_{1-y}N_y$/GaAs QWs for $y = 0$ (dashed lines) and 0.007 (continuous lines). Hydrogen dose increases from the bottom to the top of Fig. 1. Hydrogen has quite different effects on the optical properties of the two samples. In the $y = 0.007$ QW, the PL peak shifts toward higher energy for increasing hydrogen doses. At the highest dose, the PL band of the $y = 0.007$ QW overlaps the PL band of the N-free QW, whose peak energy does not sizably change with d_H. Hydrogen irradiation leads also to an increased microscopic disorder, mainly in the N-containing QW, whose PL line width is appreciably broader than that of the blank even at the lowest d_H. Finally, PL intensity increases by a factor of 3 at the lowest H dose in the $y = 0.007$ QW before decreasing at high d_H's. On the contrary, PL intensity monotonously increases with H dose in the N-free sample (up to a factor of 100) before dropping at the highest $d_H (= 690\ H_0)$.

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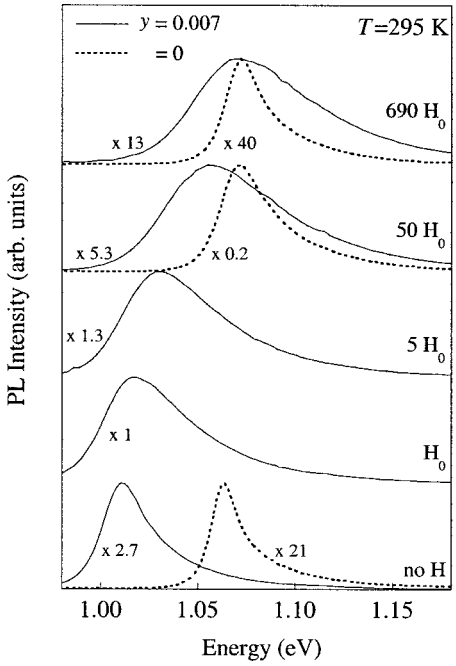

FIG. 1. Room temperature PL spectra of two hydrogenated $In_{0.34}Ga_{0.66}As_{1-y}N_y/GaAs$ QWs with $y=0.007$ (continuous lines) and $y=0.0$ (dashed lines) for different hydrogen doses ($H_0=1.0\times10^{16}$ ions cm^{-2}). All spectra have been normalized to the peak (normalization factors are given for each spectrum). Laser power density $P=70$ Wcm^{-2}.

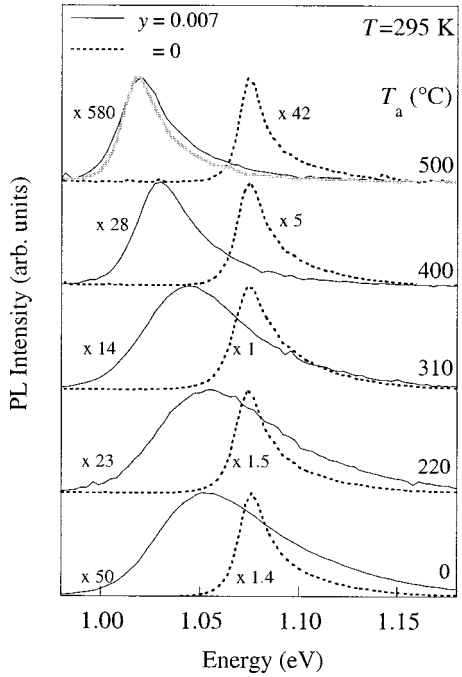

FIG. 2. Room temperature PL spectra of $In_{0.34}Ga_{0.66}As_{1-y}N_y/GaAs$ QWs hydrogenated at the dose $d_H=50$ $H_0(=5.0\times10^{17}$ ions $cm^{-2})$ for different annealing temperatures T_a. Continuous lines refer to $y=0.007$ QWs, dashed lines indicate $y=0.0$ QWs. An H-free, $y=0.007$, not annealed sample is shown by the thick gray line for ease of comparison. All spectra have been normalized to the peak (normalization factors are given for each spectrum). Laser power density is $P=20$ Wcm^{-2}.

The effects of hydrogen irradiation can be reversed by thermally annealing the sample. The N-containing QW and the N-free blank (both hydrogenated at the same dose $d_H=50$ H_0) have been annealed at various temperatures, T_a, ranging from 220 to 550 °C. The room temperature PL spectra of both samples are shown in Fig. 2 for annealing temperatures increasing from the bottom to top of the figure. The PL band of the blank (dashed lines) is not affected much by the annealing process, except for a decrease of the emission efficiency at high T_a. On the other hand, the PL band of the hydrogenated $y=0.007$ QW (continuous lines) moves toward lower energy until its line shape nearly coincides with the PL spectrum of the H-free, not annealed, $y=0.007$ QW (thick gray line).

This is summarized in Fig. 3, where the room temperature values of the half width at half maximum (HWHM) of the PL band (y axis) and the PL peak energy, E_p (x axis), of the $In_{0.34}Ga_{0.66}As_{0.0093}N_{0.007}/GaAs$ QW are shown for H doses increasing from 0 to 50 H_0 and for annealing temperature increasing from 220 to 550 °C in the sample with $d_H=50$ H_0. Linewidth data are taken at room temperature in order to avoid carrier localization effects, which affect mainly the low energy side of low T PL spectra.[8] Moreover, HWHM has been evaluated from the low energy side of the PL band in order to discard most of the contribution to the PL line width due to band filling effects at room temperature, and retain only those contributions related to the fluctuation of the potential energy arising from the random distribution of N and H atoms. E_p univocally determines the PL line width, independent of the way this value has been obtained, namely, by direct H irradiation or desorption of hydrogen in the sample with $d_H=50$ H_0. Finally, annealing at $T_a\geqslant500$ °C restores the HWHM and E_p values of the H-free $y=0.007$ QW (10 meV and 1.018 eV, respectively).

Data reported in Figs. 1–3 provide clear evidence that the band gap of (InGa)(AsN) QWs can be tuned postgrowth by changing the H content in the host lattice. Let us discuss the microscopic origin of the H related effects in (InGa)(AsN) QWs reported here. An increase of the electronic charge density around N due to its small size and high electronegativity favors the formation of a bond between H^+ and N, similar to what was theoretically proposed and ex-

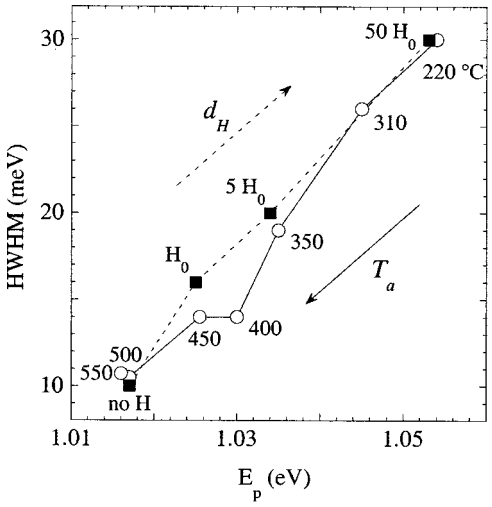

FIG. 3. HWHM of the PL band in $In_{0.34}Ga_{0.66}As_{0.993}N_{0.007}/GaAs$ QWs vs the PL band peak energy, E_p. Data are taken from room temperature PL spectra at low laser power density. Closed squares refer to a QW hydrogenated at increasing (upward arrow) H doses, d_H, open circles refer to a QW hydrogenated at $d_H=50$ $H_0(=5.0\times10^{17}$ ions $cm^{-2})$ and annealed at increasing (downward arrow) temperatures, T_a.

perimentally suggested in *p*-type GaN.[9–11] Also, quenching of the PL intensity of radiative recombinations associated to N–N pairs in GaP:N has been reported and attributed to the formation N–H bonds.[12] A ''molecular orbital'' between hydrogen and nitrogen leads to a bonding level with a point group symmetry different from (and lower in energy than) that of the original N level. This neutralizes the N electrical activity with a decrease of the effective number of N levels and an increase of the band gap. Thermal annealing breaks the N–H bonds, thus increasing back the effective number of N atoms. We stress that no band gap energy change has been observed upon annealing in the N-free hydrogenated QW (see Fig. 2) and in a H-free $y=0.007$ sample (not shown here). On the theoretical side, models developed to explain the effects of N on the (InGa)As optical gap are based on point symmetry-breaking arguments[13,14] or band anticrossing between N-related levels and conduction band extended states.[6,15] The scenario described above is consistent with these models. On the other hand, we believe that any model describing the role of N in III–N–V materials should also consider (and eventually reproduce) the neat effects of hydrogen presented here.

H irradiation and thermal annealing also affect the PL line shape and intensity. The PL bands in hydrogenated (InGa)(AsN) QWs are much broader than those in hydrogenated (InGa)As QWs, see Fig. 1. Hydrogen irradiation, therefore, increases the disorder already introduced by N in the (InGa)As lattice because of local fluctuations of the effective N concentration over the exciton size and/or different types of H–N bonds. For what concerns the PL intensity, it increases upon hydrogenation in the N-free QW (see Fig. 1) as previously reported.[16] The dependence on the dose of the PL signal of (InGa)(AsN) QWs shown in Fig. 1 should therefore be ascribed to a competition between the former process of passivation of pre-existing defects and the introduction of new nonradiative centers upon hydrogenation. Finally, the decrease of PL intensity for high H doses, see Fig. 1, or high annealing temperature, see Fig. 2, can be ascribed to bombardment damage and As desorption, respectively.

Hydrogen induced passivation of nitrogen in (InGa)(AsN) QWs highlights the peculiar nature of N in these materials. In the diluted concentration limit, nitrogen behaves as an isoelectronic impurity in GaP[17] and GaAs,[18] where it gives rise to narrow energy levels in the energy gap or in the conduction band of the host material, respectively. Present results suggest that the N associated wavefunction maintains a strongly localized ''impurity like'' character, even for nitrogen concentrations so high to strongly perturb the conduction band edge of the (InGa)As host lattice. This favors the formation of strong bonds of nitrogen with hydrogen.[19] To conclude, although further measurements, in particular far infrared absorption, and total-energy calculations based on density-functional theory are required to better elucidate the details of H–N complexes, hydrogen appears to be a powerful tool for investigating and tuning the optical gap of (InGa)(AsN) materials.

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