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Photoluminescence study of hydrogen passivation in $InAs_{1-x}N_x$/InGaAs single-quantum well on InP

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It is well known that nitrogen incorporation into III–V compounds will degrade the quality of materials. In this letter, we show that the incorporation of atomic hydrogen into InAsN/InGaAs quantum wells can effectively passivate defects and lead to enhancement of photoluminescence intensity near the band edge. After hydrogenation, the change of the optical properties is quite different from that of the annealing with nitrogen treatment. For instance, the linewidth becomes wider after hydrogenation, while the linewidth is narrower after nitrogen annealing. Through a detailed study of the photoluminescence spectra, we show that the passivation of defect bonds is the main reason for the improved optical behavior for hydrogenation, while the interdiffusion is responsible for the change after nitrogen annealing.
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Incorporation of nitrogen into III–V materials such as GaAsN and GaInNAs,[1–3] have recently drawn much attention, due to the unique properties as well as potential device applications of such materials. For example, alloy band gaps in these nitrogen-incorporation group-V materials exhibit a strong bowing effect, and they may approach zero.[4–7] The band gap of these materials can be turned from far infrared to ultraviolet,[8] and it leads to the development of a technical application of laser diodes with a wide range wavelength. One of the outstanding examples is that $In_xN_{1-x}As_yP_{1-y}$ grown on an InP substrate has been suggested as a novel compound semiconductor material system for the realization of high performance laser diodes emitting at 1.55 μm.[9] InAsN belongs to one of the mixed group-V nitride materials. It is a very promising material for midinfrared optoelectronic devices. By incorporation of nitrogen into InAs, because of the large difference in atomic size and electronegativity between As and N, the band gap of quantum well decreases.[10] With the advantage of a highly strained quantum well, one can fabricate good quality material and push laser emission of InAsN devices to the desired wavelength. However, it was found that the optical properties degrade very rapidly with increasing nitrogen concentration due to the presence of high concentration of nonradiative centers.[11] In order to push the devices of III nitrides into application, it is necessary to reduce the defects and improve the optical quality.

Introduction of atomic hydrogen into semiconductors can significantly change the electrical and optical properties of materials.[12,13] In particular, this has led to the technical application of hydrogenated amorphous silicon. The principle interest in crystalline semiconductors occurs because of its ability to passivate the electrical activity of dangling or defect bonds, leading to the enhancement of photoluminescence (PL) intensity, electron mobility, etc. It is also found that hydrogen can passivate both shallow acceptor and donor impurities in many technologically important semiconductors.[13] Additionally, it has been proven that hydrogen can be used as a sensitive probe of defect reactions providing an exciting opportunity to clarify defect microstructures. Thus, in recent years, the incorporation of atomic hydrogen into semiconductors has attracted wide interest. An extensive review on this topic has been written by Pearton *et al.*[14] Most of the previous reports of the influence of hydrogen on III–V compounds were concentrated on GaAs/AlGaAs and InGaAs/GaAs systems.[15–17] In this letter, the effect of hydrogen passivation on the photoluminescence spectra of $InAs_{1-x}N_x$/InGaAs single-quantum well (SQW) on InP is investigated. We show that hydrogenation is a very effective way to passivate defect bonds in quantum wells. In addition, we find that the result of hydrogenation is quite different than that of nitrogen annealing. The possible origin of the difference will be discussed.

All samples were grown on (001) InP substrates by a VG V-80 gas source molecular-beam epitaxy system and active nitrogen species were provided by an EPI UNI-bulb rf plasma source. For the SQWs, a 0.1-μm-thick InP buffer layer was grown at first at 450 °C, then the growth was interrupted, followed by the 400 °C growth of an InGaAs/InAs(N)/InGaAs SQW structure, with a 1 μm/h growth rate and a As/In ratio of two. The rf plasma power was turned to 300 W and nitrogen compositions were controlled by the nitrogen gas flow rate. The SQW were composed of 100-nm-thick $InGa_{0.53}As_{0.47}$ barriers (lattice matched to InP) and 30-Å-thick InAs or InAsN well layer. Finally, an InP cap layer with a thickness of 0.1 μm was grown on top of the SQW structures.

For the hydrogen passivation, we used a photochemical vapor deposition system. Due to its lack of high energy particle bombardment, this technique has been proven to be a better method for hydrogenation than conventional methods, such as ion implantation and rf plasma discharge.[13] The con-

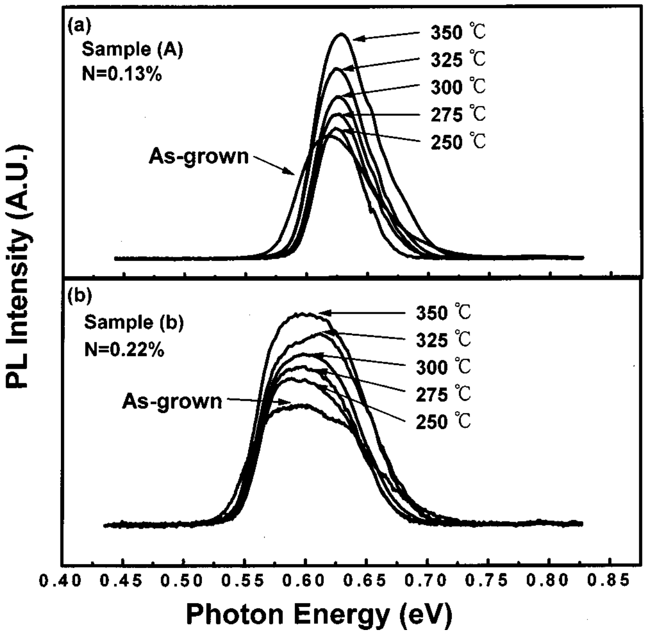

FIG. 1. Low temperature PL spectra of $InAs_{1-x}N_x$/InGaAs SQW before and after hydrogenation at different temperature for 15 min for (a) sample A with $N=0.13\%$ and (b) sample B with $N=0.22\%$.

ditions of hydrogen passivation are as follows: Hydrogen flow rate, 40 sccm; chamber pressure, 1 mbar; sample temperature from 250 °C to 350 °C; exposure time, 15 min. A detailed description of the apparatus has been given elsewhere.[13] For the rapid thermal annealing with a nitrogen atmosphere treatment, the temperature range is from 500 °C to 575 °C, and the annealing duration is fixed at 15 min.

For the PL measurements, the sample was placed inside a closed-cycle He cryostat. An argon ion laser working at 488 nm was used as the excitation source, which was modulated by a mechanical chopper. The luminescence signal was detected by a liquid nitrogen cooled InSb photodiode with a Hamamatsu P3357-02 preamplifier. These detected signals were connected to a lock-in amplifier, and were analyzed by a personal computer.

Figure 1 shows the 15 K PL spectra of $InAs_{1-x}N_x$/InGaAs SQW with nitrogen content 0.13% and 0.22%, before and after hydrogenation. We can see that the peak energy almost remains fixed after hydrogenation for both samples, but the PL intensity increases with increasing hydrogenation temperature. In order to understand the origin of the change, we analyze the thermal quenching of the PL spectra by the equation[18,19]

$$I_{\mathrm{PL}}=\frac{I_0}{1+C_1\exp\left(\frac{-E_{a1}}{kT}\right)+C_2\exp\left(\frac{-E_{a2}}{kT}\right)}. \qquad (1)$$

The low temperature PL efficiency is most likely controlled by carrier thermalization from spatial fluctuations of the band edges,[20] and followed by nonradiative recombination. The high temperature efficiency is dominated by a nonradiative path, which might be phonon emission by electron or exciton trapping at interfacial defects.[21] Thus, we define the E_{a1} as related to the localization energy, and the E_{a2} is the activation energy of nonradiative recombination process occurring at high temperature. As shown in Fig. 2, Eq. (1) can be used to describe our measurement very well. All the fitting parameters for sample B after hydrogenation at different temperatures are summarized in Table I. By comparing the results of E_{a1} of as-grown sample B with the same sample after hydrogen passivation, we find that E_{a1} decreases with increasing annealing temperature. The value of E_{a1} is 13.52 meV for the as-grown sample and 2.5 meV after hydrogenation at 350 °C. It indicates that hydrogenation can efficiently reduce the activation energy of localized carriers. In addition, as can be seen from Fig. 1, full width at half maximum (FWHM) of the PL spectra increases with increasing hydrogenation temperature.

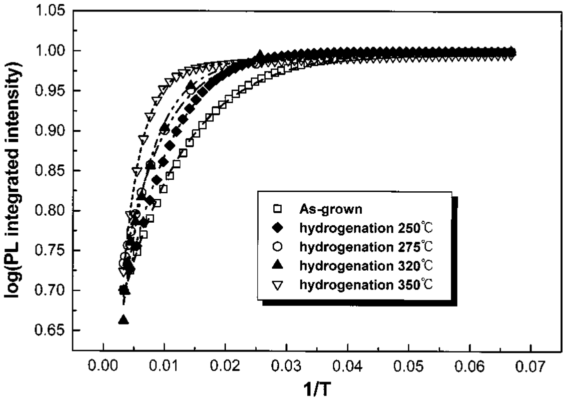

FIG. 2. Arrhenius plot of integrated PL intensity after hydrogenation at a different temperature for sample B. The dashed lines are the fitting results of Eq. (1).

By adapting the previous results of hydrogen passivation in semiconductors,[12–17] we believe that all of the aforementioned results can be attributed to the passivation of defects by atomic hydrogen. Because of the defect passivation, the PL intensity is enhanced. Additionally, because the number of carriers gone through the defect channel is reduced, more carriers can be used to fill the tail states of the band edge. Thus, due to this filling effect, the linewidth of the PL spectra becomes wider.

We now compare the result of hydrogenation with annealing under nitrogen atmosphere treatment. As can be seen in Fig. 3, after the postgrowth annealing under a nitrogen environment, the PL spectra have a blueshift, a higher intensity, and a sharper FWHM. It is worth noting that the sharper FWHM is quite different from that of hydrogenation in which the FWHM becomes wider as shown in Fig. 4. According to previous reports, these results can be attributed to the effects of As–N interdiffusion.[22,23] Because of the As–N interdiffusion, the InAsN layer tends to have a stronger alloy segregation due to the large immiscibility of the InAs–InN

TABLE I. All parameters fitted to Eq. (1) for sample B after hydrogenation at different temperatures.

Sample B	C_1	C_2	E_{a1}(meV)	E_{a2}(meV)
As-grown	0.154	0.364	13.52	7.667
Hydrogenation 250 °C	0.168	0.359	12.383	12.644
Hydrogenation 275 °C	0.157	0.372	11.736	16.611
Hydrogenation 320 °C	0.172	0.368	6.572	22.308
Hydrogenation 350 °C	0.167	0.361	2.50	31.16

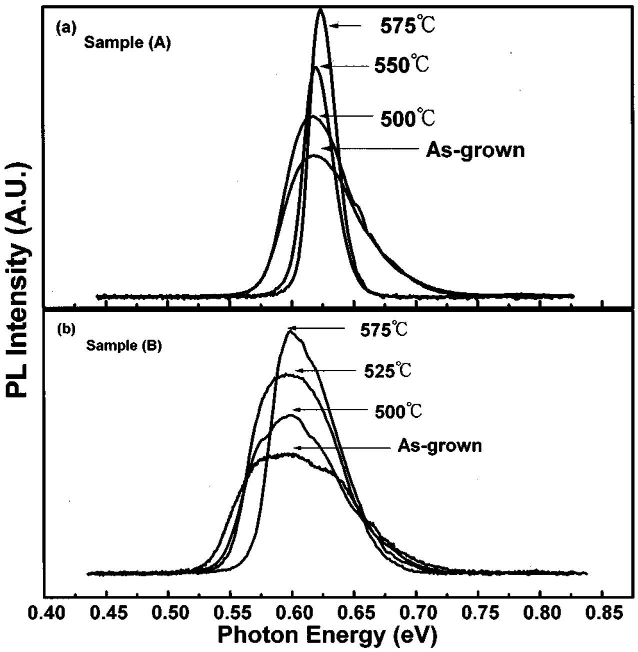

FIG. 3. Low temperature PL spectra of $InAs_{1-x}N_x$/InGaAs SQWs before annealing at a different temperature for 15 min under nitrogen atmosphere for (a) sample A and (b) sample B.

system, and hence the localization depth decreases. Thus, the PL spectrum is blueshifted and FWHM becomes narrower. Based on the different underlying origins, we therefore can understand the different behaviors between hydrogenation and nitrogen annealing. In addition, we can also infer that even though hydrogenation is an effective way to passivate defects in InAsN quantum wells, the As–N interdiffusion does not occur at the temperature of hydrogenation. Therefore, the depth of band tails remains the same, and the spectra do not have a blueshift.

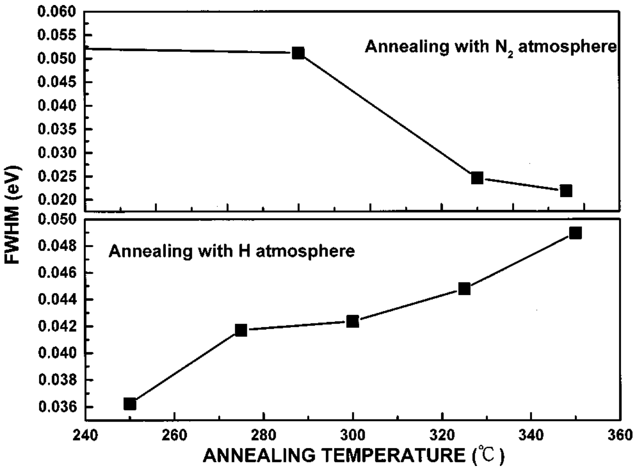

FIG. 4. Variation of FWHM of sample A after annealing at different temperature (a) nitrogen atmosphere (b) hydrogen atmosphere.

In summary, we have shown that hydrogenation is an effective way to passivate defects in InAsN alloys, and can be used to improve the luminescence properties. Our experiments have shown that the nitrogen atmosphere annealing treatment will induce As–N interdiffusion, which will decrease the potential fluctuations and reduce the linewidth. Comparing the nitrogen annealing and hydrogen treatment, we have found that the enhancement of the integrated PL intensity is larger for the case of hydrogenation. We therefore believe that hydrogenation is a more effective way to reduce defects in InAsN alloys than the process of rapid thermal annealing.

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