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Enhanced optical properties of InAs/GaAs quantum dots grown by radio-frequency hydrogen plasma-assisted molecular beam epitaxy

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Abstract
Strong enhancement of photoluminescence (PL) efficiency has been observed in a GaAs/InAs quantum dots-in-a-well structure, grown with *in situ* irradiation of atomic hydrogen supplied by a radio-frequency hydrogen plasma source. The PL enhancement and wavelength position at room temperature have been found to be stable under extensive thermal annealing up to 630 °C in vacuum. As shown by the corresponding improvement of the barrier material, the possible mechanism for PL enhancement is the reduced nonradiative recombination in the barrier region by *in situ* passivation of defects while they are generated.

(Some figures in this article are in colour only in the electronic version)

Many device applications of nanostructures, including InAs/GaAs self-assembled quantum dots, are often restrained or hampered by the unavoidable presence of imperfections due to mismatched materials, complicated growth process and low growth temperature generally employed for their formation. Many attempts have been reported to alleviate the negative effects using novel growth techniques [1] and post-growth annealing. Hydrogen has also been reported to passivate defects in bulk and quantum well materials [2] and, recently, the quantum dot structures [3]. It is also reported that continuous irradiation by atomic hydrogen during epitaxial growth is more efficient for passivation of misfit dislocations than after growth H-plasma treatment [4–6]. However, for most of the cases the improvement drops after thermal treatment above around 300 °C due to the escape of hydrogen at elevated temperature. Since stable thermal stability is desirable for device fabrication, the present work investigates the thermal stability of the improved optical properties due to hydrogen. In contrast to most of the previous work, *in situ* hydrogen exposure during growth was employed. Self-assembled InAs QDs embedded in a well structure were grown on a GaAs(0 0 1) substrate with a different exposure to hydrogen plasma generated with a radio-frequency plasma source. Order-of-magnitude enhancement in PL efficiency and peak wavelength have been maintained with up to 630 °C post-growth annealing in vacuum.

Epitaxial growth and plasma irradiation for the present work are carried out with the semi-production Riber Epineat reactor equipped with all solid sources and Veeco UNI-Bulb RF plasma source. The same equipment has been used to grow high-quality epitaxial materials previously [7]. High-purity (5 N) hydrogen gas has been supplied through two additional Millipore molecular filters and a flow rate controller to the RF plasma cell. Plasma source operated in high brightness mode at constant excitation power is equal to 400 W with zero return power. The QD structure used for the present study consists of 0.2 μm GaAs buffer, followed by a dot-in-a-well structure with 6 ML of InAs quantum dots grown in the S-K mode with 60 nm GaAs bottom barrier and 90 nm GaAs top barrier. This structure is surrounded by 150 nm thick $Al_{.3}Ga_{.7}As$ cladding layers on either side. Three identical structures, sample #84, #85 and #86, were grown under identical growth conditions except for the exposure to hydrogen plasma which was varied with the hydrogen flow rate at 0, 2, and 4 sccm. Plasma exposure was maintained from the time of oxide desorption at 250 °C to the time after growth when the substrate temperature again reached 250 °C. It took less than 5 minutes for oxide desorption at the substrate temperature of 250 °C without the As flux. Self-assembled InAs QDs have been grown in the S-K mode at 500 °C at a growth rate equal to 0.011 ML s^{-1} under the As_4 flux about 2.0×10^{-6} Torr. All the other layers have been grown at 600 °C under As rich conditions. The base pressure during H-assisted growth was about 2.7×10^{-6} Torr and 5.4×10^{-6} Torr for 2 sccm and 4 sccm of hydrogen flow rate respectively. After growth, the photoluminescence (PL) technique has been used to evaluate the optical quality of the grown samples and effects of post-growth annealing. The PL excitation source is the 488 nm line of argon-ion laser focused on a spot of about 400 μm in diameter and detected by the InGaAs photodiode. The PL intensity was calibrated with a standard sample to minimize the error of measurement to within 10%. The uniformity of the PL measurement near the center for the quarter of 2″ wafer sample was less than 5%. The size and density of the samples grown are around 5×10^9 cm^{-2} and the base diameter of the dots is estimated to be ~30 nm according to the TEM and AFM measurements. These parameters are consistent with the measurement room temperature PL peak wavelength of 1.28 μm and FWHM 30 meV.

After growth the samples were isochronally annealed for 1 h duration in vacuum about 10^{-8} Torr. During annealing, the sample surface has been covered by another piece of GaAs for protection from thermal decomposition. The temperature of annealing is measured with a thermal couple and calibrated with Al-Si alloy. All three samples #84, #85 and #86 were annealed in vacuum simultaneously. After each anneal, the PL spectrum was taken at room temperature with 1 mW excitation power.

Results of room temperature and low temperature PL spectra of as-grown samples are shown in figures 1(*a*) and (*b*), respectively. It can be seen that at room temperature the samples grown under the hydrogen plasma (#85, #86) show an order of magnitude increase from the reference sample (#84) with no hydrogen exposure. Increased hydrogen flow rate is also seen to increase the PL enhancement. The greatly enhanced PL intensity indicates improved crystalline quality. This is somewhat surprising since it is widely reported that plasma treatment is prone to defect generation due to the energetic ions present in the plasma source [8]. For each spectrum shown in figure 1(*a*), two PL peaks are present corresponding to the ground state and excited states of the QDs. The ground state peak wavelengths for the three spectra are around 1.28 μm, and the full width at half maxima (FWHM) of the main peaks are less than 30 meV. These three samples show almost identical spectra except for the intensity, indicating that similar QDs are grown under the hydrogen plasma. However at low temperature, the enhancement of the PL intensity is greatly reduced. As shown in figure 1(*b*), the three samples show comparable intensity. The peaks of the three samples are blue shifted with respect to those at room temperature by about 70 meV, very close to what is expected from Varshni's formula. The shape of the spectra shows some difference with excited state peak for the reference sample becomes less separated from the ground state when compared to its room temperature spectrum and the spectra for the other two samples grown with hydrogen plasma exposure. An attempt was made to understand the possible reasons of this difference. The deconvolution of the spectra of sample #84 with two Gaussian peaks results in a smaller separation of excited state to ground energy than that at room temperature. Since this is somewhat

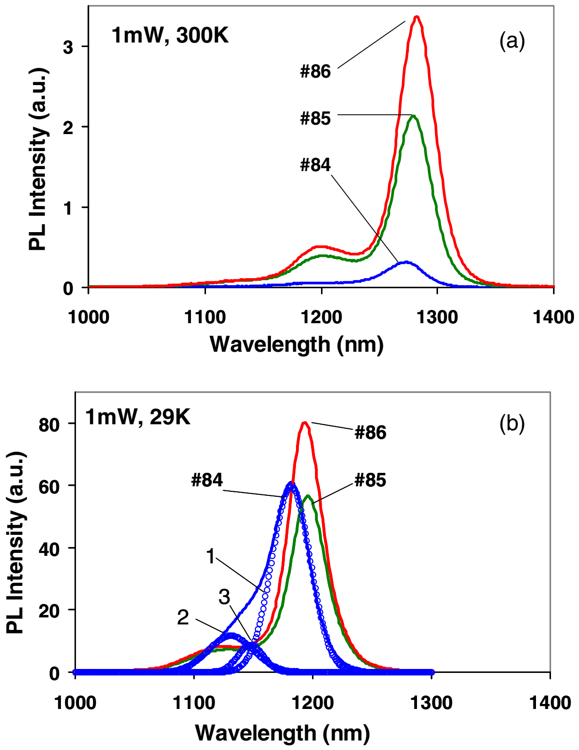

Figure 1. (*a*) Room temperature PL of three samples with peak wavelength ~1280 nm and FWHM ~30 mev; (*b*) low temperature PL with the three Gaussian deconvolution of sample #84 shown as small circles. The ground state, the excited state, and the ground of additional family of QDs are labeled 1, 2, and 3, respectively.

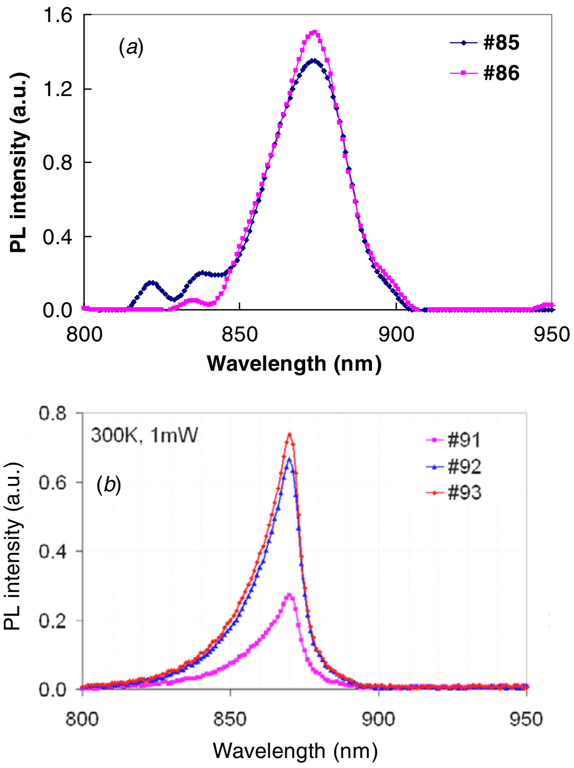

Figure 2. (*a*) Room temperature PL spectra around the GaAs bandgap transition showing the improved GaAs properties with hydrogen flow rate. The oscillations between 800 and 850 nm are due to noises; (*b*) room temperature PL spectra of GaAs layers grown with the same hydrogen exposure as the sample shown in figure 1.

unreasonable, a three Gaussian deconvolution was used and the results are shown in figure 1(*b*). The three Gaussian peaks labeled 1, 2, and 3 are, respectively, the ground state, the first excited state, and the ground state of another QD family of smaller size than the main family. The smaller size of this family of QDs results in a shallow depth from the barrier such that at room temperature carriers have enough thermal energy to escape from these shallow QDs and recombination takes place through the family of large QDs [9] or through the nonradiative recombination centers in the barrier. The extra peak is thus absent in the room temperature PL spectra (see figure 1(*a*)). This analysis indicates that the hydrogen plasma exposure may prevent the formation of this additional family of smaller QDs during growth. Detailed study is underway to clarify this point.

Similar observations on the reduced enhancement of the low temperature PL intensity have also been made by other research groups [10, 11] using *ex situ* hydrogen plasma irradiation of InAs QD samples. Qualitatively it has been explained by the rapid radiative recombination of excited carriers in QDs at low temperature, so a possible improvement of the surrounding material by hydrogen passivation cannot be revealed by PL measurement. But at higher temperatures excited carriers captured by QDs are able to escape and diffuse in the wetting and cladding layers. The properties of these layers play a more dominant role than the low temperature case. Since with the hydrogen exposure, the density of nonradiative recombination centers is reduced in these layers, the radiative recombination as observed with PL intensity is then increased over the sample with no hydrogen exposure. To provide more evidence for the above explanation, the properties of GaAs grown with the same conditions are examined below.

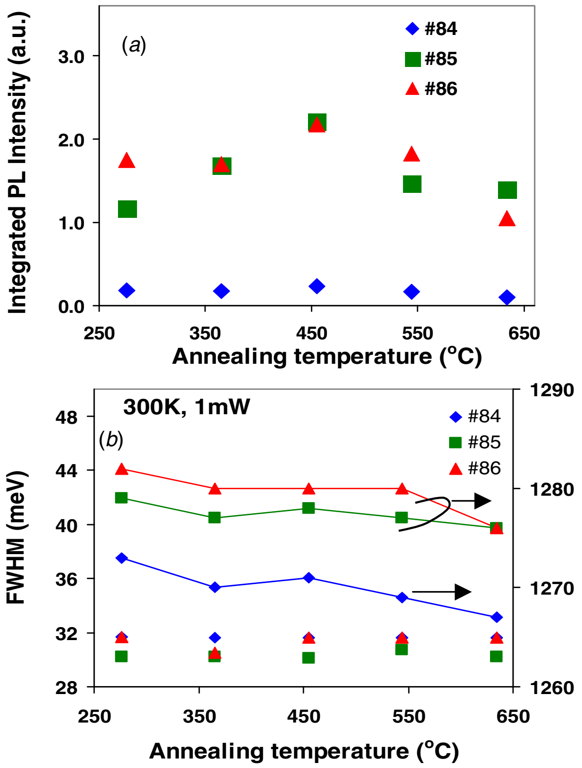

Figure 3. (*a*) Variation of integrated PL intensity with annealing temperature for 1 h isochronal annealing in vacuum. Annealing time was kept for 1 h at each temperature; (*b*) peak wavelength (right axis, in units of nm) and FWHM (left axis) changes after each annealing as a function of annealing temperature.

In PL measurement, most of the carriers are generated in the barrier layers followed by the diffusion and capture by the QDs, the properties of the barrier will affect the observed PL intensity. This is especially the case since the growth temperature for the adjacent part of the barrier is lower than the normal temperature for high material quality. To show that this is the case, the spectra corresponding to GaAs bandgap emission for the three samples are shown in figure 2(*a*). It can be seen that the PL intensity of GaAs peaks of sample #85 and #86 are increased with hydrogen flow rate while that due to #84 is too weak to be observed (not shown). To provide additional evidence for the improved GaAs properties with hydrogen exposure, a series of GaAs layers were grown at 600 °C under otherwise the same conditions as that of barrier layers for QD samples. The PL spectra for these separately grown GaAs samples are shown in figure 2(*b*). The PL intensity increased for the hydrogen-grown samples, indicating that the GaAs barrier properties are improved in the presence of hydrogen. The actual property of the GaAs barrier of the QD sample is probably improved more by hydrogen since, during the QD growth, the initial 60 nm of the barrier growth is under a temperature ramp to the steady temperature of 600 °C from the QD growth temperature of 500 °C. The explanation that the improvement of the GaAs barrier layer is responsible for the observed PL improvement has also been reported in the MOCVD growth of InGaAs/GaAs QDs using tetrachloromethane during growth, even though the growth and the test structures are very different [12].

From previous works on hydrogen passivation, the effect of hydrogen plasma treatment, as shown with the improved PL intensity, largely disappeared above 300 °C due to the out diffusion of hydrogen after the thermal treatment [9–11]. In order to investigate the thermal stability of the present enhancement effect, a one hour isochronal annealing was performed under ultra-high vacuum (UHV) conditions for temperature up to the congruent sublimation temperature. All three samples #84, #85 and #86 were vacuum annealed simultaneously, and after annealing PL was taken at room temperature with 1 mW excitation power. The integrated PL intensity of samples #85 and #86 along with the reference sample #84 after each annealing are shown in figure 3 as a function of annealing temperature. It can be seen that the enhancement of PL intensity for the sample grown under hydrogen plasma is maintained up to the growth temperature of 600 °C for the cap layer and to the final annealing temperature equal to 634 °C, slightly below the congruent sublimation temperature. Above that temperature, the intensity starts to drop as the surface of GaAs decomposes. The reference sample also shows the same trend. The peak wavelength and the FWHM after each anneal are also shown in figure 3(*b*). It can be seen that a slight blue shift in the wavelength is seen from all three samples which is a common behavior for the GaAs/InAs QDs under annealing. However the amount of blue shift is much less ($\sim$5 nm versus 100 nm) with annealing temperature for the present samples. The FWHMs also remain roughly unchanged.

In summary we have demonstrated some beneficial effects of hydrogen-assisted MBE with hydrogen plasma source. The room temperature PL intensity is about one order higher than the conventional hydrogen-free case. This improvement in PL properties is stable with extensive temperature annealing in vacuum. In contrast to prior works, the present case with RF H-plasma source shows no decrease in enhancement ratio with annealing temperature up to 634 °C with only slight blue shifts ($<$5 nm) and narrow FWHM of 30 mev at a peak wavelength of 1.28 μm. Such a stability of PL enhancement can be explained by the overall improvement of material (InAs, GaAs and AlGaAs) quality due to the reduced presence of defects or the passivation of their effects. These improvements are expected to be beneficial to device performances.

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