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In situ photoluminescence study of uncapped InAs/GaAs quantum dots

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Abstract

We present a study of photoluminescence (PL) from uncapped non-oxidized and oxidized InAs quantum dots (QDs) on GaAs substrate as a function of the thickness of a GaAs capping layer. A photoluminescence system in ultra-high vacuum that was coupled onto a molecular beam epitaxy chamber was used in order to avoid the oxidation of the quantum dot surface. We report for the first time a PL emission obtained from uncapped as-grown (non-oxidized) InAs QDs. We also report a dramatic change in the energy position and intensity of the PL as the quantum dots get closer to the top surface of the structure and make a direct comparison between the PL from non-oxidized and oxidized uncapped InAs/GaAs QDs. On the basis of these observations, we offer a physical explanation, based on oxidized versus non-oxidized uncapped QDs, for the discrepancies between previously reported results.

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

1. Introduction

Recent interest has been focused on the properties of self-organized InAs/GaAs quantum dots (QDs) due to their potential for electronic and optoelectronic device applications [1–4]. In most cases, results were obtained on QDs completely covered by a GaAs cap layer. The properties of QDs, however, are strongly dependent on their size, shape, density, or cap layer thickness [5, 6]. Therefore, the thickness of the cap layer can have a strong influence on the QD photoluminescence (PL) features. On the other hand, exposed (uncapped) QDs see a high surface potential (atmosphere) which can result in a significant shift of the energy levels [7, 8]. Moreover, surface states, strain relaxation, and oxidation (due to air exposure) can also play an important rule in the optical properties of the exposed dots [9, 10]. While these effects are important, to our knowledge, the optical properties of InAs QDs grown on a GaAs surface without or nearly without a cap layer (uncapped QDs), has not been explored until recently [8–12]. For example, Fafard [12] studied the energy levels of near-surface InAs QDs by observing the electronic shells of the QDs using state filling spectroscopy (77 K), and observed a red shift of 65 meV while decreasing the GaAs barrier from 100 to 6 nm. He suggested that the red shift was due to partial relaxation of QD strain allowed by a thin capping layer. However, for a 5 nm cap sample he reported a weak PL signal with a blue shift which he explained as due to a high (atmospheric) surface potential. Consistent with these results, Wang *et al* [8] investigated the PL (77 K) of the exposed InAs QDs on GaAs surface. They reported two PL peaks, due to two different groups of QDs, with energies higher than the conventional embedded QDs. They also explained that the blue shift was due to the strong lateral confinement resulting from the high surface potential. Meanwhile, Miao *et al* [9] observed a large red shifted PL emission from uncapped InAs QDs compared to completely capped QDs. They explained this red shift by the strain relaxation and the strong coupling of the confined states with surface states. These seemingly contradictory results suggest that it would be interesting to study the influence of atmospheric or air exposure on the optical properties of uncapped QDs.

In this paper, we report for the first time in the literature a PL emission from uncapped as-grown (non-oxidized) InAs/GaAs QDs obtained from a perfect reconstructed InAs surface in an UHV system. We also report on a drastic change in the energy position and intensity of the PL as the QDs get closer to the top surface of the structure and make a direct comparison between the PL from non-oxidized and oxidized

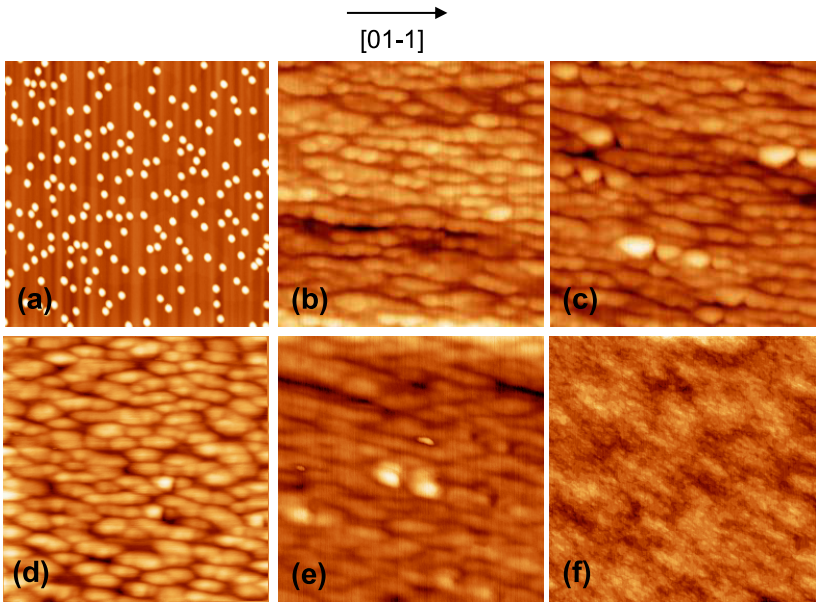

Figure 1. (1 μm × 1 μm) AFM images of InAs QD with 8 nm height covered by (a) 0, (b) 2, (c) 4, (d) 7, (e) 10, and (f) 50 nm of GaAs cap layer.

uncapped InAs/GaAs QDs. Based on these observation, we also offer a physical explanation for our observation and for the discrepancies between previously reported results.

2. Experimental details

The samples studied here were grown using a solid-source molecular beam epitaxy chamber connected to a PL system under ultra-high vacuum (UHV). A 0.5 μm GaAs buffer layer was grown on semi-insulating (100) GaAs substrates at 580 °C after oxide desorption. This was then followed by 2.2 ML of InAs and the formation of QDs at 520 °C. The dots were obtained using the Stranski–Krastanov growth mode. Cycles of 0.14 ML of InAs plus a 2 s interruption under As_4 flux were repeated until the total 2.2 ML of InAs was deposited. The QDs were next annealed for 20 s to improve the QD size distribution. The evolution of the dots was detected using *in situ* reflection high-energy electron diffraction (RHEED). The dots were then capped with 2, 4, 7, 10, and 50 nm of GaAs cap layers grown at 520 °C. InAs and GaAs growth rates were set to 0.065 and 1 (ML) s^{-1}, respectively. The PL measurements was performed in a modified Omicron variable temperature scanning tunneling microscopy (VT-STM) chamber under UHV that was maintained to be better than 10^{-10} Torr. A set of optics inside and outside the VT-STM were used to carry out the PL measurements [13]. The VT-STM chamber was coupled to a Riber MBE system in order to avoid oxidation of the semiconductor surface. The PL measurements were performed over a temperature range of 77–300 K under excitation of a 632.8 nm line of a helium–neon laser. The luminescence was detected by a cooled InP/InGaAs photomultiplier tube (Hamamatsu R5509-73) mounted on 0.5 m monochromator. After carrying out the PL measurements, the samples were moved from the UHV chamber to an *ex situ* atomic force microscope (AFM) to study the surface morphology, and then returned back to the UHV chamber to compare the PL before and after oxidation of the uncapped dots.

3. Results and discussion

Figure 1(a) shows an AFM image of the uncapped QDs with a typical dot size of ∼8 nm in height and ∼30 nm in diameter. The average QD density is about 2×10^{10} cm^{-2}. From the AFM images of the partially capped dots in figure 1, we observe that with increasing cap layer thickness, the surface changes from a domed dot to an elongated line-like dot along $[01\bar{1}]$ with a height of ∼2 nm. Since we started with dots of a height of ∼8 nm, the surface is not fully flattened by the 10 nm cap layer while with a 50 nm cap layer the surface was atomically flat. A change in the balance of the surface free energy due to the thin capping layer causes indium atoms to diffuse into the surrounding GaAs crystal and brings about material redistribution results in line-like QDs [14] in the $[01\bar{1}]$ direction due to expected anisotropic surface diffusion of group III migrating atoms.

Figure 2 shows the PL spectra under UHV at 77 K of the (a) non-oxidized covered InAs QDs with 50 nm GaAs cap layer, (b) uncapped non-oxidized InAs QDs, and (c) uncapped oxidized (due to air exposure) InAs QDs. The PL spectrum (a) in figure 2 of the non-oxidized capped dots with a 50 nm GaAs capping layer shows two peaks. The first peak at 1.066 eV with a full width at half maximum (FWHM) of 30.2 meV is due to the optical transition between the lowest lying confined valence and conduction states in the QD. Likewise, the second PL peak at 1.136 eV is due to a transition between the first excited states in the QD. In particular, an excitation power dependent PL study showed one peak at low intensity and two at higher intensities to confirm that these two peaks are related to the ground and excited states of the capped QDs.

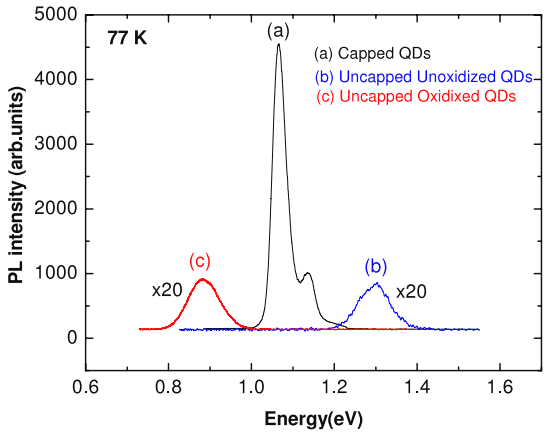

Figure 2. The PL spectra at 77 K and under UHV of the (a) non-oxidized covered InAs QDs with 50 nm of GaAs cap layer, (b) non-oxidized uncapped InAs QDs, and (c) oxidized uncapped InAs QDs.

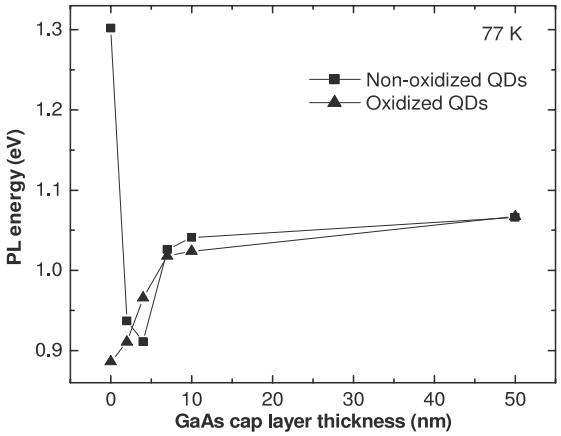

Figure 3. Energy of PL emission from non-oxidized (squares) and oxidized (triangles) InAs QDs at 77 K with different thickness of GaAs cap layer.

The PL spectrum (b) in figure 2 of the non-oxidized uncapped InAs QDs shows one peak at 1.302 eV with a FWHM of 90 meV. This peak can be interpreted as the optical transition to the ground state of the uncapped QDs. Clearly, capping the exposed dots with a 50 nm GaAs cap layer decreases the ground state emission energy of the dots by 236 meV. Along with the observed spectral difference there is also a large decrease in the PL intensity of the uncapped dots which is expected due to the increase of nonradiative recombination of the electron–hole pairs via surface states [9, 10, 15]. Moreover, for the uncapped QDs the FWHM of the ground state emission is three times larger than for the QDs with the 50 nm thick cap layer and is likely due to the surface roughness of the uncapped QDs [7, 15]. These results agree with those of Fafard [12] and Wang *et al* [8].

The PL spectrum (c) in figure 2 of uncapped dots after exposing them to air also shows one peak but substantially red shifted at 0.886 eV. This peak can be interpreted as the optical transition between the lowest lying states of the uncapped dots. These results are in agreement with those of Miao *et al* [9]. Apparently, oxidation of exposed QDs plays a significant role in the observed PL spectra. In order to understand the luminescence feature of InAs uncapped dots, the evolution of the PL with capping thickness was studied.

In figure 3, the energy of PL emission from non-oxidized (squares) and oxidized (triangles) QDs under UHV at 77 K, as a function of cap layer thickness is summarized. For the non-oxidized QDs, we first see red shift from 1.066 to 0.911 eV with decreasing cap layer thickness from 50 to 4 nm, and then we observe a dramatic blue shift to 1.302 eV while decreasing the cap layer thickness from 4 to 0 nm. It seems that there is probably a competition between two effects causing this big conversion in energy when we get closer to the surface of dots (less than 4 nm) and this will be discussed next. The red shift can be explained by the relaxation of strain in the uncovered and close to the surface InAs QDs, which cause a band gap reduction. Uncapped InAs QDs have a lattice constant larger than GaAs, they strain relaxed, and the largest strain relaxation occurs at the top of the QD [9]. The deposition of GaAs will tend to force the lattice constant back to the GaAs, and the resulting buried QDs are more strained than before capping [9]. Similar behavior has been reported by Miao *et al* [9], where they estimated a change in the InAs QDs energy gap of about 195 meV due to strain relaxation after removing the GaAs capping layer. On other hand, as the QDs get closer to the surface the structure changes from a finite GaAs barrier to quasi-infinite surface potential in UHV. In particular, the structure of the uncapped QDs can be considered as InAs QDs between two different barriers, one is the GaAs and the other is the ∼5 eV vacuum potential at the surface. The high surface potential can perturb the wave functions of the QDs near the surface casing a blue shift of the QD energy levels [7, 8, 12]. In this case, there is competition between two effects (a blue shift from the high surface potential and a red shift from strain relaxation) resulting in a net blue shift for the exposed dots. Our observations and explanations are therefore very consistent with the previous studies [7, 12].

To study the effect of oxidation due to air exposure on the uncapped dots, the samples were removed from the UHV chamber for several days and then returned to the UHV chamber to carry out a PL comparison. Looking at the PL emission evolution of the oxidized QDs in figure 3, we can see an energy shift from 1.067 to 0.966 eV with decreasing cap layer thickness from 50 to 4 nm. This behavior is similar to what we observed for non-oxidized QDs. On the other hand, with decreasing cap thickness to 0 nm, however, we observe a dramatic red shift to 0.886 eV. This behavior is opposite to what we observed for non-oxidized QDs. Here, however, as opposed to structure changes from a finite GaAs barrier to quasi-infinite surface potential in UHV, a decreasing cap layer brings the surface to a fixed thickness of oxide. That is, with air exposure of the uncapped QD sample, the InAs QDs and surrounding wetting layer are likely to be oxidized in air [16, 17]. The vacuum potential has been found from theoretical calculations and ultraviolet photoemission spectroscopy to be ∼5 eV [7, 18], with an oxide layer at the surface this value is expected to be lowered [7]. This effect and the strain relaxation results in the net red shift of 180 meV in the PL observed in this work from uncapped oxidized QDs

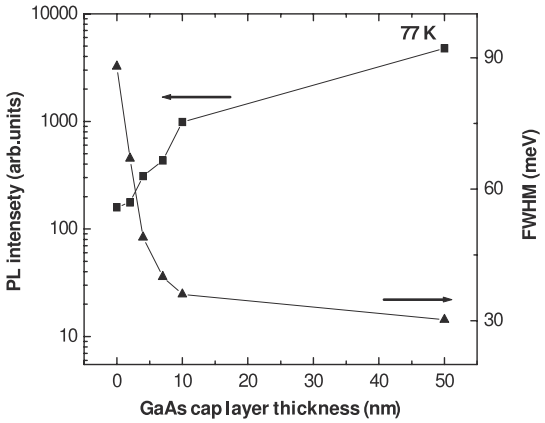

Figure 4. Intensity and FWHM of PL emission from non-oxidized QDs at 77 K with different thickness of GaAs cap layer.

compared to the capped with 50 nm GaAs QDs. This is in agreement with what has been reported by Miao *et al* [9] where they estimated a change in the InAs QDs energy gap of about 195 meV.

Figure 4 shows the evolution in the PL intensity (left axis), and the evolution in FWHM (right axis) of the non-oxidized QDs with the cap thickness. It is seen from the left axis that the PL intensity decreases with decreasing the cap thickness from 50 to 0 nm. The PL intensity of the oxidized QDs showed a similar behavior to that of non-oxidized QDs. At 50 nm cap layer the dots are deeply buried and their PL intensity shows no influence from the surface. At cap layer thickness less than 10 nm the PL intensity begins to decrease drastically due to the influence from the surface. From 10 to 0 nm cap thickness the PL intensity continues to decrease till it is 20 times lower than that of 50 nm cap layer thickness. The strong decrease in the PL intensity with decreasing the GaAs cap thickness can be explained as follow. In case of completely capped InAs QDs with GaAs cap layer, carriers can efficiently be redistributed in QDs through channels of both GaAs barriers and the underlying InAs wetting layer [8]. In the case of completely uncapped and close to the surface QDs, photoexcited carriers can hardly move from one QD to another because there is no confined electron states in the InAs wetting layer, and there are unavoidable surface defects states that trap the carriers [8]. We can say that the strong decrease in the PL intensity is due to the nonradiative recombination at the surface of the uncovered InAs QDs [7, 8], and the competition between the capture of photo carrier in the QDs and the surface states. A similar behavior was also reported by [7, 10].

It is seen from the right axis of figure 4 that the FWHM of the non-oxidized QDs increases continuously with decreasing the cap layer thickness. The FWHM of the QDs with 50 nm thick cap layer is three times smaller than for the completely uncapped dots. Surface roughness [7] and strain relaxation effect [12] is believed to cause the broadening of the uncapped dots PL spectra. The oxidized uncapped QDs showed a qualitatively similar behavior, though the line widths were slightly bigger than those of the non-oxidized QDs and this could be due to additional roughness may result from fluctuations caused by the uncontrolled formation of an oxide layer at the surface.

4. Conclusion

In summary, we report a dramatic change in the energy position and intensity of the PL as the QDs get closer to the top surface of the structure and make a direct comparison between the PL from non-oxidized and oxidized uncapped InAs/GaAs QDs. Based on these observations, we offer a physical explanation based on oxidized versus non-oxidized uncapped QDs for the discrepancies between previously reported results.

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