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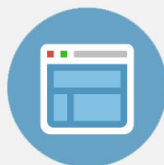
InAs quantum dot morphology after capping with In, N, Sb alloyed thin films

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Using a thin capping layer to engineer the structural and optical properties of InAs/GaAs quantum dots (QDs) has become common practice in the last decade. Traditionally, the main parameter considered has been the strain in the QD/capping layer system. With the advent of more exotic alloys, it has become clear that other mechanisms significantly alter the QD size and shape as well. Larger bond strengths, surfactants, and phase separation are known to act on QD properties but are far from being fully understood. In this study, we investigate at the atomic scale the influence of these effects on the morphology of capped QDs with cross-sectional scanning tunneling microscopy. A broad range of capping materials (InGaAs, GaAsSb, GaAsN, InGaAsN, and GaAsSbN) are compared. The QD morphology is related to photoluminescence characteristics. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4864159]

Tailoring the optical properties of InAs/GaAs quantum dots (QDs) by using a thin capping layer (CL) composed of a different material has become a common approach in the last decade. Strain reducing layers such as InGaAs and GaAsSb have been used to extend the emission wavelength of InAs QDs to the 1.3–1.55 μm telecommunications region and improve the photoluminescence (PL) characteristics.[1–6] Tensile strained GaAsN can be used as a strain compensation layer that allows the growth of stacked QD layers of high quality and uniformity.[7] Studies report an improvement of the optical properties for low N contents, accompanied by a red shift of the PL peak energy.[7,8] The quaternary alloy InGaAsN also induces strong red shifts[9,10] and long wavelength light emitting diodes have been fabricated with this approach.[11] More recently, capping with GaAsSbN has been shown to allow independent tuning of electron and hole confinement in QDs through the N and Sb content.[12] This system allows a huge versatility for band structure engineering, allowing tuning of the band alignment from type-I to different type-II configurations.

The impact of capping layers on the properties of QDs is complex. While traditionally the main effects were considered to be the modified band offsets and strain inside the QDs, it has become clear that capping layers can significantly alter the QD size and shape by affecting intermixing processes during capping.[13] One of the main driving forces behind the intermixing process is the lattice mismatch between QD and capping layer, leading to mass transport away from the QDs during capping.[14] The degree of QD erosion can be finely tuned by varying the lattice mismatch, i.e., the strain induced by the capping layer.[13,15] Besides this strain driven mechanism, surface diffusion plays an important role in determining the final QD shape as well. Larger N related bond strengths and the surfactant effect of Sb directly influence the surface diffusion and thereby the QD/capping layer morphology. A third mechanism that exerts control over the final QD shape is phase separation. The simultaneous presence of In and N, or Sb and N, in the capping layer can give rise to a non-uniform alloy. The presence of one element can influence the incorporation and the spatial distribution of the other.[16,17] All three mechanisms (strain driven mass transport, surface diffusion, phase separation) should strongly affect the electronic structure and optical properties of the QDs. To fully exploit the possible advantages of the different capping materials and the above mechanisms, a deeper knowledge of the final QD/capping layer morphology is needed. Not only the QD size and shape but also the actual composition of the capping layer around the QD is a critical parameter, which in most cases have not been studied at the atomic scale. This study aims to fill this gap in understanding by investigating the QD/capping layer morphology with cross-sectional scanning tunneling microscopy (XSTM). A broad range of capping materials (InGaAs, GaAsSb, GaAsN, InGaAsN, and GaAsSbN) are compared.

The QDs were grown by depositing 2.7 monolayers (MLs) of InAs by means of molecular beam epitaxy (0.04 ML/s). After 20 s under As overpressure, a 5.0 nm thin film of alloys containing In, N, and Sb is grown (no soak time), see Table I, followed by 10 MLs of GaAs. In samples A and B, the QDs and capping layer were grown at 450 °C and 470 °C, respectively. In sample C, the temperature was lowered by 15 °C for both layers. Next, a 50 nm thick spacer of GaAs is grown at 580 °C. In order to characterize the QDs before capping, QDs were grown on the surface of samples A and B. In addition, single layered samples were grown under the same conditions as layers 1, 2, and 3 in sample A and layers 1 and 3 in sample C for PL studies.

The XSTM measurements were performed under UHV conditions on *in situ* cleaved (110)-surfaces. All measurements were done at high negative bias voltage and low tunnel current ($V \approx -3$ V, $I \approx 40$ pA). At these conditions and with the color scale used, InAs rich regions appear bright compared to GaAs, and individual N (Sb) atoms show up as dark (bright) spots, respectively.

The average height (as measured by atomic force microscopy) and standard deviation of the uncapped QDs in

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TABLE I. Average height and standard deviation (σ) of the observed QDs in the different samples and layers. The layers marked with × could not be imaged due to bad cleavage.

	#	Capping layer material	Height (nm)	σ (nm)
Sample A	1	GaAs	3.1	0.5
	2	GaAsN, 1.0% N	3.4	0.3
	3	GaAsN, 2.5% N	3.6	0.5
	4	GaAsN, 4.0% N	×	×
Sample B	1	InGaAs, 8.0% In	3.2	0.4
	2	GaAsN, 2.5% N	3.3	0.5
	3	InGaAsN, 8.0% In, 2.5% N	4.1	0.4
	4	InGaAsN, 8.0% In, 4.0% N	4.0	0.5
	5	InGaAsN, 20.0% In, 4.0% N	×	×
Sample C	1	GaAsSb, 8.0% Sb	2.8	0.3
	2	GaAsN, 2.5% N	2.7	0.4
	3	GaAsSbN, 8.0% Sb, 2.5% N	3.1	0.3
	4	GaAsSbN, 8.0% Sb, 4.0% N	3.1	0.4
	5	GaAsSbN, 20.0% Sb, 4.0% N	×	×

samples A and B was found to be 5.1 nm ($\sigma = 0.7$ nm) and 5.2 nm ($\sigma = 0.6$ nm), respectively, confirming that the QDs in both samples are identical before capping.

We first turn our attention to the GaAsN capping layers in sample A. Figure 1(a) shows a XSTM image of the wetting layer (WL)/capping layer in layer 3. The darkest features (marked by an arrow) are N_{As} substitutional impurities in the surface plane. By counting the individual N atoms in one atomic plane, a composition profile along growth direction can be composed, see Figure 1(b). Although the statistical error is large, an average N content of $2.3 \pm 1\%$ is obtained, in agreement with the nominal 2.5%. As shown by the composition profile, N starts to be incorporated one bilayer above the start of the WL. The GaAsN layer is 5 nm thick, in perfect agreement with the intended value, and no significant N clustering is observed. The top interface is abrupt, indicating that there is no N carryover in the growth direction. This in contrast to In and Sb which are found to strongly segregate in the growth direction, as expected.[18] The reduced segregation and absence of N clustering are attributed to the larger N related bond strength.

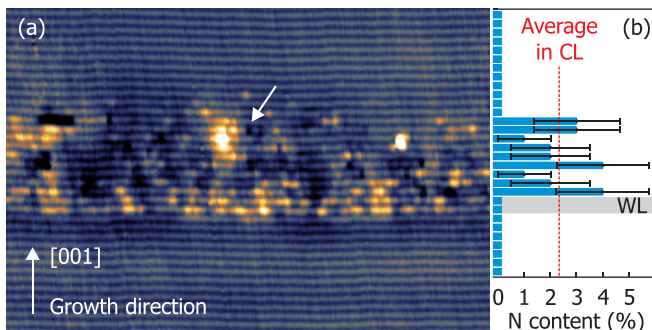XSTM images of typical QDs are shown in Figure 2. We were unable to image the last layer in all samples due to bad

FIG. 1. (a) 20 nm × 30 nm XSTM image of layer 3 in sample A (GaAsN capping), showing the WL/CL. (b) N concentration along the growth direction.

cleavage at that position, a common problem with highly strained samples. The average QD height was determined by counting the atomic layers for an ensemble of QDs and is given in Table I. The height of the capped QDs has been reduced compared to the uncapped QDs. As mentioned before, QD erosion upon capping is a well known effect driven by strain gradients.[14] Comparing the layers in sample A, we find that the QD height increases with increasing N content. Various studies report an increase in QD height when capping with a compressively strained layer.[13,15] In such a case, the strain gradients around the QDs are lowered by better lattice matching between the QD and capping layer material, reducing the mass transport to the WL during capping. In our case of a tensile strained GaAsN capping layer, the strain gradients around the QDs increase and we would expect an increase of QD erosion. However, we observe the opposite. Besides the difference in strain gradients, there is one notable difference between the current system and previously reported compressively strained QD/capping layers: Ga–N bonds are stronger than Ga–As bonds. This larger N related bond strength could reduce intermixing and surface diffusion during capping, thereby limiting QD erosion and increasing the final QD height.

It is generally assumed that N is incorporated as a homogeneous thin film on top of the whole QD layer. However, no atomically resolved study on the exact incorporation position of N atoms in GaAsN capped InAs QD layers exists. We observe that the GaAsN capping layer in samples A and B is not homogeneous; few N atoms are found directly on top of the QDs. The incorporated N atoms are mainly observed in the segregated WL. We estimate that the N incorporation is reduced by 90% on top of the QDs. This is not the case in sample C where the N is more uniformly distributed. Note that sample C was grown at a lower temperate. Since there is a big difference in lattice constant between InGaAs (QDs) and GaAsN (capping layer), N adatoms will tend to migrate away from the top of the QDs during the growth of the capping layer giving rise to the phase separation observed in samples A and B. However, the mobility of the N adatoms in sample C is reduced due to the lower growth temperature forcing N incorporation on top of the QDs. This shows that the position of N incorporation is very sensitive to the growth temperature and that phase separation might occur.

The XSTM measurements provide us with a unique data set to relate PL spectra to the morphology of the QD layers. In Figure 3, PL spectra of the QDs in the single layered set of sample A are shown. The PL peak position is found to red shift with increasing N content in the capping layer. The XSTM results show that the QD in layers 2 and 3 is higher than in layer 1. The increased height might be the reason for the observed red shift. However, the QDs in layer 3 are of nearly equal height than those in layer 2 whilst the PL red shift is much larger (79 vs. 26 meV). This rules out the increased height of the QDs as the sole cause for the red shift. The XSTM images show that there is no intermixing of N with the InAs QDs. Two options remain to explain the redshift: a reduction of the conduction band offset due to the presence of N outside the QDs or a change in the strain field inside the QDs. Previously, an extensive theoretical study showed that the strain inside InAs QDs is only marginally
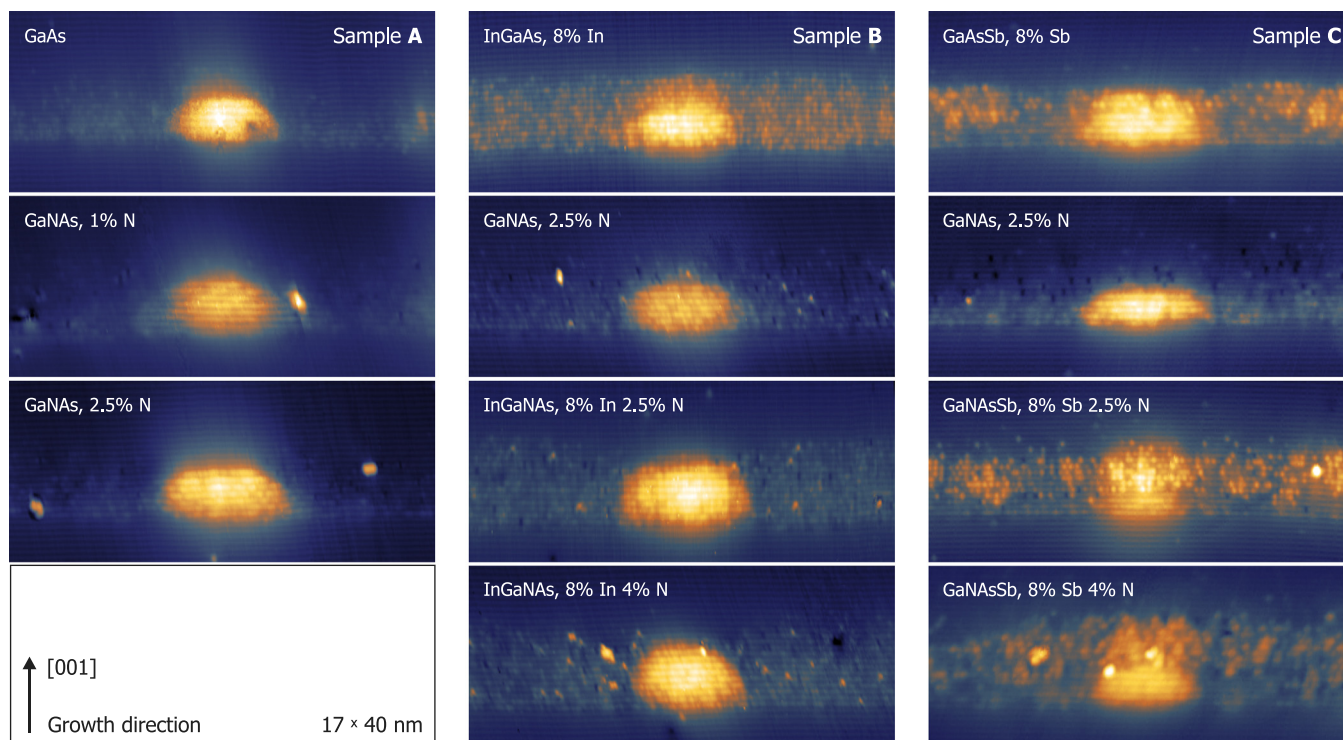
FIG. 2. Overview of typical QDs in the different samples and layers. All images are to the same scale.

affected when capping with GaAsN.[8] Given this, we suggest that the main cause for the PL red shift is the reduction of the electron confinement potential due to the presence of N in direct vicinity of the QDs. An interesting feature of the PL spectra is the strong improvement in L2 and degradation in L3 in terms of full width at half maximum (FWHM) and integrated intensity. These results are similar to those in Refs. 19 and 20. It is well known that non-radiative recombination centers appear during the growth of GaAsN and lead to degradation of the PL characteristics.[21] The current results indicate that N induced defect density is negligible for N contents around ≈1% but becomes quite relevant at higher contents of ≈2.5%.

We now turn our attention to sample B which was grown to study the interplay of In and N in the capping layer. The first capping layer consists of InGaAs without N. The capping layer is found to uniformly cover the QDs, see Figure 3. The presence of In results in a non-abrupt top interface in which the In content gradually decreases along the growth direction.
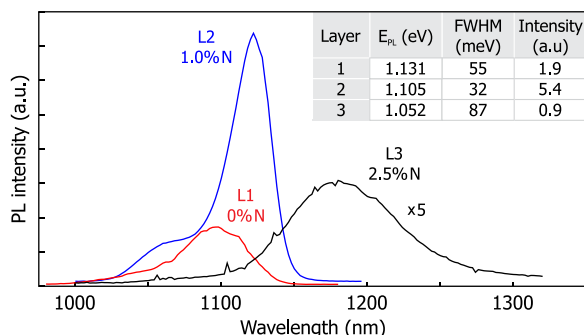

FIG. 3. PL spectra of the QDs in the single layered set of sample A (GaAsN capping).

In layer 2, a GaAsN capping layer is used. The height of the QDs is comparable to those in layer 1 (3.3 vs. 3.2 nm). As in sample A, the N is uniformly distributed in the capping layer but is absent directly above the QDs, which have a sharply defined top interface. In layers 3 and 4, InGaAsN capping layers are used. The result is a significant increase in QD height (3.1 nm vs. 4.1 nm). Just as in layer 2 (GaAsN capping), the capping layer is found to be absent directly above the QDs; both the In and N present in the capping layer migrate away from the top of the QD, which as a result is covered by pure GaAs. Despite this mass transport of capping layer constituents, intermixing with the InAs in the QD is reduced since the QD height is significantly increased and a sharp top interface is observed. The fact that there is not even InGaAs on top of the QD means that the quaternary alloy has a collective behavior in which phase separation into the ternaries, which in this case should be enhanced by the strain field of the QD, does not occur. This indicates that the In present in the capping layer is forced to migrate away from the QD by the presence of N.

The situation is different in sample C, which was grown at a lower temperature, yielding lower QDs compared to the other samples. In layer 2, the GaAsN capping layer is now covering the QDs, although there is less N present on top of the QD (≈50%) than elsewhere in the layer; N is present only in the first 4 MLs directly above the QDs, while it is observed up to 8 MLs above the QD interface level in the proximity of the QDs. This indicates that there is still some N migration away from the top of the QDs and that even lower growth temperatures are required to fully suppress this effect. In case of GaAsSbN capping (layers 3 and 4), the resulting configuration is opposite as with InGaAsN capping. The GaAsSbN capping layer is fully covering the QDs but is absent directly
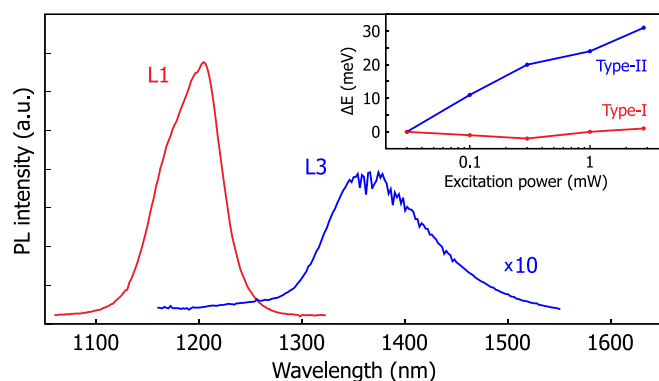
FIG. 4. PL spectra of the QD layers in the single layered set of sample C (GaAsSbN capping). (Inset) PL peak position shift of L1 and L3 as function of excitation power.

at the side facets where no Sb is observed. Furthermore, a clear compositional modulation takes place on top of the QDs forming a Sb-rich region. This is in agreement with results from scanning transmission electron microscopy studies on similar samples.[22] Since the accumulation of Sb on top of the QDs is not observed with GaAsSb capping (layer 1), it must be due to the concomitant presence of N and Sb. Despite the lower growth temperature, the quaternary alloy reorganizes itself, likely to minimize strain, giving rise to a final complex configuration. Independently of the growth temperature, it is clear that the two quaternary alloys we have used behave very differently. They show opposite mass transport phenomena: from the QDs to the surrounding capping layer with InGaAsN capping and *visa versa* with GaAsSbN capping. As the lattice mismatch between the QDs and the capping layer is similar in both cases, the different behavior of In (group III) and Sb (group V, surfactant) at the growth front should be at the origin of this difference.

All these modifications in the QD/capping layer morphology should have a strong influence on the electronic structure and optical properties of the QDs. Figure 4 shows PL spectra of the QDs in the single layered set of sample C. A red shift of 119 meV is obtained when adding 2.5% N to the GaAsSb capping layer whilst the PL degrades (the FWHM increases and the integrated intensity decreases). The PL degradation is in agreement with what was observed for sample A and can be attributed to an increase of the N-induced defect density.

The observed Sb accumulation on top of the QDs could be determinant regarding the band alignment of the structure, as PL measurements as function of the excitation power seem to indicate. The inset of Figure 4 shows the PL peak energy shift as a function of excitation power. Whilst there is no significant shift for L1 (GaAsSb capping), a clear blue shift is observed for L3 (GaAsSbN capping). This blue shift typically arises from the band bending effect induced by the spatially separated photoexcited carriers in a type-II band alignment.[23] The N induced shift of the GaAs conduction band has been estimated from the band anti-crossing model and measured to be around 300 meV for 2.5% N content.[24] Taking into account that the QD/GaAs barrier in standard InAs/GaAs QDs is in the 400–500 meV range,[25] it can be roughly estimated that the transition to a type-II system in

the conduction band would take place around 4% N content. Having a 2.5% N content, the band alignment in the conduction band should still be type-I in our case. Therefore, the type-II alignment is likely induced by Sb. Containing the same overall amount of Sb as L1, the local rearrangement (phase separation) of material within the capping layer induced by the presence of N results in a transition from a type-I to a type-II band alignment. Since GaAsSb-capped InAs QDs are known to have a type-II alignment in the valence band for a Sb content above 16%,[5,6] the compositional modulation observed in our GaAsSbN-capped QDs yields a content higher than this value.

To summarize, we have investigated the morphology and PL characteristics of InAs QDs after capping with ternary (GaAsN, InGaAs, GaAsSb) and quaternary (InGaAsN, GaAsSbN) thin films. Adding N to GaAs capping layers reduces QD erosion during capping (attributed to reduced intermixing and surface diffusion due to large N related bond strengths) and red shifts the PL peak position due to a reduction in the electron confinement potential. At low N contents (≈1%), the N induced defect density is found to be negligible whilst the PL characteristics are improved. Our results show that the position of N incorporation is very sensitive to the growth temperature but can be accurately controlled. Quaternary capping layers result in more complex QD morphologies. The InGaAsN alloy behaves as a collective in which phase separation does not occur. This is in contrast to the GaAsSbN alloy where the presence of N results in compositional modulations: Sb-rich regions form on top of the QDs. As a result of the phase separation, the band alignment is tuned from type-I to type-II. The current results illustrate the importance of strain driven mass transport, surface diffusion, and phase separation in determining the final QD/capping layer morphology and shows how subtle effects related to the local morphology can strongly influence the electronic structure and optical properties of QDs.

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