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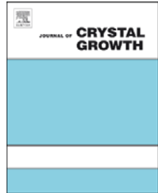

Morphology and stress evolution of InAs QD grown and annealed *in-situ* at high temperature

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ABSTRACT

The post growth annealing of InAs quantum dots (QDs) at relatively high temperature was investigated by an *in-situ* stress cantilever beam setup. For samples annealed at 500 °C, stress accumulated during QD formation relaxes below the value which was built-up during wetting-layer growth. AFM images taken at different annealing stages reveal that QDs ripen first and then dissolve within 10 min of annealing. These observations are explained by a combination of In desorption, especially at the beginning of annealing, and interdiffusion between Ga and In.

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1. Introduction

Quantum dots (QDs) have been investigated in recent years because of their potential applications for optoelectronic devices [1]. One of the most common methods of QD preparation is heteroepitaxial growth in the Stranski-Krastanow mode. The driving force for the transition from 2D layer-by-layer growth to 3D dot growth is the mismatch stress which is accumulated during 2D growth and then partially relaxes by the formation of 3D dots. Upon post growth annealing, 3D dots usually undergo morphological changes whereby the misfit stress is further reduced. In the case of InAs QDs on GaAs(001), ripening from small to large dots (Ostwald-ripening) has been reported [2,3]. For InAs QDs on GaAs(001) annealed at high temperatures, dissolution of QDs occurs as Heyn [4] and Lee et al. [5] observed in the transition in reflection high energy electron diffraction (RHEED) patterns. It has been reported [6] that intermixing of GaAs with InAs is significant at higher temperatures and it was observed that the dot volume increases due to the additionally incorporated GaAs [7]. Contrarily, it was also found that interdiffusion has a pronounced effect on the dissolution of embedded InAs QDs in GaAs [8].

The exact processes during annealing at high temperatures are thus not clear yet and shall be investigated in this paper. The stress evolution is measured during annealing using an *in situ* cantilever beam setup. Additionally, atomic force microscopy (AFM) images are taken at different annealing times and high-resolution transmission electron microscopy (HRTEM) is used to determine the structural properties. Our experimental results reveal that for annealing at high temperature, although In desorption influences the ripening behavior of QDs seriously, the dissolution of QDs is a result of combined In desorption and interdiffusion between Ga and In.

2. Experimental details

The samples were prepared in a III–V semiconductor molecular beam epitaxy chamber equipped with a cantilever beam setup to measure stress curves during growth and following post-growth annealing [9]. The epi-ready GaAs(001) substrates measuring $25 \times 5 \times 0.15\,mm^3$ were clamped on one side to allow the free end to bend during measurements. A capacitance technique combined with a lock-in assisted signal detection system was used to measure the deflection of the free end in real-time [10]. Using Stoney's equation [11], the film force *FF*, defined as the force per film width, was calculated from the substrate bending. Before InAs deposition, the GaAs substrates were degassed at 300 °C (thermocouple reading) for 2 h followed by oxide desorption at 605 °C. Then, a 500 nm thick GaAs buffer layer was deposited. The growth rate of GaAs and InAs are 0.93 and 0.05 ML/s respectively.

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Growth was carried out under As rich conditions with a As background pressure of 2×10^6 mbar. From previous studies, it is known that the critical thickness for InAs dot formation is around 1.5–1.8 monolayers (ML) for the temperature range considered in this study. To compare with films which consist of a wetting layer (WL) only, we deposited InAs for 30 s (corresponds to 1.5 ML InAs), while for films composed of WL and QDs, we deposited InAs for 45 s (corresponds to 2.3 ML thick InAs). All films were grown at 500 °C and then kept at the growth temperature for annealing. The As background pressure was also kept stable. The film force curves are measured and are depicted versus time in this paper. To investigate the morphological evolution during ripening of QDs, these films remained uncapped. The annealing behavior of the quantum dots was monitored by keeping the samples at the growth temperature for a given time and then rapidly quenching them to room temperature for AFM studies.

3. Results and discussion

Fig. 1 shows the film force curves measured during growth and following annealing of the WL sample (dotted line) and the QDs sample (solid line) at 500 °C respectively. Upon opening of the In shutter, a linear increase in film force is observed for both samples. The linear increase remains for the WL sample during half minute deposition until annealing starts, then the film force decreases with the annealing time. While for the QD samples, the linear increase to ~2.2 N/m is remained for 0.58 min (corresponding to the critical thickness of ~1.7 ML), as shown in the inset of Fig. 1, which shows the film force curve during 45 s (2.3 ML) InAs deposition. The dashed line guides the linear increase in the film force curve. With further InAs deposition, the increase of film force becomes slower and proceeds with a small slope up to a value of 2.5 N/m. This is, as expected, due to a partial release of stress during the change from 2D layer by layer growth to 3D island formation and growth. After annealing the QD sample for 10 min, the film force decreases from 2.5 to 0.8 N/m. In contrast to the QD samples, annealing has a relatively minor influence on the WL samples, for which the film force decreases from 2.0 to 1.2 N/m.

Fig. 2 shows the morphology of the WL films imaged by AFM after annealing at 500 °C for 10 min. Small islands of about 1–2 ML height are visible on the surface of the film. Similar to the transition from 2D layer-by-layer to 3D island growth, these mounds lead to the reduction of the stress observed in the *FF* curve. However, the formation of these mounds is not primarily driven by misfit stress, but rather a result of a dewetting process during annealing [12]. According to a theoretical study [13], InAs forms a liquid-like layer on the surface of GaAs at high temperatures above ~500 °C. The resulting high mobility allows In atoms to rearrange on the surface, thus providing a kinetic mechanism for the mound formation.

During annealing of the QD sample for 10 min at 500 °C, the film force decreases with a gradually decreasing slope and drops to a value lower than the value of the WL curve after 2 min. Then, the film force proceeds with same slope as the WL's after 4 min annealing, finally reaching a value of 0.8 N/m which is below the value reached by the WL sample. Therefore, the existing QDs promotes an additional force decrease. The possibilities for the additional film force decrease during annealing of QD samples are the formation of dislocations and In desorption. To investigate the formation of dislocations, HRTEM images were measured. As shown in Fig. 3, HRTEM images reveal that every atom is on the perfect crystal site after QD formation and after 10 min annealing, indicating that no dislocations were formed. This was confirmed by large area scans (not shown) in which also no dislocations were found. Additionally, no distinct and well-defined 3D islands were detected in cross-sectional TEM of the annealed samples (see Fig. 3b).

Another possibility for the additional decrease in the *FF* of the QDs films annealed at high temperature is desorption of In, which would lead to a continuous decrease in the average height of the QDs during annealing. To investigate this possibility, we recorded AFM images at various stages during annealing, as shown in Fig. 4.

To obtain these images, the samples were annealed for a given time and then rapidly quenched to room temperature. Interestingly, the dots appear to ripen at first, but then their density decreases down to a point, where no dots are visible in large AFM ($10 \times 10\,\mu m^2$) or TEM scans. To obtain a better understanding, we

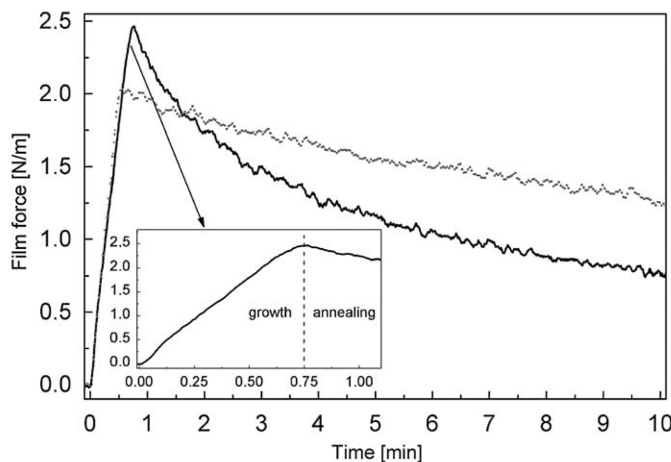

Fig. 1. Film force measured during growth and annealing of InAs films for 10 min at 500 °C. Dotted lines correspond to 1.5 ML (30 s deposition) InAs WL-films, solid lines correspond to 2.3 ML (45 s deposition) thick InAs WL plus QDs films. Inset is the evolution of film force during growth of 2.3 ML (45 s deposition) InAs. The dashed line guides the linear increase of the film force.

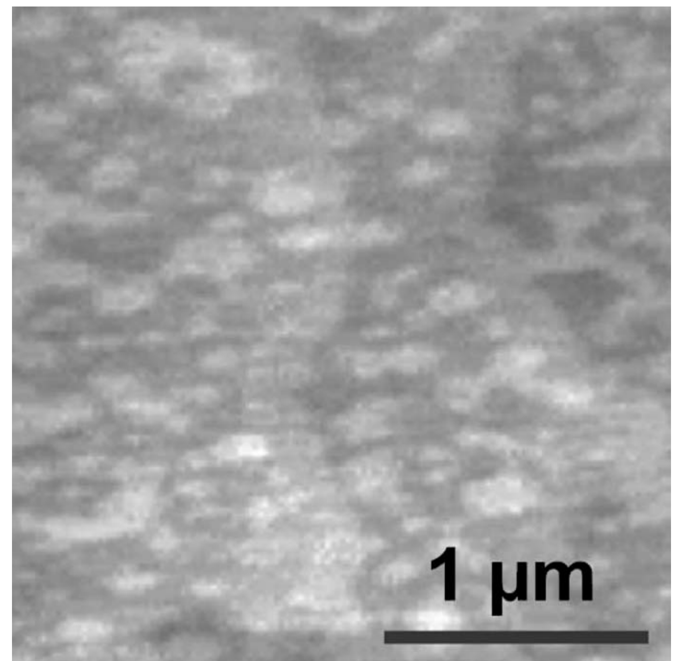

Fig. 2. AFM images of the WL sample taken after annealing for 10 min at 500 °C. The *z*-scale is 1 nm.

extracted normalized histograms of the dot height and dot radius as a function of annealing time, as shown in Fig. 5 with the mean values given in Fig. 6.

The mean radius r_{mean} increases while the mean height h_{mean} decreases during the first minute of annealing. With another 1.5 min annealing, both r_{mean} and h_{mean} remains constant while the density of QDs decreases. Considering typical Ostwald-ripening of QDs, the mean height and mean radius should increase. However, we observe that the mean height decreases at the beginning of annealing. This indicates, as reported by Heyn [4] and Lee et al. [5] that In desorption takes place. Furthermore, this also shows that In desorbs faster from the top of QDs.

Using general free energy calculations, Tersoff [14] has shown that when QDs nucleate from $In_xGa_{1-x}As$ wetting layer, the In concentration of the QDs is enhanced over the In concentration of the wetting layer. Moreover, as studied by Joyce [7] and Heyn et al. [15,16] the $In_xGa_{1-x}As$ alloy and In composition increase from the inner center of the QDs to the top. Furthermore, Heyn reported that the activation energy for In desorption from dots is higher than that for In desorption from wetting layer. Combining Tersoff's theory and Heyn's studies, it is clear that once annealing starts, InAs desorbs faster from dots than from wetting layer while QDs try to approach an energetically favorable composition. In such a closed system (QDs plus wetting layer), the dots can only obtain additional In from the wetting layer. This leads to a lower In concentration for the QD sample's wetting layer than in a pure wetting layer sample. Also this process promotes a faster In desorption from the QD sample compared to the wetting layer sample. Considering that the *FF* of the QD sample is mainly coming from QDs and $In_xGa_{1-x}As$ wetting layer when annealing starts due to the above process, InAs desorbs faster from the QD sample. It is expected that after annealing for a while the *FF* of the QD sample would be lower than that of the WL sample, which is composed nominally of 1.5 ML InAs. Our measurements confirm this expectation.

The decrease of the *FF* of the QD sample is faster than that of the WL sample once annealing starts. The decrease of the *FF* of the QD sample is due to QD ripening, InAs desorption combined with rearrangement of material from the wetting layer and the dots, while the decrease is mainly due to rearrangement of surface morphology for WL sample. As the ripening process contributes less to relieve stress and InAs desorbs slower with time, the decrease of *FF* is getting slower as shown from the *FF* curve.

Furthermore, analyzing AFM images in more detail with annealing times longer than 2.5 min, h_{mean} starts to increase again while r_{mean} still decreases. The increase in h_{mean} shows that the growth of dots is becoming more pronounced again compared to In desorption. Finally, after about 5–7.5 min, a slight increase in h_{mean} and an almost constant r_{mean} are measured while the density of the dots continues to decrease down to the dissolution of QDs. The dissolution of the dots at this stage of annealing cannot be

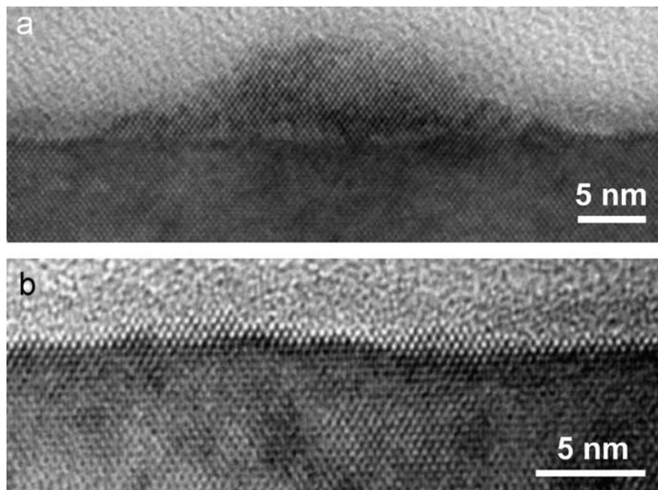

Fig. 3. HRTEM images of 2.3 ML thick InAs QDs films deposited at 500 °C taken (a) before annealing and (b) after annealing for 10 min.

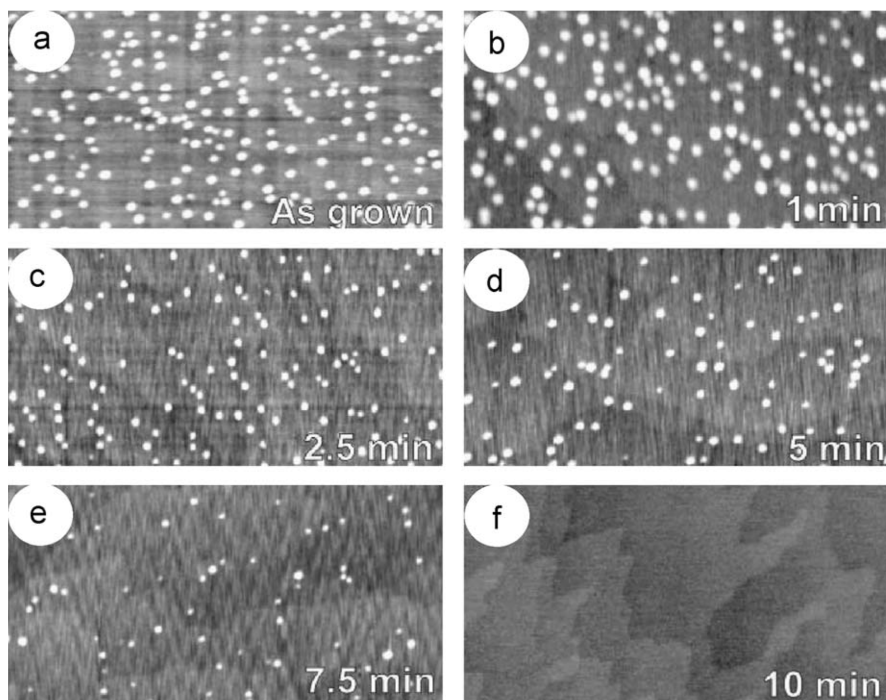

Fig. 4. $2 \times 1\ \mu m^2$ AFM images of 2.3 ML thick InAs films deposited at 500 °C: (a) before annealing, (b) post-growth annealing for 1 min, (c) 2.5 min, (d) 5 min, (e) 7.5 min and (f) 10 min.

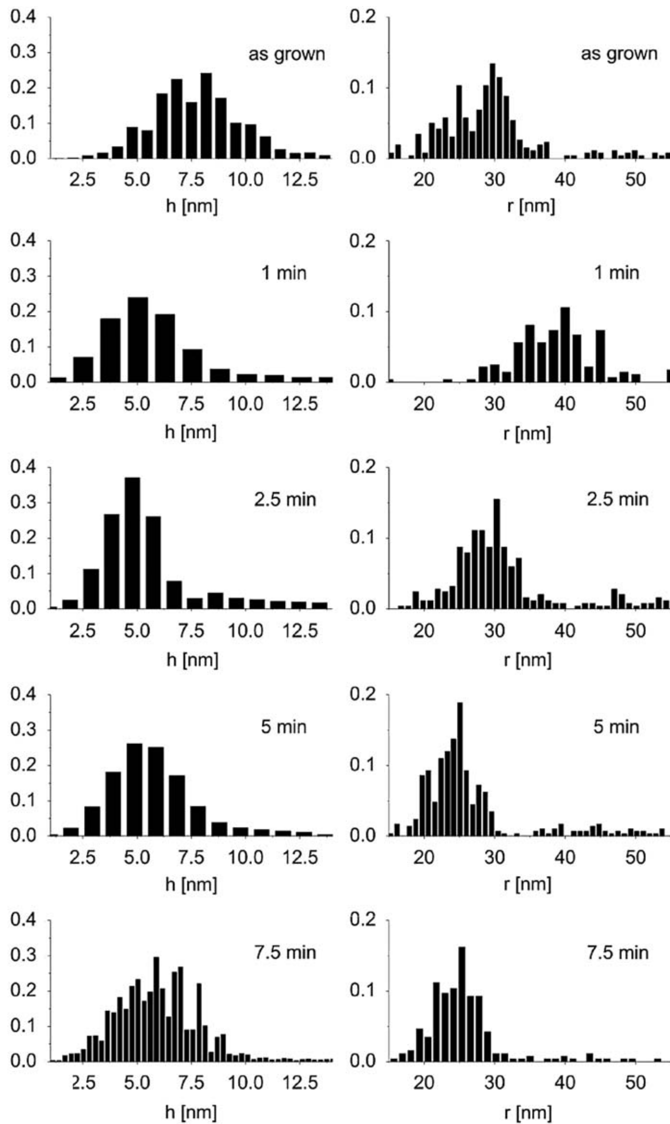

Fig. 5. Normalized histograms of the dot height (left) and dot radius (right) distribution for increasing annealing times.

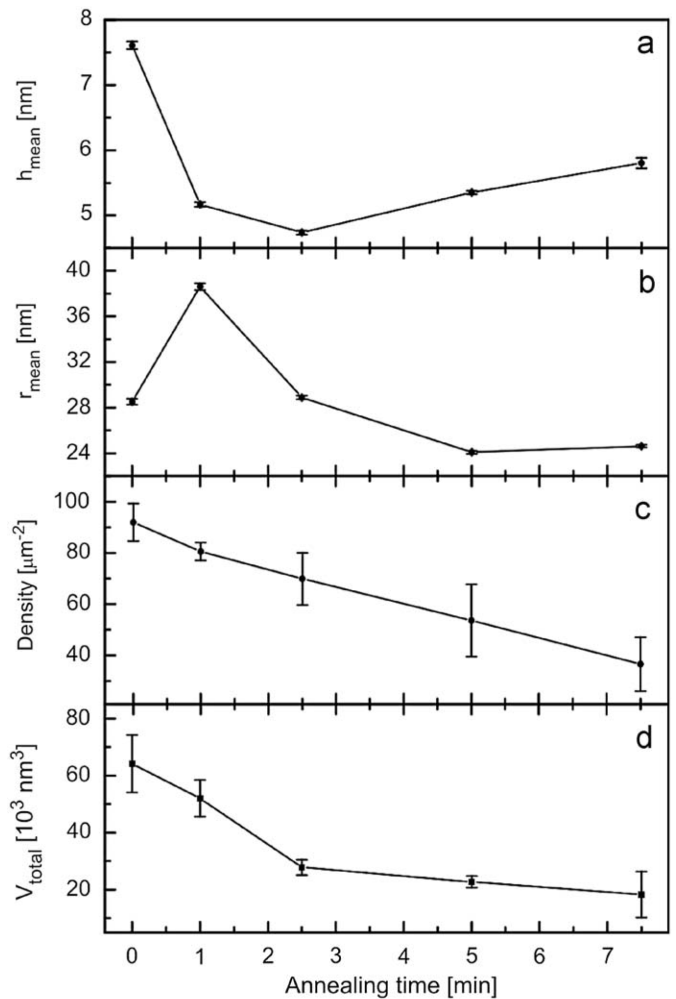

Fig. 6. Evolution of (a) height, (b) radius, (c) density and (d) total volume of dots with annealing time.

explained by In desorption alone, because this would require a continuous decrease in the mean dot height.

The standard ripening theory of particles, i.e. the growth of larger grains by dissolution of smaller grains, can be explained in the following way. For a supersaturated solid solution, to each degree of the supersaturation Δ of grains, there exists a critical radius $R_{cr} = \alpha/\Delta$ (α is a constant associated with the interphase surface tension) at which the grain is in equilibrium with the solution. When the particle radius is larger than the critical size, it grows, otherwise it dissolves. Using this theory and considering interdiffusion, which is relatively strong at elevated temperatures [6], we can explain the observed annealing behavior as follows. In our case, Δ is the concentration of InAs for QDs. At the beginning stage of annealing, the In concentration in dots is high, leading to a small critical size. Ripening of dots can still be observed. With further annealing, due to desorption of In and interdiffusion between Ga and In, the In concentration decreases and the critical size increases. Eventually, the increase of critical size overtakes the increase of the dot size, i.e. $dR_{cr}/dt > dr/dt$. Dots with sizes smaller than the critical size shrink and eventually dissolve. After a certain time, the critical size is larger than the largest dot size, i.e. $R_{cr} > r$. At this point, all dots have dissolved. This process is clearly seen in AFM images taken at later annealing stages.

4. Conclusions

We have studied the film force evolution of InAs/GaAs QDs during post growth annealing using an *in situ* cantilever beam setup in combination with atomic force microscopy. We find that existence of QD promotes In desorption. For annealing at 500 °C, the evolution process of QD can be explained by considering interdiffusion between Ga and In atoms and desorption of In. The eventual dissolution of QDs should be attributed to the interdiffusion between Ga and In.

References

[1] D. Bimberg, M. Grundmann, N.N. Ledentsov, Quantum Dots Heterostructures, Wiley, Chichester, 1999.
[2] K. Poetschke, L. Mueller-Kirsch, R. Heitz, R.L. Sellin, U.W. Pohl, D. Bimberg, N. Zakharov, P. Werner, Physica E 21 (2004) 606.
[3] T.J. Krzyzewski, T.S. Jones, J. Appl. Phys. 96 (2004) 668.
[4] Ch. Heyn, Phys. Rev. B 66 (2002) 075307.
[5] H. Lee, R.R. Lowe-Webb, W. Yang, P.C. Sercel, Appl. Phys. Lett. 71 (1997) 2325.

[6] P.B. Joyce, T.J. Krzyzewski, G.R. Bell, B.A. Joyce, T.S. Jones, Phys. Rev. B 58 (1998) R15981.
[7] B.A. Joyce, T.S. Jones, J.G. Berk, J. Vac. Sci. Technol. B 16 (2005) 2373.
[8] B. Lita, R.S. Goldman, J.D. Phillips, P.K. Bhattacharya, Surf. Rev. Lett. 7 (2000) 539.
[9] R. Koch, G. Wedler, J.J. Schulz, B. Wassermann, Phys. Rev. Lett. 87 (2001) 136104-1-1.
[10] D.M. Schaadt, D.Z. Hu, K.H. Ploog, J. Vac. Sci. Technol. B 24 (2006) 2069.
[11] G.G. Stoney, Proc. R. Soc. London A 32 (1909) 172.
[12] R.P. Mirin, A. Roshko, M. van der Puijl, J. Vac. Sci. Technol. B 20 (2002) 1489.
[13] D.J. Bottomley, Appl. Phys. Lett. 72 (1998) 783.
[14] J. Tersoff, Phys. Rev. Lett. 81 (1998) 3183.
[15] Ch. Heyn, A. Bolz, T. Maltezopoulos, R.L. Johnson, W. Hansen, J. Cryst. Growth 278 (2005) 46.
[16] Ch. Heyn, D. Endler, K. Zhang, W. Hansen, J. Cryst. Growth 210 (1999) 421.