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Published in:
Applied Physics Letters

DOI:
10.1063/1.2719662

Published: 01/01/2007

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Pohjola, P., Hakkarainen, T., Koskenvaara, H., Sopanen, M., Lipsanen, H., & Sainio, J. (2007). Tensile-strained GaAsN quantum dots on InP. *Applied Physics Letters*, *90*(17), 1-3. [172110]. https://doi.org/10.1063/1.2719662

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Citation: Appl. Phys. Lett. **90**, 172110 (2007); doi: 10.1063/1.2719662
View online: http://dx.doi.org/10.1063/1.2719662
View Table of Contents: http://aip.scitation.org/toc/apl/90/17
Published by the American Institute of Physics

Tensile-strained GaAsN quantum dots on InP

P. Pohjola, T. Hakkarainen, H. Koskenvaara,[a] M. Sopanen, and H. Lipsanen
Micro- and Nanosciences Laboratory, Micronova, Helsinki University of Technology, Tietotie 3, Espoo FIN-02015 HUT, Finland

J. Sainio
Laboratory of Physics, Helsinki University of Technology, Otakaari 1, Espoo FIN-02015 HUT, Finland

(Received 18 December 2006; accepted 2 March 2007; published online 26 April 2007)

Self-assembled quantum dots are typically fabricated from compressive-strained material systems, e.g., InAs on GaAs. In this letter, self-assembled quantum dots from tensile-strained GaAsN on InP are demonstrated. GaAsN on InP has type-I band alignment. Stranski-Krastanov growth mode is not observed, but *in situ* annealing of the uncapped samples results in the formation of islands. Photoluminescence spectra from the buried GaAsN show separate peaks due to a wetting layer and islands around the energies of 1.3 and 1.1 eV, respectively. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2719662]

The Stranski-Krastanov (SK) growth of coherently strained islands has been under extensive study during the last two decades. In this growth mode a wetting layer and coherently strained three-dimensional islands are formed during the growth process. The research has been concentrated on compressively strained material systems such as Ge/Si,[1] InAs/InP,[2] InP/GaInP,[3] InGaAs/GaAs,[4] InP/GaAs,[5] and GaInNAs/GaAs.[6] Also tensile three-dimensional islands have been fabricated from, e.g., PbSe on PbTe.[7] The formation of islands is not, however, always happening in tensile-strained growth: when growing $Ga_{0.75}In_{0.25}As$ on InP only holes were observed.[8] Another problem with tensile-strained systems is that tensile islands have typically larger band gap than the host material. Therefore, these islands cannot confine carriers and are not quantum dots. However, at least one tensile-strained system, i.e., $GaAs_{1-x}N_x$ on InP, theoretically has type-I band alignment at certain nitrogen compositions and can confine both electrons and holes. GaAs/InP heterojunction on InP substrate has a type-II band alignment in which only holes are confined in GaAs. The conduction and valence band offset energies are approximately 172 and 550 meV, respectively.[9] Because the incorporation of nitrogen reduces the band gap of GaAsN (Refs. 10 and 11) by lowering the conduction band edge,[12] it is expected that the transition to type-I interface would occur with a nitrogen composition of about $x \approx 0.013$. In this letter, we present growth studies of the GaAsN-on-InP system with a goal to achieve type-I quantum dot structures.

The sample growth was carried out in a horizontal metal-organic vapor-phase epitaxy (MOVPE) reactor at atmospheric pressure using hydrogen as carrier gas. The precursors were trimethylindium, trimethylgallium, tertiarybutylphosphine (TBP), tertiarybutylarsine (TBAs), and dimethylhydrazine (DMHy). First, a 100-nm-thick InP buffer layer was grown at 610 °C on a vicinal semi-insulating InP (100) substrate. After the growth of the buffer layer, the temperature was lowered under TBP flow to the growth temperature of the GaAsN layer. The GaAsN layers were deposited at different temperatures varied in the range of 530–610 °C. The TBAs/III and DMHy/V ratios were 2 and 0.92, respectively. With these flows the DMHy/TBAs ratio corresponds to a nitrogen composition of ~5.5% in the layer in this reactor.[10] All the growth temperatures mentioned are thermocouple readings and all the layer thicknesses are nominal deposition thicknesses.

To study surface morphology by atomic force microscopy (AFM), part of the samples were left uncapped. Some of the uncapped samples were cooled down to room temperature directly after the growth of the GaAsN layer. For the other uncapped samples, a thermal annealing was performed by raising the temperature to 610 °C for 20 s under TBAs and DMHy partial pressure, after which the samples were cooled down. X-ray photoelectron spectroscopy (XPS) measurements were performed on the uncovered GaAsN layers to investigate if nitrogen had been incorporated.

The rest of the samples were fabricated for optical measurements. The GaAsN layer was capped with an InP barrier layer grown at 610 °C. The optical characterization was performed with low temperature photoluminescence (LT-PL) at 9 K. The 488 nm line of an argon ion laser was used for excitation. The luminescence light was dispersed with a 0.5 m monochromator and a liquid-nitrogen-cooled germanium detector was used for detection.

First, for reference, thin layers (1-6 ML) of GaAs were grown on the InP buffer layer. The TBAs/III ratio was varied in the range of 2-20 to study the effect of As/P exchange on the surface morphology. The V/III ratio of 2 was found to give the smoothest initial surface indicating the smallest As/P exchange. This TBAs/III ratio also gives a good incorporation of nitrogen into GaAsN on GaAs and it is also the minimum for high quality GaAsN.[10] The growth rate was varied between 2.8 and 8.5 Å/s, which corresponds to 1–3 ML/s for GaAs. The growth rate of 5.0 Å/s was chosen because no significant differences were observed.

Next, the growth of GaAsN was investigated by depositing 6 ML of GaAsN on InP at different temperatures between 530 and 610 °C. At the temperatures of 530–580 °C no islands were formed. At 610 °C few islands were formed but the material had otherwise accumulated to wirelike structures. Therefore, clear SK growth mode could not be observed. Furthermore, the growth temperature of 610 °C is

[a]Author to whom correspondence should be addressed; FAX: +358-9-4513128; electronic mail: hannu.koskenvaara@tkk.fi

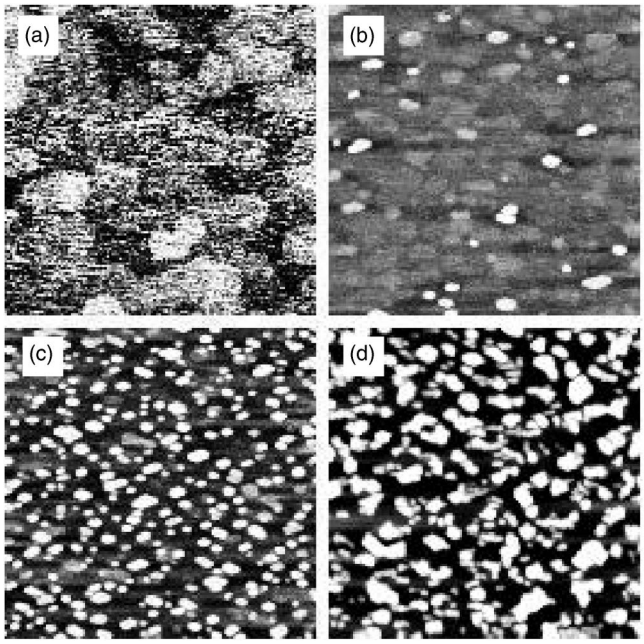

FIG. 1. AFM images of GaAsN layers with thicknesses of (a) 3 ML, (b) 4 ML, (c) 5 ML, and (d) 6 ML deposited on InP at the temperature of 530 °C. The samples were annealed *in situ* at 610 °C for 20 s. The scan size is $1 \times 1\ \mu m^2$.

not very attractive to obtain type-I GaAsN/InP quantum dots because the nitrogen composition has been found to decrease radically with increasing growth temperature.[10,13]

It has been found out that thermal annealing can be used to enhance island formation.[14] To both optimize the nitrogen concentration and to form islands, the samples were grown at 530 °C with varying GaAsN deposition thicknesses (3-6 ML) and then were *in situ* annealed at 610 °C for 20 s. Figure 1 shows AFM images from the annealed samples. The sample with the 3-ML-thick GaAsN layer (a) has large two-dimensional islands with a height of 1-2 ML. When 4 ML of GaAsN is deposited and annealed (b), three-dimensional (3D) islands start to form. The areal density and the average height of the islands are 4×10^9 cm^{-2} and 3.5 nm, respectively. The deposition of 5 ML (c) leads to 3D islands with a larger density of 3.8×10^{10} cm^{-2} and an average height of 4.0 nm. When 6 ML is deposited and annealed (d), the shape of the larger islands becomes unsymmetrical. This is characteristic for islands that are relaxed.[3,15,16] However, the larger islands are quite small, mainly 8–12 nm in height, for relaxation. For comparison, compressively strained InP islands on InGaP lattice matched to GaAs (001) have been found to be defect-free up to heights of 22.5 nm.[3] The absolute value of the relative lattice mismatch $\Delta a/a$ is almost the same in both of these cases. To determine whether the GaAsN islands are relaxed or not, further studies are needed.

Figure 2 shows the effect of the deposition thickness on the areal density (a) and average height (b) of the 3D islands. The 3D islands have been divided into smaller type-*A* (height $\leqslant$7 nm) and larger type-*B* (height $>$7 nm) islands. According to Fig. 2(a) the critical thickness for 3D island formation is somewhere between 3 and 4 ML. The areal density of the smaller islands increases from 4.0×10^9 to 3.8×10^{10} cm^{-2} when the deposition thickness is increased from 4 to 5 ML. The average height of the small islands is about 4.0 nm. In the case of 6 ML, the areal density decreases to 1.5

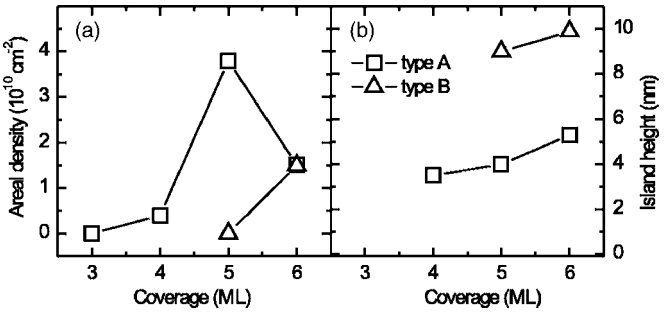

FIG. 2. (a) Areal density and (b) average height of the GaAsN islands as a function of coverage. A and B stand for islands that are $\leqslant$7 and $>$7 nm high, respectively.

$\times 10^{10}$ cm^{-2} because of island coalescence. At the same time the areal density of the larger islands increases to 1.5 $\times 10^{10}$ cm^{-2}. The average height of the large islands is 9.9 nm. This kind of behavior has been reported, e.g., for SK InAs islands on InP.[2]

Figure 3 shows LT-PL spectra of buried GaAsN layers with different nominal thicknesses. The peaks in the energy range of 1.25–1.37 eV seem to originate from the GaAsN wetting layer (WL). The multiple peaks in the 3 ML sample correspond to different areas of the WL having 1 ML difference in thickness. These 1 ML fluctuations are also observed in the AFM image of the uncovered layer in Fig. 1(a). With the coverages of 4 and 5 ML, the critical thickness is reached and islands are formed. The luminescence peak centered at 1.05 eV originates from the islands. When the deposition thickness is increased to 6 ML, the PL intensity clearly decreases. This can be explained by enhancement of the nonradiative recombination due to dislocation formation associated with the relaxation of the type-*B* islands. In addition, the wetting layer luminescence begins to dominate.[16] To study even thicker layers of GaAsN, two samples with coverages of 10 and 20 ML were grown. Luminescence peaks originating from the islands were not observed at all from these samples.

To examine the nature of the radiative transitions observed in the GaAsN samples, a GaAs reference sample was grown. The reference sample had a 6-ML-thick layer of GaAs buried between InP layers. Figure 4 shows the LT-PL spectra from this sample and a GaAsN sample grown with the DMHy/V ratio of 0.92. WL peaks at about 1.34 eV can be seen in both samples. In the GaAs reference sample, the peak results from a type-II transition between the InP con-

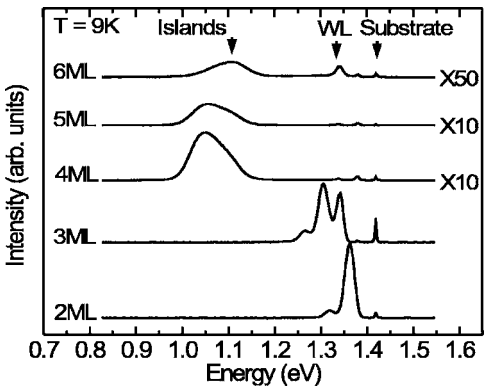

FIG. 3. LT-PL spectra from the samples with various thicknesses of buried GaAsN layers on InP.

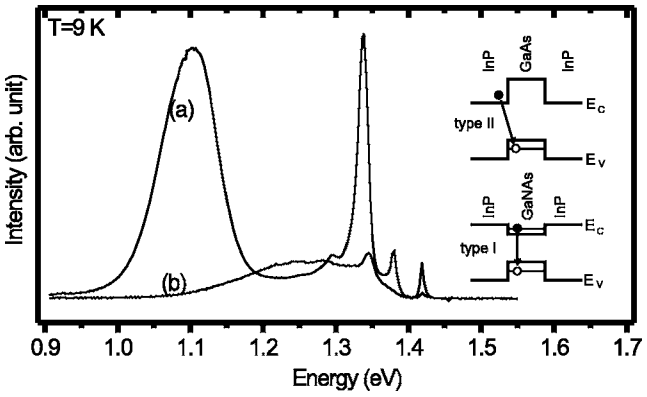

FIG. 4. LT-PL spectra of samples with a 6-ML-thick buried layer of (a) GaAsN grown with the DMHy/V ratio of 0.92 and (b) GaAs. Energy band structures of the GaAs/InP and the GaNAs/InP QWs and respective transitions are shown in an inset.

duction band and the GaAs WL quantum well (QW). In the GaAsN sample the wetting layer peak is approximately at the same wavelength as in the GaAs sample. This can be explained by the fact that nitrogen modifies mainly the conduction band and does not have a noticeable effect on the valence band.[12] The band structure and the energy states of the GaAs/InP and GaAsN/InP quantum wells are shown in the inset of Fig. 4. Energy of the type-II WL peak is close to the band gap of InP because the carrier states in a very narrow QW are very near to the barrier potential. Several WL QW peaks result from the monolayer thickness variations in the WL.

In the LT-PL of the GaAs sample, a broad peak centered at 1.28 eV with a full width at half maximum (FWHM) of 162 meV is observed. In the GaAsN sample a peak related to islands is centered at 1.1 eV and has a FWHM of 82 meV. Narrower and more intense peak in the GaAsN sample suggests that there may be a type-I transition in GaAsN quantum dot (QD), whereas type-II transition produces a weaker and broader peak in the GaAs sample. Also the wetting layer peak is strong in GaAsN sample. This can be explained by the low confinement potential in the GaAsN conduction band of the GaAsN QDs. Thermal excitation throws electrons out from the shallow QD potential well and they recombine in the WL QW.

The energetic positions of the peaks obtained from the GaAsN samples do not correspond to the values calculated from a simple potential well model. The calculated values for the assumed nitrogen composition of $x=0.055$ are somewhat lower. To investigate if any mixing of materials has occurred and if any nitrogen has really been incorporated, an uncapped 6-ML-thick GaAsN sample was investigated by XPS. XPS results show that there are nitrogen, phosphorus, and indium on the top atomic layers of the sample. This indicates that nitrogen has really been incorporated into the GaAsN layer. It is also possible that mixing of materials in the interface of GaAsN and InP layers is occurring. This cannot be asserted for sure because the thickness of the wetting layer is not known. Therefore, XPS signal could be partly originated from the buffer layer between the islands. However, mixing of materials does explain quite naturally the reason for the observed difference in the measured and calculated positions of the PL peaks.

In summary, tensile-strained thin GaAsN layers were grown on InP by MOVPE. Stranski-Krastanov growth mode was not observed, but *in situ* annealing of the uncapped samples at 610 °C resulted in the formation of islands. The critical thickness for island formation was found to be between 3 and 4 ML. The LT-PL spectra of GaAsN samples showed separate peaks due to WL and islands around the energies of 1.3 and 1.1 eV, respectively. The PL and XPS results also indicate that nitrogen had been incorporated into the layers and that some mixing between GaAsN and InP may have occurred.

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