



The morphology of an InP wetting layer on GaAs

M. Mattila*, M. Sopanen, H. Lipsanen

Optoelectronics Laboratory, Helsinki University of Technology, P.O. Box 3500, FIN-02015, Espoo, Finland

Received 26 August 2003; received in revised form 4 February 2004; accepted 4 February 2004

Available online 2 April 2004

Abstract

The effects of material intermixing, group V atom desorption and exchange on the surface morphology of InP wetting layers on GaAs substrates were studied by varying the growth temperature and coverage in metalorganic vapor phase epitaxy. Tertiarybutylphosphine (TBP) was used as the phosphorus source and the surface morphology was characterized by atomic force microscopy. The observations showed that the morphology depends strongly on the growth parameters and deteriorates with increasing temperature and decreasing InP coverage. It was verified that the main reason for the morphology impairment is the strongly temperature dependent group V atom exchange and desorption within several monolayers on the sample surface during exposures of the GaAs surface to TBP. However, a smooth morphology could be obtained within a wide temperature range by depositing at least a complete monolayer of InP.

© 2004 Elsevier B.V. All rights reserved.

PACS: 81.05.Ea; 68.55.–a; 68.55.Jk

Keywords: InP; GaAs; Morphology; Exchange reaction

1. Introduction

The epitaxial growth of heterostructures is a common means of band structure tailoring in modern electronic and optoelectronic components. It is well known that the growth of epitaxial layers is categorized into different modes which describe the evolution of the layer. Under certain conditions a lattice mismatched layer can grow in the coherent Stranski–Krastanow (SK) mode in which self-assembled islands are formed on top of a wetting layer a few monolayers thick [1]. This growth mode has been observed in many systems such as InAs/GaAs [2] and InP/GaAs

[3]. From energy-based considerations, the occurrence of the SK mode can be explained by the interplay of the surface free energies of the two materials and the interfacial free energy which includes the strain energy of the layer [4]. However, since the commonly used epitaxial techniques, such as molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE), are non-equilibrium methods, other effects must also be taken into account. For example, rather high temperatures are required during MOVPE growth to ensure proper precursor decomposition. On the other hand, at high temperatures adatom desorption [5] and material intermixing at heterointerfaces [6] are non-negligible. Therefore, the growth of materials in the SK mode is affected by the growth parameters. For instance, the abruptness of the interface between the substrate and the SK wetting layer or a quantum well

* Corresponding author. Tel.: +358-9-451-5312;
fax.: +358-9-451-3128.
E-mail address: marco.mattila@hut.fi (M. Mattila).

can be controlled by using optimized gas switching sequences [7].

A particular material system exhibiting the aforementioned intermixing effects is InP on GaAs. As long as these effects are under control the material system has numerous applications. For example, thin InP layers have been used for passivation of GaAs surfaces [8] and near-surface $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum wells [9]. The InP/GaAs material system exhibits Stranski–Krastanow island growth for InP layers thicker than the critical thickness of about 2.2 ML [10]. The self-organized islands have been used as stressors to produce strain-induced quantum dots [11]. The interface quality of MOVPE-grown quantum wells has been studied and optimized in the In(Ga)P/GaAs material system by photoluminescence measurements [12], ellipsometry [13] and reflectance anisotropy spectroscopy [14].

In this work, we have investigated the effects of growth temperature and group V purging on the morphology of MOVPE-grown ultra-thin InP layers on GaAs. We show that a thin InP layer on GaAs can be grown maintaining the smooth morphology of the semiconductor surface within a wide range of temperatures.

2. Experimental procedure

The samples were grown in an atmospheric-pressure horizontal MOVPE reactor [15] using trimethylgallium (TMGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs), and tertiarybutylphosphine (TBP) precursors. The substrate material was vicinal semi-insulating (1 0 0) GaAs. After deoxidizing the substrates at 700 °C for 5 min a 150 nm thick GaAs buffer layer was grown to achieve an atomically flat surface. After growing the buffer layer the growth was interrupted for 1 s under TBP flow to purge the residual TBAs from the reactor. All InP layers were grown at a nominal growth rate of 1.5 ML/s and a V/III ratio of 100. The nominal InP coverage and growth temperature were varied in the range of 0.3–1.8 ML and 610–655 °C, respectively. All reported temperatures are thermocouple readings which have been measured in a similar reactor to be about 50 °C higher than the actual sample surface temperatures (at 650 °C) [16]. The samples were cooled down to 400 °C under TBP

flow immediately after the growth of the InP layers. Cooling time from 600 to 400 °C was measured to be about 100 s. To study the effect of arsenic to phosphorus exchange and group V desorption on the sample morphology, samples containing only the GaAs buffer layer were cooled down to 400 °C from different temperatures under TBP flow. The morphology of the samples was characterized by contact-mode atomic force microscopy (AFM) in air ambient using chemically sharpened silicon nitride tips. We have assumed that the oxide on the sample surface is conformal with the semiconductor surface [17].

3. Results and discussion

The effect of InP coverage on the sample morphology was studied by depositing 0.3–1.8 ML of InP on GaAs at 610, 635, and 655 °C. AFM images from the samples grown at 635 °C are shown in Fig. 1. The images show that at nominal coverages above 1 ML, yet below the Stranski–Krastanow transition threshold, the sample morphology is mainly two dimensional (2D). The layers grow mainly by 2D island nucleation, lateral growth and coalescence with increasing coverage. Consequently, during the growth of 1 ML the morphology varies from a smooth stepped surface to an irregular surface consisting of small separate 2D islands, yet the morphology remains mainly 2D. This growth mode was observed in every sample with more than 1 ML of InP and is typical for the InP/GaAs system on a vicinal substrate [10]. However, in the samples with InP coverages of 0.3–0.8 ML small pits can be observed on the surface. In the samples grown at 635 °C the average diameter and depth of these pits are 30 and ~1 nm, respectively. The areal density is 10^9 to 10^{10} cm^{-2} , decreasing with increasing InP coverage. The depth of the pits suggests also group III atom desorption or migration in addition to arsenic to phosphorus exchange and arsenic desorption during growth or cooling. As a consequence of these processes there may be a thin ternary $\text{GaAs}_x\text{P}_{1-x}$ or quaternary $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ layer on the surface. The strain induced by the lattice mismatch between the layer and the GaAs buffer is known to cause the material on the surface to rearrange and to form pits and clusters in material systems such as GaInP/GaAs [18], GaAs/GaSb [19] and InAs/InP [20].

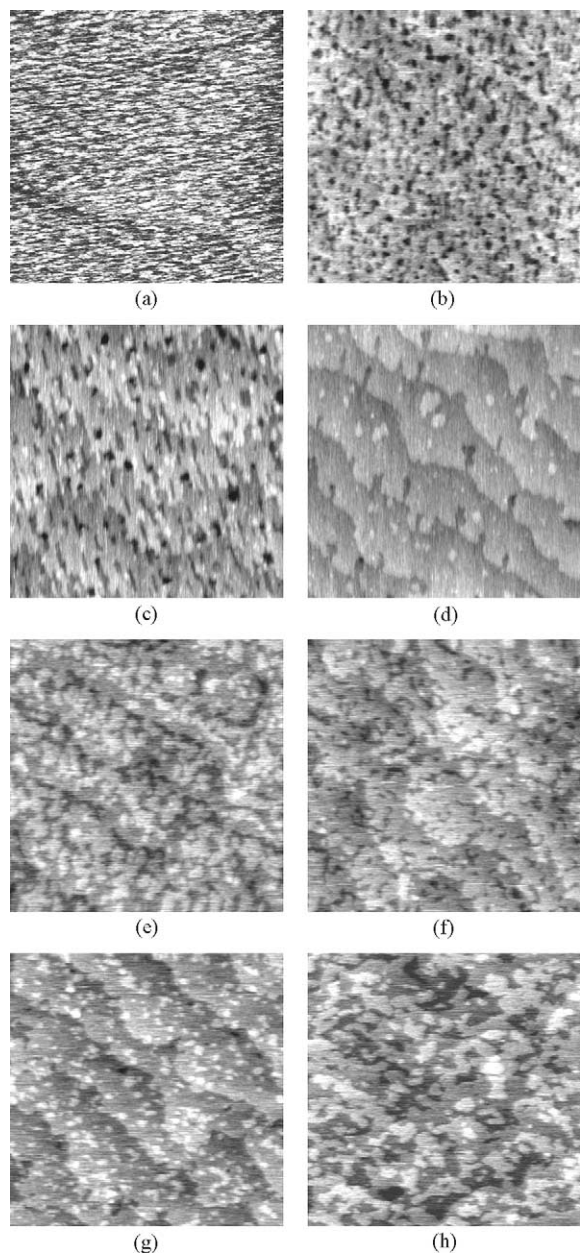


Fig. 1. AFM image from a sample grown at 635 °C with an InP coverage of (a) 0.0 ML; (b) 0.3 ML; (c) 0.5 ML; (d) 0.8 ML; (e) 1.2 ML; (f) 1.5 ML; (g) 1.8 ML; (h) 2.1 ML. The coverage of 0.0 ML corresponds to a GaAs sample cooled down from 635 °C under TBP flow. The scan size is $1 \mu\text{m} \times 1 \mu\text{m}$ and the height range is 3 nm.

Material intermixing, arsenic to phosphorus exchange, and group V desorption each can have an impact on the surface morphology. To see the effect of

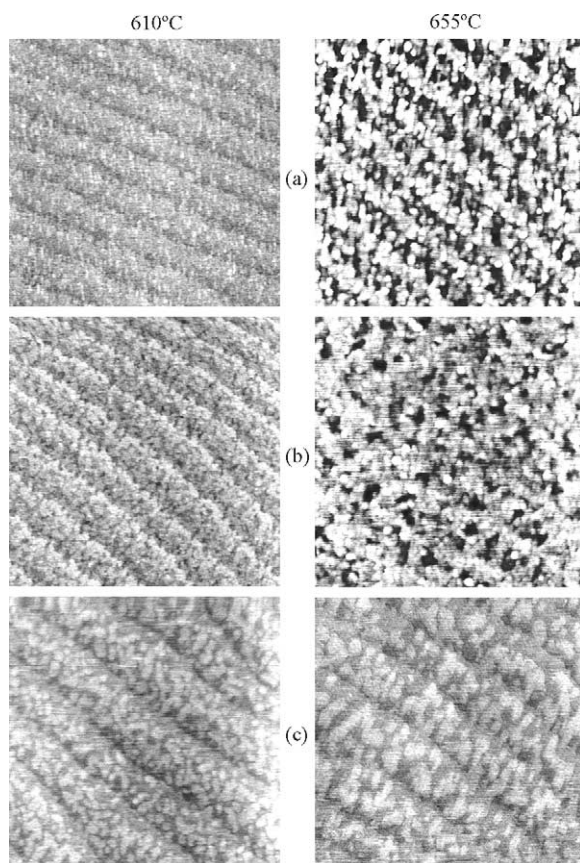


Fig. 2. AFM image from (a) a GaAs surface cooled down from two different temperatures under TBP flow; (b) a sample with 0.3 ML; (c) 1.2 ML InP coverage deposited at two different temperatures. The scan size is $1 \mu\text{m} \times 1 \mu\text{m}$ and the height range is 3 nm.

group V atom exchange and desorption alone, three GaAs samples were cooled down to 400 °C under TBP flow from 610, 655, and 675 °C, respectively. Fig. 2(a) shows AFM images from the samples cooled down from 610 to 655 °C. For comparison, Fig. 2(b) and (c) shows AFM images from the samples with 0.3 and 1.2 ML InP, respectively. The images show that at the lower temperature of 610 °C the sample morphology remains 2D for all three InP coverages. At 655 °C, on the other hand, the morphology clearly depends on the InP coverage. For high coverages the morphology is 2D, but becomes 3D with decreasing coverage. The surface roughness was characterized by the average height variation on the sample surface measured from the AFM images. Fig. 3 shows this average height variation for GaAs samples cooled down under TBP

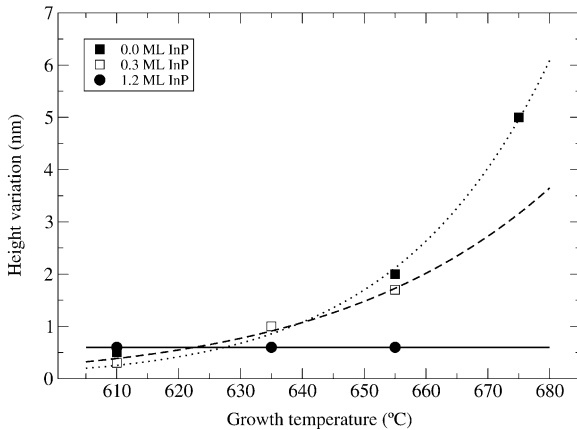


Fig. 3. Average height variation vs. growth temperature on the surface of a 1.2 ML InP sample (filled circles), 0.3 ML InP sample (hollow squares) and a GaAs sample cooled down under TBP flow (filled squares). The curves are exponential fits to the measured data.

flow from different temperatures and for InP samples grown at different temperatures with InP coverages of 0.3 and 1.2 ML. Due to the exponential temperature dependence, it is assumed that most changes of the surface morphology are produced immediately at the beginning of the cooling, i.e. at the highest temperature. Figs. 2 and 3 clearly show that for samples with InP coverages of less than about 1 ML the surface morphology is strongly temperature dependent. For example, monolayer steps and terraces can be resolved in samples grown at 610 °C, whereas in the samples grown at 655 °C the morphology is 3D and dominated by nanometer-sized islands, clusters and pits. On the other hand, at InP coverages above 1 ML the morphology remains 2D and is basically independent of the temperature at least in the range of 610–655 °C. Although the areal density and size of the 2D islands varies, the sample surface has no nanometer-scale 3D features.

We explain the observed behavior by considering the InP layer as a protective layer between the GaAs buffer and the TBP ambient in the MOVPE reactor. At coverages above 1 ML, the InP layer fully covers the buffer layer and can prevent arsenic to phosphorus exchange and arsenic desorption from taking place at temperatures between 610 and 655 °C. Our observations do not rule out the possibility of some arsenic to phosphorus exchange or arsenic desorption on the

topmost arsenic layer during the gas switching sequence between the growth of the GaAs buffer and the InP layer, because this would still result in the smooth surface seen in the AFM images. This reaction is rather likely because it has been shown to take place rapidly under MOVPE conditions when a group V terminated GaAs surface is exposed to phosphine (PH₃) [14]. Based on our observations, the drastic change in the surface morphology seen in the samples grown at high temperatures and with coverages below 1 ML is the result of extensive arsenic to phosphorus exchange and arsenic desorption extending several monolayers below the surface of the buffer layer.

Although these conclusions are somewhat speculative since AFM is not capable of studying dynamic processes but merely measures their final outcome, it is well known that a GaAs(1 0 0) surface is very stable at normal growth temperatures under TBAs stabilization. Therefore, the processes which alter the sample surface morphology as seen in the AFM images must stem from the presence of TBP in the reactor.

The group V exchange and desorption can also be enhanced by group III atom migration, exchange and desorption. During these processes group V atom planes deeper in the lattice are exposed to TBP and further exchange and desorption reactions can take place. Nevertheless, according to Fig. 3, the main reason for the 3D morphology is the arsenic to phosphorus exchange or arsenic desorption since there is only a slight difference between the morphology of the GaAs samples cooled down under TBP flow and the InP samples with 0.3 ML InP. Height variations comparable to these were also observed in samples with InP coverages of 0.5 ML (images not shown).

4. Conclusion

Thin InP layers were grown by MOVPE on vicinal GaAs substrates and the effect of growth temperature and coverage on the sample morphology was characterized by atomic force microscopy. All InP coverages were below the critical coverage of the Stranski–Krastanow transition. At coverages above 1 ML, the surface morphology remained 2D in the growth temperature range of 610–655 °C. Below 1 ML the morphology was observed to be 2D only for samples grown at 610 °C.

A 3D surface morphology with clusters of several nanometers in height was observed in the samples grown at 635 and 655 °C. Highly similar results were obtained from GaAs samples exposed to TBP during cooling. Thus, it was concluded that in this case the main reason for the 3D morphology at elevated temperatures is the arsenic to phosphorus exchange and arsenic desorption. For InP coverages smaller than the critical coverage for the SK transition, the 2D surface morphology can be preserved in a wide range of temperatures by depositing at least a complete monolayer of InP.

References

- [1] D.J. Eaglesham, M. Cerullo, *Phys. Rev. Lett.* 64 (1990) 1943.
- [2] J.M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, O. Vatel, *Appl. Phys. Lett.* 64 (1994) 196.
- [3] J. Ahopelto, A.A. Yamaguchi, K. Nishi, A. Usui, H. Sakaki, *Jpn. J. Appl. Phys. Part 2* 32 (1993) L32.
- [4] J.H. van der Merwe, E. Bauer, *Phys. Rev. B* 39 (1989) 3632.
- [5] O. Féron, Y. Nakano, Y. Shimogaki, *J. Cryst. Growth* 221 (2000) 129.
- [6] S. Sudo, Y. Nakano, M. Sugiyama, Y. Shimogaki, H. Komiyama, K. Tada, *Thin Solid Films* 313/314 (1998) 604.
- [7] T. Nittono, S. Sugitani, F. Hyuga, *J. Appl. Phys.* 78 (1995) 5387.
- [8] Y. Wada, K. Wada, *Appl. Phys. Lett.* 63 (1993) 379.
- [9] H. Lipsanen, M. Sopanen, M. Taskinen, J. Tulkki, J. Ahopelto, *Appl. Phys. Lett.* 68 (1996) 2216.
- [10] M. Berti, A.V. Drigo, G. Rossetto, G. Torzo, *J. Vac. Sci. Technol. B* 15 (1997) 1794.
- [11] M. Sopanen, H. Lipsanen, J. Ahopelto, *Appl. Phys. Lett.* 66 (1995) 2364.
- [12] S.W. Chiou, C.P. Lee, J.M. Hong, C.W. Chen, Y. Tsou, *J. Cryst. Growth* 206 (1999) 166.
- [13] T. Nakano, Y. Nakano, Y. Shimogaki, *J. Cryst. Growth* 221 (2000) 136.
- [14] J. Jönsson, F. Reinhardt, M. Zorn, K. Ploska, W. Richter, J. Rumberg, *Appl. Phys. Lett.* 64 (1994) 1998.
- [15] M. Sopanen, H. Lipsanen, J. Ahopelto, *Appl. Phys. Lett.* 67 (1995) 3768.
- [16] M.E. Heimbuch, A.L. Holmes Jr., C.M. Reaves, M.P. Mack, S.P. DenBaars, L.A. Coldren, *J. Electron. Mater.* 23 (1994).
- [17] F. Reinhardt, B. Dwir, G. Biasiol, E. Kapon, *Appl. Surf. Sci.* 104/105 (1996) 529.
- [18] Y.Q. Wang, Z.L. Wang, T. Brown, A. Brown, G. May, *Thin Solid Films* 397 (2001) 162.
- [19] Q. Xie, J.E. Nostrand, J.L. Brown, C.E. Stutz, *J. Appl. Phys.* 86 (1999) 329.
- [20] B. Wang, F. Zhao, Y. Peng, Z. Jin, Y. Li, S. Liu, *Appl. Phys. Lett.* 72 (1998) 2433.