Appl. Phys. A 73, 161–165 (2001) / Digital Object Identifier (DOI) 10.1007/s003390100854

Applied Physics A
Materials
Science & Processing

Island dissolution during capping layer growth interruption

L.G. Wang[1,*], P. Kratzer[1,], M. Scheffler[1], Q.K.K. Liu[2]**

[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany
[2] Abteilung Theoretische Physik, Hahn-Meitner-Institut, Glienicker Str. 100, 14109 Berlin, Germany

Received: 29 January 2001/Accepted: 30 January 2001/Published online: 3 April 2001 –

Abstract. A possible scenario for the dissolution of partially capped quantum dots was investigated. This model is based on the consideration of the total free energy being a sum of elastic and surface energies as the quantum-dot material redistributes itself as a second wetting layer on top of the capping layer. Quantitative results were obtained for the case of InAs/GaAs quantum dots that are partially capped by GaAs. We compare our results with supporting experimental evidence.

PACS: 68.65.+g; 81.15.Hi; 68.35.Bs; 71.15.Nc

Self-assembled islands of InAs on GaAs formed in the Stranski–Krastanow growth mode have attracted much attention; they could be used as quantum dot (QD) structures in promising applications in opto-electronic devices such as QD lasers [1]. In this growth mode, three-dimensional InAs islands spontaneously form on a wetting layer after a critical film thickness has been exceeded. The islands formed in this way are overgrown subsequently with a capping layer material that has a wider energy band gap, usually GaAs. For the use of the resulting nanostructures in laser devices, it is crucial that these islands are homogeneous in size and shape. However, as well as islands small enough to operate as QDs, the stochastic nature of nucleation and growth may simultaneously produce either islands of larger sizes that are still pseudomorphic with the substrate lattice and hence coherently strained or even larger ones that have relaxed by incorporation of dislocations. It would be highly desirable to eliminate both types of larger islands by suitable procedures during the growth of the capping layer.

As a contribution to the discussion on ways to create QDs of homogeneous size, we show how the wetting phenomenon can be exploited for the dissolution of these large coherent islands. Our model includes a growth interruption of the capping layer after a certain thickness has been reached such that the smaller islands are completely covered while the larger ones are partially capped. For the latter that are coherently strained, relief of the elastic strain energy can take place, i.e., lowering of the free energy, if the island material redistributes itself as a second (partial) wetting layer on top of the interrupted capping layer. On resumption of the capping layer growth the islands that are embedded are then of smaller size. For the rest of this article it is to be understood, unless otherwise stated, that our terminology "dissolution of islands" and other similar expressions are meant to imply the additional formation of a second partial wetting layer from the island material.

Different elements of this model have been invoked in the qualitative discussions of experimental findings, which we shall review briefly. The issue of material redistribution was first addressed in the context of growth of stacked InAs QDs in a GaAs matrix by molecular beam epitaxy (MBE) [2]. Alternating layers of InAs and GaAs were deposited on the sample. Cross-sectional transmission electron microscope (TEM) images showed flattened InAs islands separated by GaAs layers, despite the nominal GaAs deposition (15 Å on the average) being not enough to cover the InAs islands. It was postulated that the initially uncovered part of the InAs island dissolved to form a partial second wetting layer. Furthermore, In atom evaporation from the exposed part of the island and the surface migration of Ga towards the latter from the surroundings would then enclose the remaining InAs to give the InAs island a flattened shape.

In another experiment, InAs islands grown by MBE on Si-doped GaAs [3] were examined by atomic force microscopy (AFM) after a thin overgrowth of GaAs. The AFM profiles showed substantial material redistribution among the partially covered islands as well as the formation of pits at the same sites.

Most recently, partially covered (by GaAs) InAs islands grown on GaAs by molecular vapor phase epitaxy (MOVPE) have been investigated [4–8]. The GaAs deposition used to

*Present address: Solid State Theory, National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, Col. 80401, USA
**Corresponding author.
(Fax: +49-30/8413-4701, E-mail: kratzer@fhi-berlin.mpg.de)

form the partial capping layer was varied systematically. Redistribution of InAs was again confirmed. For the various stages of the redistribution process, data were collected from several experimental probes: Firstly, in situ reflectance anisotropy spectroscopy (RAS) was used to monitor the surface reconstruction and chemical composition of the capping layer before and during the growth interruption. Secondly, the effect of the growth interruption was investigated by AFM on samples cooled down after the interruption. Indeed, in some samples, pits as deep as the GaAs partial overgrowth were detected at the sites of the partially covered islands. Thirdly, cross-sections of fully overgrown samples were inspected using high-resolution transmission electron microscopy (HRTEM). The different probes unequivocally revealed elimination of the large islands and the formation of a second wetting layer. However, one must note that these islands that are dissolved are so large that they most probably contain dislocations.

On the theoretical side, quantitative studies are still lacking. Until now only general theoretical estimates of the redistribution of InAs from the island to form a second partial wetting layer have been given, based on spatial variations of the chemical potential [2].

In the present work, we evaluate a sequence of values for the total free energy as the material is depleted from the partially covered island to form the second wetting layer. We have adopted a hybrid method to calculate the total energy E^{tot} by decomposing it into contributions from the elastic strain of the pseudomorphic island and the surrounding substrate and capping layer, E^{elast}; from the surface energy of the facets of the island and the interior walls of the hole, E^{surf}; and from the second wetting layer, E^{wl}:

$$E^{\mathrm{tot}} = E^{\mathrm{elast}} + E^{\mathrm{surf}} + E^{\mathrm{wl}}. \tag{1}$$

The strain energy E^{elast} is calculated with the continuum model using the finite-element method (FEM), while the other two terms are calculated ab initio by the density functional theory (DFT). The principle of this hybrid theory has been demonstrated to be useful in the analyses of the QD size under various experimental conditions [9–11] and the optimum shapes of the QDs [12–14]. For a particular realization of the proposed scenario for the depletion process, we attempt to quantify the driving force for the material redistribution of the partially covered InAs islands by GaAs, making use of the latest experimental data [8]. In disentangling these contributions, we find that none of the three terms can be neglected.

The most detailed experimental results that show simultaneous occurrence of island dissolution and formation of a second wetting layer that would lend themselves to comparison with our calculations are those of Steimetz et al. [8]. However, a direct comparison is still premature as the islands observed to have dissolved were so large that very probably they contained dislocations, while we have concentrated on coherent islands.

The time evolution of material redistribution during the growth interruption and the rate at which it occurs are eventually governed by the kinetics of the microscopic processes involved. While a qualitative interpretation of the redistribution process has been attempted on the basis of a phenomenological treatment [2], a quantitative understanding of this phenomenon must start with the identification of the driving force, i.e., the energy gain associated with the redistribution. The energetics of the transformation process from three-dimensional clusters to a wetting film of InAs is determined by both the elastic energy relief and the changes of the surface energy. Our present study to elucidate the relative importance of the elastic strain energy and surface energy makes a useful, and possibly necessary, contribution to the eventual understanding of the fascinating phenomenon of matter redistribution. We have not included in the study In atom segregation or intermixing with Ga atoms in the matrix. It is clear that its effect cannot be neglected [3, 15]. However, for want of a reliable quantitative description of this phenomenon at present, we deem it more prudent not to undermine our quantitative results with any other theories that are too speculative.

1 Theory

1.1 Hybrid approach

Details of the surface energy calculations are similar to previous works [12–14], and are therefore only summarized briefly here. The surface energy of the island facets and the formation energy of the InAs layer on the GaAs substrate are calculated using DFT [16] in conjunction with the pseudopotential approach [17]. A slab model is used to describe the surface, and the bottom layer is fixed and passivated by pseudohydrogen atoms [18]. The local-density approximation to the exchange-correlation energy-functional [19] is applied; and the atoms are represented by fully separable norm-conserving ab initio pseudopotentials [20–22]. The electronic wave functions are expanded into plane waves with the energy cut-off of 10 Ry. The Brillouin zone integration of the electron density is performed using special $\boldsymbol{k}$-point sets [23]. Apart from the atoms in the bottom layer and the pseudohydrogen atoms, the atoms in the supercell are relaxed until the forces on the atoms are smaller than 25 meV/Å. The value of the surface energy depends on the chemical potential, which is determined by the chemical environment (e.g., As partial pressure and temperature in the reactor). To calculate the elastic energies, we have used the continuum elasticity theory simulated by the FEM [12–14, 24]. The values of the moduli of elasticity of InAs and GaAs have been taken from the literature [13, 25]. The lattice mismatch between InAs and GaAs that gives rise to the elastic energies is $\alpha := (a_{\mathrm{GaAs}} - a_{\mathrm{InAs}})/a_{\mathrm{InAs}} = -6.7\%$, where a_{GaAs} and a_{InAs} are the lattice constants of GaAs and InAs, respectively. For the FEM simulations, the size of the unit cell is suitably chosen to be consistent with the latest experimental observations of island dissolution [8]. Periodic boundary conditions were applied to the side planes of the unit cell. The eight-node hexahedral finite elements were used. Their density was incrementally increased in the parts of the island and the capping layer where the elastic energy density was large until we finally arrived at an estimated accuracy of 5% for the total elastic strain energy.

1.2 Model of the hole formation process

In order to gain quantitative insight into the process of hole formation, we investigate a simple model of how a large island transforms itself into a hole. We assume that the material

gradually diffuses away from the island via surface diffusion and forms a homogeneous wetting layer with increasing thickness on the GaAs capping layer. Contributions to the energetics that drive the transformation process come from the elastic energy relief, as well as from changes in the surface and interface energy. The latter turns out to be very small, and is neglected in the following analysis. Since the newly formed wetting layer is typically very thin (InAs coverage < 1 ML), its formation energy must be obtained from ab initio calculations.

The lower surface energy of InAs compared to most GaAs surfaces generally favors the formation of a wetting layer [11]. Figure 1 illustrates this important fact, displaying the energies of the stable reconstructions under As-rich conditions, for pure GaAs, pure InAs and a wetting layer corresponding to 0.4 ML InAs coverage, where the film formation energy has its minimum (see [9]). The thermodynamics of wetting depends on growth conditions, here described by the chemical potential μ_{As}. Spontaneous wetting occurs for the GaAs $\beta 2(2\times 4)$ surfaces as well as for $c(4\times 4)$ for moderately As-rich conditions. For the present analysis, we assume the chemical potential $\mu_{\mathrm{As}} = \mu_{\mathrm{As(bulk)}} - 0.15$ eV, indicated by the arrow in Fig. 1, because the surface reconstruction of the capping layer is then sensitive to the In content, and switches from GaAs $c(4\times 4)$ to InAs (2×4) whenever In becomes available. Such sensitivity has been reported in RAS measurements [8]. From Fig. 1, however, it is also obvious that for $\mu_{\mathrm{As}} \sim \mu_{\mathrm{As(bulk)}}$ any InAs film with the $\beta 2(2\times 4)$ reconstruction will have a higher surface energy than the GaAs $c(4\times 4)$ surface and is hence energetically unfavorable. Therefore, theory allows us to identify a regime where hole formation could be suppressed in the most As-rich growth conditions conceivable, with InAs islands co-existing with the bare GaAs $c(4\times 4)$ substrate. We shall make further remarks in connection to this later.

For a more detailed discussion of the energy gain, we focus on a specific simple geometrical shape for the large coherent island, an island with $\{111\}$ and $\{\bar{1}\bar{1}\bar{1}\}$ side facets. The island base length is about 21 nm and its height is 15 nm. The value of the base length lies between 17 nm [2] and 34 nm [3].

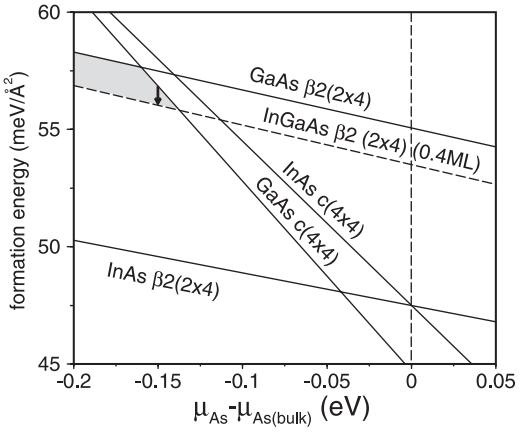

Fig. 1. Calculated surface energy (*solid line*) and film formation energy (*dashed line*) as a function of the As chemical potential for various GaAs (001) and InAs (001) surfaces. Depending on indium content and surface relaxation, the formation energy of an InGaAs film lies inside the *shaded region*

In [2], partial dissolution of InAs islands was discussed in the growth of a stack of QDs. In [3], growth interruption after very thin GaAs capping led to the observation of pits at the sites of the previously partially covered islands. We shall show later that a complete dissolution of the islands is possible. Hence, pits could be the final result of material diffusion. The relatively high aspect ratio adopted for the island is consistent with some of the InAs islands observed [26]. Moreover, this is also consistent with our thermodynamic approach, since the equilibrium shape of large InAs islands was found to be dominated by the $\{111\}$ and $\{\bar{1}\bar{1}\bar{1}\}$ side facets [13].

We assume that first the top of the island levels off (Fig. 2b), and a truncated top surface with $\{001\}$ orientation forms. This might have occurred already when the island forms, before the deposition of the capping layer. Without loss of generality, our analysis could also start with the step shown in Fig. 2b. In the next step, a "crater" forms inside the island (Fig. 2c). The hole formation process may end with a partially filled hole (Fig. 2d), or with the complete removal of the island material, apart from a thin wetting layer covering the interior walls of the hole (Fig. 2e). The overhanging walls in Fig. 2d and e are motivated by the experimental observation that the orifice of the holes is typically narrower when the capping layer growth is interrupted at a slightly larger thickness [8].

We analyse the energetics associated with various stages of the transformation, using a partitioning of total energy

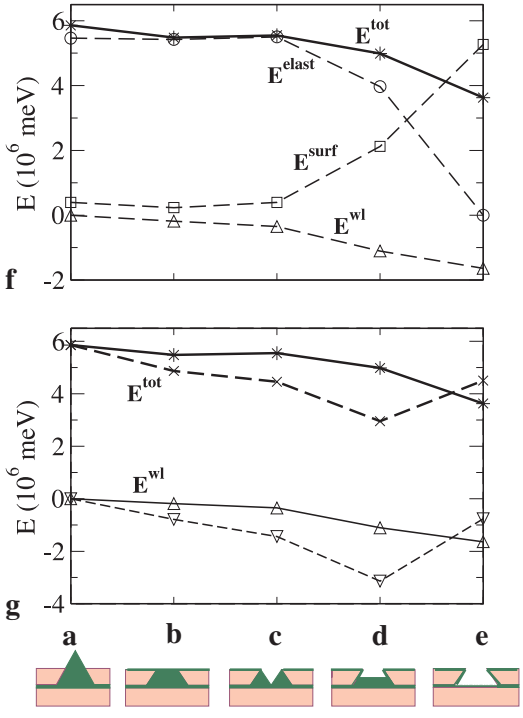

Fig. 2. a–e Schematic of the transformation from a large InAs island partially overgrown by a GaAs capping layer to a hole in five steps. **f** The energetics in the case of a density of partially covered three-dimensional islands equal to 4.4×10^9 cm^{-2}. The calculated total energy (*solid line*) and its contributions (*dashed lines*) [see (1)] for the various stages of island dissolution are shown. **g** The energetics for a density of 4.4×10^9 cm^{-2} (*solid lines*) compared with those for a density of 10^{10} cm^{-2} (*dashed lines*). For the latter, full depletion of the hole is energetically unfavorable

according to (1). For islands of different sizes before the redistribution, the elastic strain energy E^{elast} would scale approximately linearly with the island volume V. E^{surf} is the surface energy of the InAs facets of the island itself and the interior walls of the hole (in the case of Fig. 2d and e). It scales with the volume of the original island V as $V^{2/3}$. The wetting layer contribution E^{wl} is given by the difference between the surface energy of GaAs $c(4\times4)$, $\gamma_{\mathrm{c}(4\times4)}$, and the formation energy of the wetting layer, $\gamma_{\mathrm{f}}(\theta_{\mathrm{In}})$, multiplied by the surface area. We are working under conditions where a structural phase transition $c(4\times4)/\beta2(2\times4)$ occurs, around $\mu_{\mathrm{As}} = \mu_{\mathrm{As(bulk)}} - 0.15\,\mathrm{eV}$. Although the energy gain *per area* from the wetting layer formation is small ($< 1\,\mathrm{meV/\AA^2}$), its overall contribution could be significant due to the large area involved in the wetting. We assume that the redistributed material, stemming from all partially covered islands, is distributed evenly into a wetting layer. For the numerical analysis, we consider a density of partially covered three-dimensional islands of $n = 4.4\times10^9\,\mathrm{cm^{-2}}$, implying that an average area of 150 nm × 150 nm on the capping layer surrounds each island. Formally, the wetting layer contribution can be written as $E^{\mathrm{wl}} = (\gamma_{\mathrm{f}}(nV/l) - \gamma_{\mathrm{c}(4\times4)})/n$, where l is the monolayer thickness and the function γ_{f} is taken from previous calculations [10].

Numerical values for the total energy and its contributing parts for the case described above are shown in Fig. 2. The elastic energy relief favors island dissolution, since the buried part of the island is under (compressive) strain. The surface energy term can have either sign. When going from the situation depicted in Fig. 2a to Fig. 2b, E^{surf} decreases, because the removal of the tip of the pyramid leads to a reduction of surface area. At the same time, the material that is removed is on the whole unstrained. Hence, there is no change in E^{elast}. From steps b to e, the surface area of the pure InAs facets plus the interior walls of the hole increases, and thus E^{surf} increases again. However, the sum of the three contributions indicates that dissolution of the island and hole formation are still energetically favorable. The sum of E^{surf} and E^{elast} alone varies very little between steps a and e, and we can hence exclude the idea that the elastic strain relief alone could drive the formation of holes. Actually, we can see that the total energy follows the tendency of E^{wl} (Fig. 2g), which implies that the wetting effect plays a key role in island dissolution.

In the above calculations, the In content in the wetting layer increases from steps a to e, as follows from mass conservation. As shown previously [9], the formation energy γ_{f} is minimal for an InAs coverage of 0.4 ML, and increases linearly for rather thick films (more than a few ML). For this reason, the spreading out of the material from the partially overgrown islands onto the capping layer is energetically favorable only up to a certain thickness of the wetting layer, i.e., a certain amount of transferred material. After that, the diffusion of InAs away from the hole will stop, even if the hole remains partially filled with InAs. The density and size of the partially capped islands at the beginning will decide the amount of InAs that will remain in the holes at the end. For the density and size considered above, we find that the holes appearing in place of the islands are fully depleted at the end. For a higher density of the large islands ($10^{10}\,\mathrm{cm^{-2}}$), the half-depleted hole (Fig. 2d) has the lowest energy (see Fig. 2g). If we take the recent experimental observations as possible examples [8], the density of the large islands would have been typically much lower, and hence our theory predicts that coherent islands transform into fully depleted holes.

Various aspects of our findings above could be used to gain insight into reported cases of interrupted capping layer growth found in the literature. Closely matching our model are the experimental observations reported in [8], in which the islands dissolved are probably too large to be coherent. Nevertheless, pits of a depth corresponding to the thickness of the GaAs capping layer have been measured by AFM. Similar deep pits have also been reported in [3] and [27].

We have discussed two possible factors that could stop the diffusion of material out of the islands to form the second wetting layer. The chemical environment that determines the chemical potential could make even the start of the formation of a second wetting layer energetically unfavorable. Alternatively, the diffusion would stop after the second wetting layer has reached a certain thickness, because it has become energetically unfavorable to grow any further. Our choice of chemical potential reflects the situation found in [8], where the second wetting layer formed with material exhausted from the partially covered islands. In [3] and [27], the second wetting layer was not sought, although material diffused from the islands seemed to have piled up around the pit left behind. Our present thermodynamic equilibrium consideration has not included this morphology. On the other hand, one needs to have a better knowledge of the corresponding chemical potential before one can deduce whether this rim pile-up is energetically more favorable than a second wetting layer. In addition, we cannot exclude the possibility of an activation barrier between the wetting layer formation and the pile-up morphology. Our model clearly could display different sizes of pit formed according to the height of the partial capping layer. This matches nicely with experimental observations [3, 8, 27].

2 Conclusion

We have presented a theoretical investigation of growth interruption during GaAs capping of InAs islands. Recent reflectance anisotropy spectroscopy measurements during growth and post-growth analysis via AFM and TEM have motivated us to study the redistribution of partially covered InAs islands into a second fractional wetting layer. Our study is based on a thermodynamic equilibrium consideration. The total energy has been calculated in a previously tested hybrid model. The bulk strain energy was evaluated by continuum elasticity theory implemented using the finite element method and the surface energy by ab initio density functional theory. We have shown that with the choice of the chemical potential which corresponds to the reported growth condition wetting of the GaAs capping layer by InAs from the partially covered islands takes place. This is mainly driven by the lowering of the surface energy.

Acknowledgements. We acknowledge helpful discussions with E. Steimetz, J.-T. Zettler, W. Richter and R. Heitz. This research project was supported in part by the Deutsche Forschungsgemeinschaft, Sfb 296.

References

1. N. Kirstaedter, N.N. Ledentsov, M. Grundmann, D. Bimberg, V.M. Ustinov, S.S. Ruvimov, M.V. Maximov, P.S. Kope'ev, Z.I. Alferov, U. Richter, P. Werner, U. Gösele, J. Heydenreich: Electron. Lett. **30**, 1416 (1994)
2. N.N. Ledentsov, V.A. Shchukin, M. Grundmann, N. Kirstaedter, J. Böhrer, O. Schmidt, D. Bimberg, V.M. Ustinov, A.Y. Egorov, A.E. Zhukov, P.S. Kop'ev, S.V. Zaitsev, N.Y. Gordeev, Z.I. Alferov, A.I. Borovkov, A.O. Kosogov, S.S. Ruvimov, P. Werner, U. Gösele, J. Heydenreich: Phys. Rev. B. **54**, 8743 (1996)
3. J.M. Garcia, G. Medeiros-Ribeiro, K. Schmidt, T. Ngo, J.L. Feng, A. Lorke, J. Kotthaus, P.M. Petroff: Appl. Phys. Lett. **71**, 2014 (1997)
4. E. Steimetz, T. Wehnert, K. Haberland, J.-T. Zettler, W. Richter: J. Cryst. Growth **195**, 530 (1998)
5. J.-T. Zettler: Prog. Cryst. Growth Charact. Mater. **35**, 1 (1998)
6. F. Reinhardt, J. Jönsson, M. Zorn, W. Richter, K. Ploska, J. Rumberg, P. Kurpas: J. Vac. Sci. Technol. B **12**, 2541 (1994)
7. E. Steimetz, J.-T. Zettler, F. Schienle, T. Trepk, T. Wethkamp, W. Richter, I. Sieber: Appl. Surf. Sci **107**, 203 (1996)
8. E. Steimetz, T. Wehnert, H. Kirmse, F. Poser, J.-T. Zettler, W. Neumann, W. Richter: J. Cryst. Growth **221**, 592 (2000)
9. L.G. Wang, P. Kratzer, M. Scheffler, N. Moll: Phys. Rev. Lett. **82**, 4042 (1999)
10. L.G. Wang, P. Kratzer, N. Moll, M. Scheffler: Phys. Rev. B **62**, 1897 (2000)
11. L.G. Wang, P. Kratzer, M. Scheffler: Jpn. J. Appl. Phys. **39**, 4298 (2000)
12. E. Pehlke, N. Moll, A. Kley, M. Scheffler: Appl. Phys. A **65**, 525 (1997)
13. N. Moll, M. Scheffler, E. Pehlke: Phys. Rev. B **58**, 4566 (1998)
14. Q.K.K. Liu, N. Moll, M. Scheffler, E. Pehlke: Phys. Rev. B **60**, 17 008 (1999)
15. Q. Xie, P. Chen, A. Madhukar: Appl. Phys. Lett. **65**, 2015 (1994)
16. W. Kohn, L.J. Sham: Phys. Rev. **140A**, 1133 (1965)
17. M. Bockstedte, A. Kley, J. Neugebauer, M. Scheffler: Comput. Phys. Commun. **107**, 187 (1997); http://www.fhi-berlin.mpg.de/th/fhimd
18. K. Shiraishi: J. Phys. Soc. Jpn. **59**, 3455 (1990)
19. J.P. Perdew, A. Zunger: Phys. Rev. B **23**, 5048 (1981)
20. D.R. Hamann: Phys. Rev. B **40**, 2980 (1989)
21. L. Kleinman, D.M. Bylander: Phys. Rev. Lett. **48**, 1425 (1982)
22. M. Fuchs, M. Scheffler: Comp. Phys. Commun. **116**, 67 (1999); http://www.fhi-berlin.mpg.de/th/fhimd
23. H.J. Monkhorst, J.D. Pack: Phys. Rev. B **13**, 5188 (1976)
24. *MARC User's Guide* (MARC Analyses Research Corporation, Palo Alto 1996)
25. K.-H. Hellwege, A.M. Hellwege (Eds.): *Landolt-Börnstein, Physics of Group IV Elements and III-V Elements*, New Series, Group III, Vol. 17, Part a (Springer-Verlag, Berlin 1982) pp. 204,287
26. S. Ruvimov, P. Werner, K. Scheerschmidt, U. Gösele, J. Heydenreich, U. Richter, N.N. Ledentsov, M. Grundmann, D. Bimberg, V.M. Ustinov, A.Y. Egorov, P.S. Kop'ev, Z. Alferov: Phys. Rev. B **51**, 14 766 (1995)
27. A. Lorke, R.J. Luyken, A.O. Govorov, J. Kotthaus, J.M. Garcia, P.M. Petroff: Phys. Rev. Lett. **84**, 2223 (2000)