Quantitative Model of Heterogeneous Nucleation and Growth of SiGe Quantum Dot Molecules

Hao Hu, Hongjun Gao, and Feng Liu

Phys. Rev. Lett. **109**, 106103 — Published 7 September 2012

DOI: 10.1103/PhysRevLett.109.106103

Quantitative Model of Heterogeneous Nucleation and Growth of SiGe Quantum Dot Molecules

Hao Hu,[1,2] Hongjun Gao,[2] and Feng Liu[1,*]

[1]*Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, USA*

[2]*Institute of Physics, Chinese Academy of Science, Beijing 100190, China*

Using a multiscale approach combining continuum model with first-principle calculation, we develop a quantitative theoretical model for heterogeneous nucleation and growth of quantum dot molecule (QDM) —a few islands "strain bonded" by a pit in heteroepitaxy of thin films, in contrast to homogeneous nucleation and growth of isolated strained islands on surface. We show that the critical size and energy barrier for island nucleation next to a pit is substantially reduced with the increasing pit size, but the reduction approaches to an upper bound of $\sim 85\%$ and $\sim 72\%$ for the size and barrier, respectively. Our model also predicts a self-limiting effect on island growth, resulting from an intriguing interplay between island-pit attraction and island-island repulsion, that drives the island size to increase linearly with the pit size, which explains a long-standing puzzle of experimental observation.

PACS numbers: 68.55.A-, 68.35.Md, 81.07.Ta

Nucleation and growth of strained islands in heteroepitaxy of thin films has attracted much recent interest because of their applications as quantum dots (QDs) in the next-generation electronic and optoelectronic devices[1–3]. A special class of QDs is the so-called QD molecules (QDMs), consisting of a few QDs "bonded" together by elastic strain field through, e.g., a pit in the surface[4–17]. The QDMs, on the one hand, are scientifically interesting, exhibiting intriguing nucleation and growth behavior different from a single QD; on the other hand, they are technologically appealing, offering novel potential applications based on the inter-QD electronic coupling within a QDM as well as the inter-QDM interactions.

Relatively speaking, one may consider the nucleation of isolated QDs on surface without pit as *homogenous* nucleation[18, 19], and the nucleation of QDMs, i.e., the nucleation of a few islands mediated by a pit as *heterogeneous* nucleation. The theory of homogeneous nucleation of QD has been long established at the continuum level[19–21], which provides us with a good qualitative understanding. Furthermore, augmenting continuum theory with first-principle calculation, a quantitative model for homogeneous nucleation has been developed[22], which predicted the critical size for Ge/SiGe QDs in excellent agreement with the experiment. However, despite of extensive experimental studies of QDMs in both SiGe[3–13] and III-V systems[14–17], the theoretical models of heterogeneous nucleation and growth of QDM is much less developed.

Previous studies based on 2D step model[6] and 3D finite element analysis[10, 23] have identified the importance of island-pit and island-island interactions in affecting the thermodynamics and kinetics of nucleation and growth of QDMs, in particular reducing the critical size and energy barrier to enhance the island nucleation next to a pit[6, 10, 23] and limiting the island size growth[11]. However, some fundamental questions concerning with the QDM still remain to be answered, especially at a more quantitative level. How much will the critical size and energy barrier for island nucleation be reduced as a function of pit size? Is the reduction bounded or unbounded (i.e., continues indefinitely) with the increasing pit size? If bounded what are the bounds? Also, can we explain the puzzling experimental observation[11] that the self-limited island size shows a linear dependence on the pit size?

In this Letter, we develop a quantitative model to better understand the physical mechanisms underlying the kinetics of heterogeneous nucleation and growth of QDMs by combining the 3D continuum model with first-principle parameter inputs. We show that a key factor in affecting the kinetics of QDM nucleation and growth is the changing balance between the island-pit attraction and the island-island repulsion at the different stages of island growth, which is absent in the homogenous nucleation and growth of QDs (isolated islands). We quantify the critical size and energy barrier for nucleation of SiGe

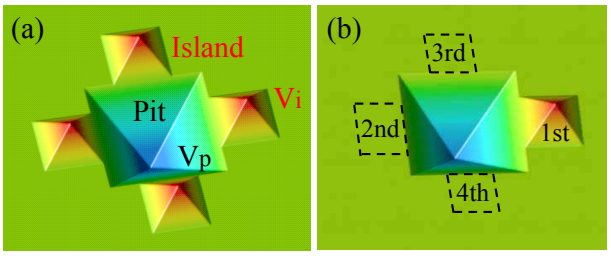

FIG. 1: (Color online) (a) 3-D Schematic illustration of a QDM with four QD nucleated/grown concurrently around the pit; (b) Schematic illustration of QDs nucleated sequentially in a QDM.

QDs as a function of pit size. We show that the size and barrier are reduced by the presence of pit but with an upper bound of reduction that approaches to $\sim 85\%$ and $\sim 72\%$, respectively, if the pit size would go to infinity. As a pleasant surprise, our model also predicts a linear dependence of the self-limiting island growth size on pit size, resolving the long-standing experimental puzzle.

3D continuum model of QDM—the reduction of critical size and nucleation barrier. As shown by previous 2D continuum model[6] and 3D finite element analysis[10, 23], the key difference between heterogeneous nucleation of QDMs and homogeneous nucleation of QDs lies in island-pit and island-island interactions. Therefore, we will first formulate a heterogeneous nucleation theory of QDMs by extending the homogeneous nucleation theory[19–21] with the inclusion of the these interactions[23, 24]. As a model system, we consider the type of QDM consisting of four faceted islands surrounding a pit with the same facet (see Fig. 1a), as observed in the growth of SiGe films on Si substrate. The experimental data of SiGe QDMs[4–13] are the richest and most complete for comparison. On the other hand, this choice will not lose the generality of the theoretical model, and some qualitative conclusions drawn from our theory are applicable to III-V and other QDMs.

We assume the four islands in the QDM to have equal volume (V_i) sitting around a pit of volume V_p with a seamless facet continuation, as shown in Fig. 1. We may consider the QDs to nucleate concurrently around the pit as shown in Fig. 1a, then the total energy per island in the QDM is derived in the dimensionless form as[24]

$$E = (3V_i^{2/3} - 2V_i) + \frac{-16V_pV_i + (1+4\sqrt{2})V_i^2}{9(V_p^{1/3} + V_i^{1/3})^3}. \quad (1)$$

Or we may consider the QDs to nucleate sequentially one by one around the pit as shown in Fig. 1b, then the total energy per island is slightly different from Eqs. (1)[24] (see Fig. 2 and related discussion below).

The first two terms in Eq. (1) are the energies of an isolated island[19]. The third term includes the strain-induced island-pit and island-island elastic interaction energies[25, 26]. The critical size $V_c^0 = (4\Gamma/9\varepsilon_0)^3 \cot^2\theta$ and energy barrier $E_c^0 = (4\Gamma)^3 \cot\theta/(9\varepsilon_0)^2$ for homogeneous nucleation[19] are used as the reference volume and energy, respectively. $\Gamma = \gamma_f \csc\theta - \gamma_w \cot\theta$ is the surface energy increment, and $\gamma_f(\gamma_w)$ is the surface energy of island/pit facet (wetting layer); θ is the island/pit facet angle. ε_0 is the scaled elastic energy density.

The island-pit and island-island interactions are dipolar in nature. The misfit strain induces a distribution of elastic forces on the surface of island and pit, but pointing in opposite directions[19]. Consequently, the island-pit interaction is attractive, and the island-island interaction is repulsive. It is these island-pit and island-island interactions and their complex interplay that give rise to some new interesting features of nucleation and growth of QDMs. Figure 2a shows E as a function of V_i for different V_p, in comparison with the case of homogeneous nucleation ($V_p = 0$). We can see that the presence of the pit lowers the island energy; the larger the pit is, the lower the energy will be.

In the case of sequential nucleation (Fig. 2b), the energy barrier and critical size is smallest for the first island due to only the island-pit attraction, and increases slightly in ascending order from the second, to the third and to the fourth island due to the increasing island-island repulsion. Because the island size at the nucleation stage is much smaller than the pit size and also because the island-island distance is larger than island-pit distance, the island-pit attraction (E_{ip}) is always dominating over the island-island repulsion (E_{ii}) so that energy barrier and critical size for four islands are very close and are all much smaller than those on the flat substrate without pit. This analysis shows that the larger the pit, the more favorable it is for nucleation of multiple islands next to the pit to form a QDM, consistent with what seen in most experiments[17]. Therefore, the dominance of attractive island-pit interaction over repulsive island-island interaction is responsible for the preferred nucleation of a few islands next to a pit to form QDMs.

Quantitative analysis with first-principle data inputs—the upper bounds on the size and barrier reduction. The decrease of island energy leads to reduced critical size (V_c) and energy barrier (E_c) for island nucleation next to a pit, and hence an enhanced kinetic rate of nucleation in QDMs. For a quantitative analysis, we follow the same scheme [22] performed previously for Ge QDs on Si(001). We note that QDMs form only in the low misfit SiGe alloy film but not in the pure Ge film on Si(001), a point we will discuss in more detail later. Specifically we choose the composition of $Si_{0.7}Ge_{0.3}$ as in the experiment[10, 11]. The strain energy density scales quadratically with strain. For the pure Ge QD, the strain energy density[22] is $\varepsilon_0 = 270meV/nm^3$, and for the $Si_{0.7}Ge_{0.3}$ QD, it is $\varepsilon_0 = 24.3meV/nm^3$. For Γ, it is more

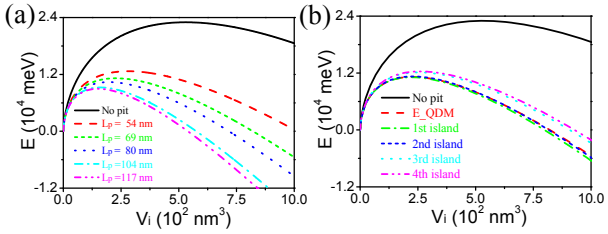

FIG. 2: (Color online) (a) Total energy per island in a QDM vs. the island volume for different pit sizes, the energy of isolated island nucleation is shown (black) for comparison; (b) Total energy of sequentially nucleated islands vs. the island volume for $V_p = 20$ (reduced unit) and $V_{is} = 5$ (reduced unit).

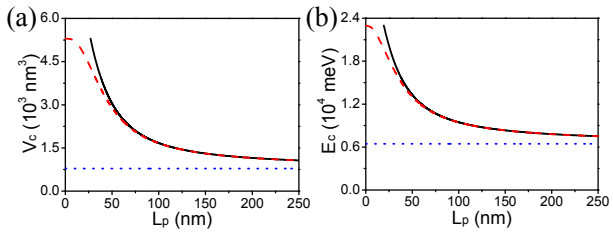

FIG. 3: (Color online)(a),(b) Critical sizes and energy barriers for island nucleation in a QDM (black solid curve) and one island nucleation next to a pit (red dashed curve) as a function of pit base size, dotted line indicates the asymptotic value at the limit of $V_p \gg V_i$.

complicated. It is well-known both the (105) QD facet[3] and the (001) wetting layer[27] surfaces consist of almost pure Ge in the SiGe alloy film due to surface segregation. So, roughly we may estimate the Γ using the strain scaled pure Ge (105) and (001) surface energies (Fig. 4 in Ref. 28). Because the surface composition and reconstruction and wetting layer thickness are not exactly known[28], the exact value of Γ for $Si_{0.7}Ge_{0.3}$ is uncertain. But we can bracket its limiting values in between 100 meV/nm^2 and 500 meV/nm^2, with the lower bound having the critical size for alloy QD approaching to that of pure Ge QD while the upper bound ensuring the critical size below the size observed in the experiment[10, 11]. In our calculation, we choose the $\Gamma = 150 meV/nm^2$, which gives the best agreement with the experimental results.

We calculate the critical size and energy barrier for the $Si_{0.7}Ge_{0.3}$ QD without pit to be $V_c^0 = (4\Gamma/9\varepsilon_0)^3 \cot^2\theta = 5.3 \times 10^2\ nm^3$ (corresponding to a base size of $\sim 25\ nm$) and energy barrier $E_c^0 = (4\Gamma)^3 \cot\theta/(9\varepsilon_0)^2 = 2.3 \times 10^4\ meV$, respectively. Then, from the E(V_i) plot (Fig. 2a), we numerically derive the critical size (V_c) and energy barrier (E_c) next to a pit as a function of pit size (V_p), as shown in Fig. 3a and 3b. Both V_c and E_c decrease quickly with the increasing V_p initially, and then slow down and saturate when V_p becomes large.

It is interesting to note that the reduction of critical size and energy barrier for island nucleation by the presence of pit has an upper bound, namely, the reduction doesn't go indefinitely but gradually saturates to a fixed amount with the increasing pit size. The asymptotic values of V_c and E_c at the infinite V_p are derived as

$$E = 3V_i^{2/3} - 34V_i/9. \qquad (2)$$

Taking $dE/dV_i = 0$, we obtain $V_c = (9/17)^3 \simeq 14.8\%$ and $E_c = (9/17)^2 \simeq 28\%$ at this limit, shown as the dashed lines in Fig. 3a and 3b, respectively, which correspond to a maximum reduction by 85.2% and 72% for the size and barrier. For example, the critical size for the $Si_{0.7}Ge_{0.3}$ QD can be reduced from $5.3 \times 10^2\ \mathring{A}^3$ to the $0.78 \times 10^2\ \mathring{A}^3$. We note that the saturation values correspond to the reduced critical size and energy barrier for island nucleation near the edge of two semiinfinite facets (the (001) and (105) facets in the present case), which has indeed been seen in some experiments (see, e.g., Fig. 2b in Ref. [29]).

Self-limiting growth—the linear dependence of island size on pit size. Next, we show our model prediction of a self-limiting effect on the growth of QDMs. Once the islands nucleate next to the pit, they tend to grow bigger. Interestingly, we found that initially when islands are small, the magnitude of attractive island-pit interaction energy (E_{ip}) increases faster than the repulsive island-island interaction energy (E_{ii}) with the increasing island size (V_i), as shown in Fig. 4a for the case of $L_p = 80\ nm$. Thus, the overall interaction energy initially favors island growth to enhance island-pit attraction. Later on when islands grow bigger, however, the situation reverses and E_{ii} increases with V_i faster than E_{ip}. Consequently, the overall interaction energy subsequently inhibits island growth to avoid island-island repulsion. This leads to a self-limiting growth on island size, characterized with an island size (V^*) of minimum interaction energy.

To derive (V^*), we denote E_{ipi} as the sum of all the interactions, which is plotted vs. V_i in Fig. 4a. E_{ipi} decreases with the increasing V_i initially for small V_i, favoring the island growth, but reaches a minimum (V^*) beyond which E_{ipi} increases with the increasing V_i, inhibiting island growth. V^* depends on V_p, and in Fig. 4b we plot the numerical solutions of island base size L_i^* ($V^* = L_i^{*3} \tan\theta/6$) as a function of pit base size L_p ($V_p = L_p^3 \tan\theta/6$), which shows an surprising linear dependence. These analyses indicate that the self-limiting effect is caused by an intriguing competition between the island-pit attraction and island-island repulsion as a function of island size (the role of island-island repulsion on self-limiting growth has been pointed out before[11]). Most surprisingly, not only our model predicts a linear dependence of island size on pit size (Fig. 4b) in perfect agreement with the experiment (see Fig. 7 in Ref. 11), but also quantitatively a slope very close but less than unity, i.e., the island base size is always slightly smaller than the pit base size as observed in the experiment[10, 11].

The self-limiting effect that our model reveals indicates that there exists a preferred island growth size corresponding to each given pit size, and further scales linearly with pit size. It implies that as the pit size varies, the preferred island size varies in linear proportion to the pit size as shown in Fig. 4b. This is in excellent agreement with the experiment, albeit our model cannot give the dynamics of island and pit growth. Furthermore, after QDMs mature (see discussion below), at the later stage of growth there is another interesting experimental observation of conformal growth of QDM where pit and islands evolve concurrently with their size ratio remains

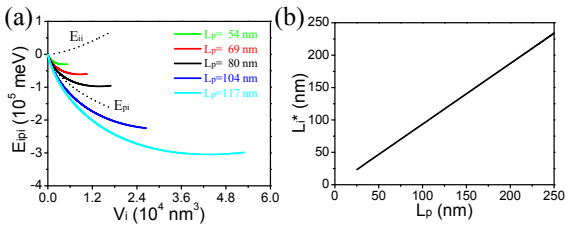

FIG. 4: (Color online)(a) Total strain induced elastic interaction energy (E_{ipi}) in a QDM vs. island volume (V_i) for different pit volume (V_p). Dotted lines show the pit-island and island-island interaction energies vs. V_i for $L_p = 80\ nm$. (b) The island base size L_i^* of minimum interaction energy as a function of the pit base size L_p.

almost constant [10]. Therefore, the pit and island size ratio is predominantly determined by the self-limiting effect in the early stage of growth before QDM maturation, as our model demonstrated.

Additional points of discussion. In the above discussion, we assume the island nucleate next to the pit, as seen in many experiments. More generally, the island-pit attraction should also operate at larger island-pit separation, but with smaller magnitude as the attraction decreases with the separation (L) as $\sim L^{-3}$. For an island at a distance of L to a pit, the island energy (in reduced unit) is[24]

$$E = 3V_i^{2/3} - 2V_i - 2V_pV_i/9V_L \qquad (3)$$

where we set $V_L = L^3 \tan\theta/6$. And the critical size and energy barrier can be calculated as

$$V_c = (1 + V_p/9V_L)^{-3}, \quad E_c = (1 + V_p/9V_L)^{-2} \qquad (4)$$

Apparently, the reduction of critical size and energy barrier increases with the decreasing L. The islands prefer to nucleate as close to the pit as possible and in the best scenario they nucleate right next to the pit to form the QDMs with a seamless facet continuation from pit to island. This is consistent with experimental observations that under some growth conditions when island density is high, the islands may also assemble around the pits, in addition to forming QDMs[8].

In accordance with the experiments, we performed our quantitative analysis of QDMs for the $Si_{0.7}Ge_{0.3}$ alloy system of intermediate strain. An experimental growth phase diagram[11] has been set up, which shows that QDM nucleates/grows at intermediate temperature, growth rate and misfit strain; pit forms at low temperature, high growth rate and low misfit strain; islands (QDs) forms at high temperature, low growth rate and high misfit strain. This is consistent with our findings of relative energy barrier for nucleation. In the descending order, we have $E_b^{QD} > E_b^{QDM} > E_b^{pit} \sim 0.0$. For high misfit strain, the energy barrier for QD (isolated island) nucleation is small so that $kT \sim E_b^{QD}$, and kinetics allows island nucleation first on the surface preempting pit formation, because pit can only form with sufficient film thickness after $t > t_c^{pit}$, where t_c^{pit} is the minimum thickness required for pit formation beyond wetting. For low and intermediate misfit strain, $kT < E_b^{QD}$, QD nucleation on surface is suppressed with too high a barrier. However, pits may form without a barrier ($E_b^{pit} \sim 0.0$) by coalescence of stepped mounds (roughened surfaces) without a truly nucleation process, as the film grows sufficiently thick, which has also been shown by kinetic Monte Carlo simulations[26]. Our model shows that the energy barrier and critical size for island nucleation can be reduced by pit. Thus, upon pit formation, the island can again nucleate next to the pit to form QDMs for the intermediate strain when $kT \sim E_b^{QDM}$ but not for the low misfit strain when $kT < E_b^{QDM}$.

Lastly, we briefly discuss our model prediction of a self-selective process on island shape transformation, triggered mostly by island-pit interaction. It is well-known that the islands exhibit a shape transformation in the QDM, similar to the isolated 3D islands with a kinetically limited height growth[30], or a truly 2D island[31]. Qualitatively, we can show that island in a QDM always favor to elongate along the pit edge ($t > s$) due to the island-pit attraction, in contrast to an isolated island that may elongate in two energy degenerate direction. However, in both cases, when the island grows bigger, its width tends to be a constant, and its length increase linearly with island size. For the case of QDM, as the four islands continue to elongate along the pit edge, they eventually meet and merge into a mature QDM, which agrees well with the experiments (see, e.g., Fig. 3 in Ref. 11), while an isolated island may grow its length indefinitely. Quantitatively, we predict the island base size (width) for a pure Ge hut island is 18.6 nm, which is in excellent agreement with the most recent experiment[32]. While for the $Si_{0.7}Ge_{0.3}$, we calculated the isolated island base size (width) to be $\sim$ 105 nm, but within the QDM, the island base size is reduced to $\sim$ 77 nm for $L_p = 82\ nm$, which is again consistent with that observed in the experiments[10, 11].

We have focused on the case of single QDM consisting of faceted pit and islands. More generally, pit may adopt different shapes and depths, which may alter the island location [17]. In particular, for very steep pits, nonlinear elastic effect may become important to affect island growth. For an array of pits, the pit-pit interactions should be taken into account[33]. Also, the faceted SiGe QDMs we study form at intermediate temperatures. At high temperature, non-faceted pits and islands may form without a barrier, via a surface roughening process [34]. These situations are beyond the scope of present work but interesting for future study.

The work at Utah is supported by DOE-BES program(DE-FG0204ER46148). The work at Beijing is supported by NSFC, the ” “973“ project and CAS.

* Corresponding author: fliu@eng.utah.edu

[1] G. Katsaros et al., Nature Nanotech. 5, 458 (2010).
[2] G. Vantarakis, I. N. Remediakis, and P. C. Kelires, Phys. Rev. Lett. 108, 176102 (2012).
[3] X. B. Niu, G. B. Stringfellow, and Feng Liu, Phys. Rev. Lett. 107, 076101 (2011).
[4] A. G. Cullis, D. J. Robbins, A. J. Pidduck, and P. W. Smith, J. Cryst. Growth 123, 333 (1992).
[5] A. J. Pidduck, D. J. Robbins, A. G. Cullis, W. Y. Leong, and A. M. Pitt, Thin Solid Films 222, 78 (1992).
[6] D. E. Jessson, K. M. Chen, S, J. Pennycook, T. Thundat, and R. J. Warmack, Phys. Rev. Lett. 77, 1330 (1996).
[7] J. A. Floro et al., Phys. Rev. B 59, 1990 (1999).
[8] X. Deng, and M. Krishnamurthy, Phys. Rev. Lett. 81, 1473 (1998).
[9] J. L. Gray, R. Hull, and J. A. Floro, Appl, Phys. Lett. 81, 2445 (2002); T. E. Vandervelde et al., Appl. Phys. Lett. 83, 5205 (2003).
[10] J. L. Gray, N. Singh, D. M. Elzey, R. Hull, and J. A. Floro, Phys. Rev. Lett. 92, 135504 (2004).
[11] J. L. Gray et al., Phys. Rev. B 72, 155323 (2005).
[12] . L. Gray, R. Hull, and J. A. Floro, J. Appl, Phys. 100, 084312 (2006).
[13] O. G. Schmidt et al., IEEE Journal of Selected Topics in Quantum Electronics 8, 1025 (2002).
[14] R. Songmuang, S. Kiravittaya, and O. G. Schmidt, Appl. Phys. Lett. 82, 2892 (2003).
[15] S. Suraprapapich et al., J. Cryst. Growth 301-302, 735 (2007).
[16] Zh. M. Wang, B. L. Liang, K. A. Sablon, and G. J. Salamo, Appl. Phys. Lett. 90, 113120 (2007); K. A. Sablon, Zh. M. Wang, G. J. Salamo, L. Zhou, and D. J. Smith, Nanoscale Res. Lett. 3, 530 (2008).
[17] G. Vastola et al., Phys. Rev. B 84, 155415 (2011).
[18] Note that in a broader sense, the surface mediated nucleation is considered as heterogeneous nucleation relative to the homogeneous bulk nucleation.
[19] J. Tersoff, and F. K. LeGoues, Phys. Rev. Lett. 72, 3570 (1994).
[20] V. A. Shchukin, N. N. Ledentsov, P. S. Kopev, and D. Bimberg, Phys. Rev. Lett. 75, 2968 (1995).
[21] H. Hu, H. -J. Gao, and F. Liu, Phys. Rev. Lett. 101, 216102 (2008).
[22] G. H. Lu, and F. Liu, Phys. Rev. Lett. 94, 176103 (2005).
[23] I. Goldfarb, L. Banks-Sills, and R. Eliasi, Phys. Rev. Lett. 97, 206101 (2006).
[24] See EPAPS online supplementary information.
[25] F. Liu, Phys. Rev. Lett. 89, 246105 (2002).
[26] F. Liu, Modeling and Simulation of Strain-Mediated Nanostructure Formation of Surface, in:M. Rieth and W Schommers(eds.), Handbook of Theoretical and Computational Nanotechnology, Chapter 10, 577-625 (2006).
[27] F. Liu and M. G. Lagally, Phys. Rev. Lett. 76, 3156 (1996).
[28] G. H. Lu, M. Cuma, and F. Liu, Phys. Rev. B 72, 125415 (2005).
[29] B. Yang, F. Liu and M. G. Lagally, Phys. Rev. Lett. 92, 025502 (2004).
[30] J. Tersoff, and R. M. Tromp, Phys. Rev. Lett. 70, 2782 (1993).
[31] A. H. Li, F. Liu, and M.G. Lagally, Phys. Rev. Lett. 85, 1922 (2000).
[32] Private communication with O. G. Schmidt.
[33] P. Liu, C. Lu, and Y. W. Zhang, Phys. Rev. B 76, 085336 (2007).
[34] J. Tersoff, B. J. Spencer, A. Rastelli, and H. von Kanel, Phys. Rev. Lett. 89, 196104 (2002).