Diffusion Dynamics during the Nucleation and Growth of Ge/Si Nanostructures on Si(111)

F. Ratto,[1,*,†] A. Locatelli,[2] S. Fontana,[2] S. Kharrazi,[3] S. Ashtaputre,[3] S. K. Kulkarni,[3] S. Heun,[4] and F. Rosei[1,*,‡]

[1]*INRS Energie, Matériaux et Télécommunications, Université du Québec,*
1650 Boulevard Lionel Boulet, J3X 1S2 Varennes (QC), Canada
[2]*Sincrotrone Trieste SCpA, SS 14 Km 163.5, 34012 Basovizza, Italy*
[3]*DST Unit on Nanoscience, Physics Department, University of Pune, Pune 411007, India*
[4]*Laboratorio Nazionale TASC-INFM-CNR, Area Science Park, SS 14 Km 163.5, 34012 Basovizza, Italy*

(Received 17 November 2005; published 8 March 2006)

We report a low energy electron microscopy study of the relation between self-organized Ge/Si(111) nanostructures and their local environment. By comparison with Monte Carlo simulations, three-dimensional islands are shown to display a substantial tendency towards self-ordering. This tendency may result from the diffusive nature of the nucleation processes. The size of individual nanostructures does not significantly correlate with the distance between neighboring islands. Thus energetic factors are thought to govern the competition among coexisting nanostructures to capture the deposited mass.

DOI: 10.1103/PhysRevLett.96.096103 PACS numbers: 68.55.Ac, 68.37.Nq, 68.60.Dv, 81.07.Ta

The self-organization of three-dimensional (3D) nanostructures as a result of semiconductor heteroepitaxy is an important phenomenon in crystal growth [1,2]. In this context Ge nanostructures on Si(111) represent a model system, with a view to applications in micro- and optoelectronics. The growth of germanium on low index silicon surfaces is known to follow the Stranski-Krastanov (SK) mode [3]; i.e., 3D islands nucleate due to a roughening transition from a critically thick wetting layer (WL). Ge nanostructures embedded within a Si matrix are expected to behave as artificial atoms, or quantum dots. The positioning and relative dimensions of self-organized 3D islands identify critical issues both for a fundamental understanding and for future device engineering. In this Letter, we pursue the following questions: (i) Do self-organized 3D nuclei display a tendency towards self-ordering? (ii) What factors govern the relative growth of individual nanostructures; i.e., what is the competition among different nuclei to gather the mass deposited on the surface?

Both issues can be described in terms of kinetic processes based on diffusion, nucleation, and capture [4]. The development of a 3D island arises from the growth of a stable nucleus. The latter generally results from a collision process involving a number of diffusing adatoms greater than a critical threshold [5]. The occurrence probability of such a collision event is proportional to the local density of adatoms. Upon formation, the critical nucleus starts capturing the diffusing atoms in its neighborhood, thus giving rise to a local decrease in the adatoms's density. Within this adatom-depleted region the probability of nucleating a second island is correspondingly reduced [6]. On an isotropic surface, the consequences of this phenomenon may be naively pictured as an isotropic repulsion among nuclei. This could result in a tendency towards a local compact ordering of the islands. Self-ordering would be merely kinetically driven, i.e., would not follow from any minimization of the system potentials. On the other hand, energetic factors would lead to a similar configuration [7]. Order may be induced by either a preexisting stress pattern in the WL [8] or elastic interactions among nuclei [9]. A hexagonal array would follow from the symmetry of the Si(111) surface and the isotropic character of island-island interactions. Despite this, most experimental reports depict a random scattering of self-organized nuclei [10]. The growth of the islands as well might be governed by diffusive phenomena [11]. In this context deposited atoms would tend towards and be captured by—on average—the closest nuclei. The process could then be described by the *Mulheran capture zone model* [12,13], projecting a correlation between the growth rate of every island and the area of the relevant cell in the Voronoi tessellation [14]. Thus the competition among neighboring nuclei for gathering the mass supplied to the surface would follow local laws. On the other hand, a growth process not consistent with the Mulheran model could be related to energetic factors. These might either prompt deposited atoms to preferentially reach islands for reasons else than their geometric proximity, or the 3D islands to unevenly exchange mass afterwards [15]. Under these circumstances some nuclei would reach a thermodynamically steadier structure than others and develop thereafter at a different pace [16]. Here we test these concepts by comparing the output of model descriptions with our experimental results.

Our experiments were performed by depositing 10 monolayers (ML) Ge from a molecular beam source on clean Si(111) surfaces kept at different temperatures T, in an ultrahigh vacuum environment (base pressure $\sim 10^{-10}$ mbar). The surface morphology was imaged *in situ* by low energy electron microscopy (LEEM) with a lateral resolution of ~ 10 nm [17].

By acquiring LEEM movies during the growth process, Ge/Si(111) islands have been dynamically observed to grow with undetectable lateral movement (see movie file in EPAPS material [18]). Thus we can approximate their centers of mass with the relevant nucleation sites. This in turn allows us to infer experimentally the nuclei layout. To probe traces of self-ordering among nuclei, we have analyzed the distribution of the cell areas in the Voronoi tessellation associated with the centers of mass of the mature islands. Figure 1 displays a LEEM micrograph of a sample grown at 400 °C and describes some of the geometrical concepts that we have exploited for this analysis. The experimental distributions have been matched with results from Monte Carlo (MC) simulations, where a continuous amount of order is introduced in a 2D distribution of points. In our simulations nuclei are approximated as geometric points, which is important to prevent the issue of possible overlap between nanostructures [19].

While simulating disorder may be easily obtained by generating a random scattering of nucleation sites, modeling partial ordering requires a more complex mathematical framework. Preliminary speculation on the expected local symmetry of arrays of nuclei is required. In this context the choice of the (111)-oriented Si substrate is crucial: because of the symmetry and isotropic nature of the surface and of the possible interactions between nuclei, islands should tend to arrange in a hexagonal lattice. Starting with the hexagonal *ordered configuration*, a continuous lattice distortion was operated. This was carried out by defining an isotropic Gaussian probability of finding a nucleus one distance apart from the original site of the hexagonal lattice. The deformation is thus governed by the width σ of this Gaussian distribution, which primarily defines the degree of disorder. In the simulations, σ is expressed in units of a typical length, chosen as the nearest neighbor distance in the ordered configuration. We have generated scatterings of nuclei with increasing values of σ, and computed the relevant statistics. This allows one to define a function $\Im$ that associates with any value of σ a distribution for the Voronoi cell areas. Details on the simulations will be reported elsewhere [20]. Figure 2 displays some values of $\Im$ together with the results for the random scattering of nuclei. The normalized distributions progressively broaden and become more positively skewed with increasing σ, converging towards the random limit. For $\sigma = 0$ the surface is perfectly ordered with hexagonal symmetry. By increasing σ, it progressively becomes disordered up to the limit $\sigma \rightarrow \infty$, which represents complete disorder (random distribution). One major advantage of our approach consists in its local character, which allows one to discern order in systems with limited long-range coherence. This is the expected situation, e.g., for the diffusion mediated SK nucleation of semiconductor nanostructures [21].

Figure 3 displays the result of the comparison between the simulated and experimental distributions. At every deposition temperature T the experimental distributions are not consistent with the random limit, the measured Ge/Si(111) islands exhibiting much narrower and more symmetric statistics. To provide a quantitative estimate of the degree of order that affects the nuclei's layout, we have fitted the measured distributions to the function $\Im$ of σ defined above. We have thus obtained an estimate of the value of σ that best mimics the experimental statistics at each deposition temperature. Compared to the random limit, the agreement with the experimental data has significantly improved. The quasihexagonal model allows one to vary simultaneously the mode, width, and skewness of the distributions in such a way as to reproduce the experimental measurements. The right panel of Fig. 3 shows the dependence of σ on the deposition temperature. The best estimates of σ lie in the range 0.3–0.5, which is an indication of substantial local order. Furthermore, T seems to exert little influence on the efficiency of the driving forces

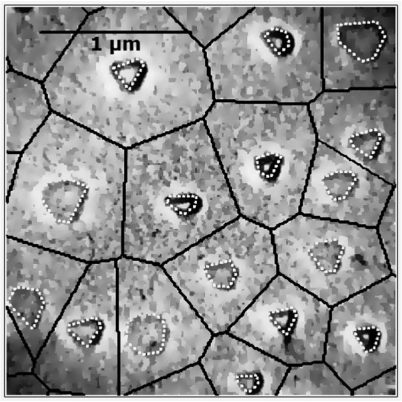

FIG. 1. $2.6 \times 2.6\ \mu\text{m}^2$ LEEM image of a sample prepared by depositing 10 ML Ge on a clean Si(111) substrate kept at 400 °C. Black lines indicate the perimeters of the Voronoi tessellation as associated with the positions of the centers of mass in the islands's distribution. White dotted lines enclose the areas of individual 3D structures.

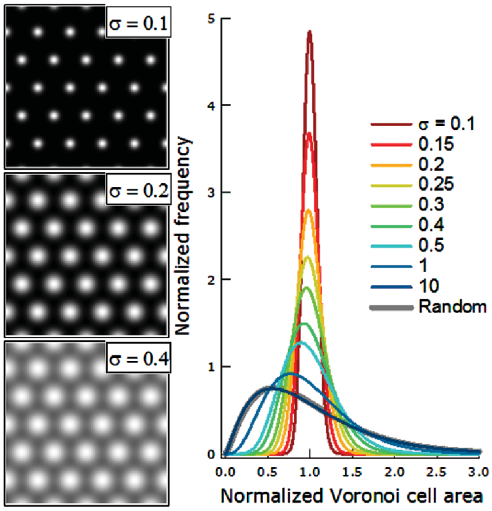

FIG. 2 (color). Selected values of $\Im$ at different σ, showing the statistics of the Voronoi cell areas at given amounts of order. The panels at the left display selected examples of the probability distributions employed to generate the quasihexagonal arrangement of islands in our MC simulations.

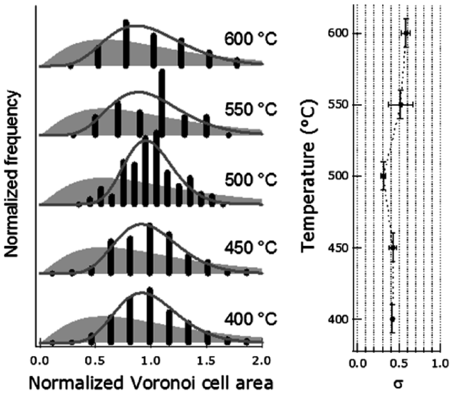

FIG. 3. Comparison between the experimental distributions (ticks on the horizontal axis), the random limit (light shadowed curves), and the best fits to the function of σ (continuous dark gray lines). The right panel displays the dependence of the distortion parameter σ on T.

that are responsible for partial self-ordering; i.e., self-similarity is observed [22].

If strain relaxation were dominating the tendency towards self-ordering, the internal energy of the system should feature a minimum corresponding to complete order and different metastable configurations with high degeneracy. Since entropy would promote disorder, the degree of order would exhibit a maximum at a finite deposition temperature. Conversely, let us assume that the nucleation processes are governed by diffusion with negligible energetic implications. If the phenomenon were to depend on T exclusively through the diffusion length, the characteristic distances would increase with T, yet the degree of order would be unaffected by T. Our results seem to support the latter scenario. However, since the role of temperature is not thoroughly characterized, we cannot unambiguously assign order to a specific driving force. Experimental evidence for diffusion mediated nucleation processes has been provided for Ge/GaAs by measuring a narrow distribution for the nearest neighbor distances [23]. Analogous results have been reported for InAs/GaAs and Ge/Si(001) islands. In the first case a partial hexagonal self-ordering was observed, yet not accounted for [24]. In the second, the phenomenon has been partially attributed to a scattering of nuclei with an exclusion zone defined as the average lateral dimensions of the nanostructures [25]. Our analysis does not account for the size of individual islands, which is *a priori* unrelated to the arrangement of the nucleation sites.

In the following, we focus on the competition among nuclei to collect the deposited mass and to grow. This issue is discussed in general terms by analyzing the consequences of the possible competition between kinetic and energetic factors [26]. The nucleation of islands is known to occur almost simultaneously, resulting from the very large size of the critical nucleus (close to 10 atoms in the case of Ge/Si(111) [27]). If the subsequent growth were determined by kinetic factors only, the process would be well described by geometrical based models [28,29]. In particular, the essence of the phenomenon would be described by the Mulheran capture zone model. On the other hand, growth dynamics not consistent with the capture zone picture should be ascribed to energetic factors.

Since Ge/Si(111) island areas and volumes are correlated [30], the model's validity can be verified by evaluating the correlation between island areas and the Voronoi cell areas. Our approach consists of plotting the former as a function of the latter and estimating the degree of linear correlation by Pearson's r coefficient. Figure 4 summarizes the results we have obtained at different temperatures. We note that r is significantly less than unity at each single T; i.e., there is consistently little linear correlation. Thus energetic factors crucially affect the competition between islands to gather the available mass. Nonetheless, the increase of r with T indicates that kinetic factors become more important. The geometrical consequences of the capture zone model do not depend in principle on the temperature. When evaluating r by including results obtained at different T, the correlation becomes significant. This stems from a decrease in the island density, i.e., an expansion of the average Voronoi cells, which corresponds to an increase in the average volumes of individual nanostructures. Nonetheless, at each single T, Mulheran's model provides a poor description of this system; i.e.,

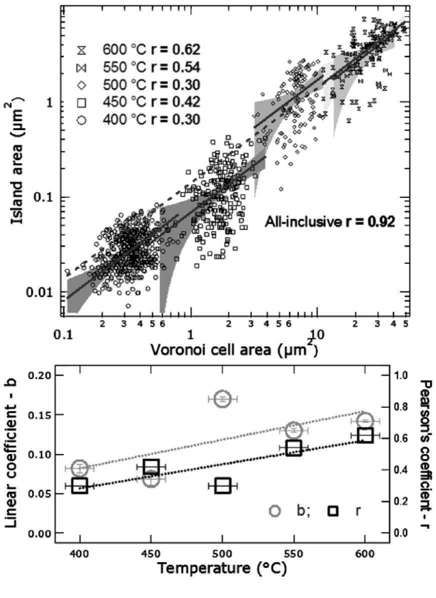

FIG. 4. Relationship between the island areas and the relevant Voronoi cell areas. Although the linear parameter b is positive at every T (as shown by the 99.73% confidence bands superimposed on the image), Pearson's r is consistently indicative of a poor correlation (the value $r = 0.92$ was calculated by comparing islands grown at different T). The lower panel displays the behavior of the linear coefficient b (slope of the linear fit) and of r as a function of T.

Voronoi cells and island volumes do not correlate *locally*. This suggests that energetic interactions among islands lead to local nonuniformities in the mass density. We speculate coexisting islands with different sizes and morphologies may exhibit different chemical potentials [17]. This could drive an unbalanced diffusion of adatoms at the surface. While many efforts have been directed towards the relative stability of different islands in Ge/Si systems [31,32], the present Letter contains the first experimental evaluation of the balance between kinetics and energetics in determining the nanostructures's volume distribution.

In conclusion, we have demonstrated that self-organized Ge/Si(111) islands display a significant tendency towards self-ordering, which is usually and critically underestimated by visual inspection of real space images of the surface. This may be associated with the diffusive character of the nucleation processes and should be taken into account in growing arrays of nanostructures. Moreover, we have demonstrated that the geometrical arrangement of the nuclei does not univocally determine the islands's growth. Factors that are to be ascribed to energetics crucially determine the process of mass-sharing among coexisting nanostructures. This result should also be taken into account for device engineering, and should motivate further research so as to identify the origin of these thermodynamic unbalancing components.

F. Ratto acknowledges the ICCS and FQRNT for financial support. S. K., S. A., and S. K. K. are grateful to ICTP for financial assistance. S. K. K. thanks DST and UGC India for support. F. Rosei acknowledges funding from NSERC of Canada, and salary support from FQRNT and the CRC Program. We gratefully acknowledge helpful discussions with M. Tomellini, M. Fanfoni, and R. Rosei.

---

*To whom correspondence should be addressed.

†Electronic address: ratto@emt.inrs.ca

‡Electronic address: rosei@emt.inrs.ca

[1] B. Voigtländer, M. Kawamura, N. Paul, and V. Cherepanov, J. Phys. Condens. Matter **16**, S1535 (2004).

[2] C. Teichert, Phys. Rep. **365**, 335 (2002).

[3] F. Rosei, J. Phys. Condens. Matter **16**, S1373 (2004).

[4] For a recent review, see M. Fanfoni and M. Tomellini, J. Phys. Condens. Matter **17**, R571 (2005).

[5] M. Zinke-Allmang, Thin Solid Films **346**, 1 (1999).

[6] J. A. Venables, Philos. Mag. **17**, 697 (1973).

[7] R. A. Puglisi, G. Nicotra, S. Lombardo, C. Spinella, G. Ammendola, M. Bileci, and C. Gerardi, Surf. Sci. **550**, 119 (2004).

[8] A. Ronda and I. Berbezier, Physica (Amsterdam) **23E**, 370 (2004).

[9] V. A. Shchukin, N. N. Ledentsov, P. S. Kop'ev, and D. Bimberg, Phys. Rev. Lett. **75**, 2968 (1995).

[10] N. Motta, A. Sgarlata, F. Rosei, P. D. Szkutnik, S. Nufris, M. Scarselli, and A. Balzarotti, Mater. Sci. Eng. B **101**, 77 (2003).

[11] M. Brinkmann, S. Graaf, and F. Biscarini, Phys. Rev. B **66**, 165430 (2002).

[12] P. A. Mulheran and J. A. Blackman, Phys. Rev. B **53**, 10 261 (1996).

[13] S. Pratontep, M. Brinkmann, F. Nüesch, and L. Zuppiroli, Phys. Rev. B **69**, 165201 (2004).

[14] The surface is divided into sectors that are associated with each particle and are defined as the sets of points that are closer to a given particle rather than to any other.

[15] Y. Enomoto, Surf. Sci. **493**, 585 (2001).

[16] P. Raiteri and L. Miglio, Phys. Rev. B **66**, 235408 (2002).

[17] F. Ratto, F. Rosei, S. Cherifi, A. Locatelli, S. Fontana, S. Heun, P. D. Szkutnik, A. Sgarlata, N. Motta, and M. De Crescenzi, J. Appl. Phys. **97**, 043516 (2005).

[18] See EPAPS Document No. E-PRLTAO-96-090610 for a LEEM movie. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

[19] This assumption can be further justified. Partial disorder is treated here as a perturbation of a periodic lattice of nuclei. By virtue of the low ratio between the average island sizes and average Voronoi cell areas overlap among nuclei can be safely neglected, at least up to the point when the perturbation leads to almost complete disorder.

[20] F. Ratto and F. Rosei (unpublished).

[21] Ordered clusters of nuclei would expand simultaneously with no long-range coherence, giving rise to a high density of antiphase boundaries.

[22] The error bars associated with the values of σ mainly depend on the limited statistics, which determines the minimum possible bin size in the experimental histograms. The larger the bin size, the coarser the estimate of σ.

[23] Y. N. Yang, Y. S. Luo, and J. H. Weaver, Phys. Rev. B **46**, 15 387 (1992).

[24] J. M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, and O. Vatel, Appl. Phys. Lett. **64**, 196 (1994).

[25] B. Cho, T. Schwarz-Selinger, K. Ohmori, and D. G. Cahill, Phys. Rev. B **66**, 195407 (2002).

[26] M. Meixner, E. Schöll, V. A. Shchukin, and D. Bimberg, Phys. Rev. Lett. **87**, 236101 (2001).

[27] A. A. Shklyaev, M. Shibata, and M. Ichikawa, Surf. Sci. **416**, 192 (1998).

[28] M. Li, M. C. Bartelt, and J. W. Evans, Phys. Rev. B **68**, 121401(R) (2003).

[29] J. G. Amar, M. N. Popescu, and F. Family, Surf. Sci. **491**, 239 (2001).

[30] F. Rosei, Ph.D. thesis, University of Rome La Sapienza, 2001.

[31] F. M. Ross, R. M. Tromp, and M. C. Reuter, Science **286**, 1931 (1999).

[32] F. Montalenti, P. Raiteri, D. B. Migas, H. von Känel, A. Rastelli, C. Manzano, G. Costantini, U. Denker, O. G. Schmidt, K. Kern, and L. Miglio, Phys. Rev. Lett. **93**, 216102 (2004).