Control of Ge/Si intermixing during Ge island growth

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The surface energy and growth kinetics during Ge deposition on Si(001) were modified by growing the films in a phosphine environment. Islands were formed under a H_2 flux as well as in a PH_3/H_2 atmosphere, but the morphologies were different. The presence of PH_3 not only affects the island shape and size but also the composition profile. The dramatical inhibition of Ge/Si intermixing during growth leads to islands richer in Ge compared to undoped islands. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3078289]

The control of growth kinetics is the determining factor for tailoring composition profiles of epitaxial nanostructures.[1] In fact, the composition of self-assembled epitaxial nanocrystals rarely matches the nominal value. The mechanisms as well as the driving forces for intermixing[2–6] have been investigated in detail, underscoring the importance of kinetics and thermodynamics in establishing the island composition profile. It has been demonstrated that during annealing experiments, the environment plays a fundamental role in the diffusion processes, influencing the island size, shape, and composition evolution toward equilibrium.[6]

The effect of different environments and surfactants during growth has been extensively studied for the Ge-Si:Si(001) epitaxial system. When foreign species are absorbed on a substrate, adatom diffusion and island formation are kinetically inhibited without significantly affecting the crystal quality.[7] It has been shown that by adjusting the growth front chemistry one may control the surface morphology as a result of kinetics or thermodynamics.[7–10] For example, distinct surfactants were found to suppress Ge island size evolution on Si(001) substrates[7,8] and also impede Ge/Si intermixing.[10,11] Conversely, Ge island shape and size can vary as a consequence of including phosphine (PH_3) in the growth environment.[12,13] The importance of the surface chemistry in film morphology has been thoroughly substantiated. Nevertheless, very little is known concerning the composition of films and nanostructures formed under different environmental conditions.

Here, we discuss the effect of the phosphine environment during growth on the composition profile of Ge–Si islands. We demonstrate that PH_3 produces not only an island shape change but a significant enrichment of Ge when contrasted to islands formed in a H_2 ambient. This observation reveals suppressed Ge/Si intermixing during island growth, resulting from the modified surface energy caused by PH_3.

Two samples were grown by chemical vapor deposition in a commercial reactor. For the reference sample, after baking the 150-nm-diameter Si(001) wafer in H_2 at ~1150 °C, a Si buffer layer was grown at 1080 °C using SiH_2Cl_2. The wafer was cooled to 600 °C and 11.2 eq-ML of Ge was deposited at 3 ML/min from a GeH_4 (0.033 Pa) gas source under H_2 (1.3 kPa) atmosphere (sample U). After the Ge deposition, the sample was cooled first in H_2 and then in N_2. In order to evaluate the degree of Ge/Si intermixing during island growth and evolution, a second sample was grown under the same conditions as U but utilizing a PH_3/H_2 (0.0018 Pa PH_3) flux (sample D). The two gases were mixed and the flow stabilized in a separate manifold before the mixture was introduced into the deposition chamber. The island composition was inferred by selectively etching both samples simultaneously in the same 31% H_2O_2 solution. The etchant used is known to remove Ge_xSi_{1-x} for $x>0.65$ at fast rates.[14] However, for $x<0.65$, the etching rate is negligible, thus allowing us to investigate isocomposition surfaces. The samples were characterized before and after the etching by Atomic Force Microscopy (AFM) and subsequent detailed statistics were carried out on 4 μm^2 regions.

Figures 1(a) and 1(b) show the AFM images of samples U and D. Different island morphologies with distinct sizes can be observed: pyramids ($h=2.3\pm0.8$ nm, $d=30.7\pm16.3$ nm), domes ($h=15.3\pm1.8$ nm, $d=67.3\pm27.8$ nm), and superdomes ($h=28.3\pm11.1$ nm, $d=134.8\pm123.0$ nm) for sample U and mounds ($h=1.8\pm0.7$ nm, $d=22.3\pm10.0$ nm), minidomes ($h=7.5\pm2.4$ nm, $d=34.6\pm17.8$ nm), and superpyramids ($h=29.0\pm2.5$ nm, $d=122.2\pm50.0$ nm) for sample D, where h is the height and d is the lateral dimension of the islands. As previously reported,[13] each doped island family is smaller than its corresponding undoped island. The three different populations of each sample can be seen in the statistics of Figs. 1(c) and 1(d). For sample U, the most widely reported island shape (pyramids, domes, and superdomes) cluster around characteristic sizes, suggesting a particular average Ge content.[15] The scatter plot shown in Fig. 1(d) nevertheless shows a wider distribution of volumes for islands with small sizes (mounds and minidomes), whereas for the larger islands (superpyramids), a tighter island size distribution is observed.

The PH_3/H_2 flux modifies the system surface energy, leading to an abrupt change in shape from minidomes to superpyramids, as indicated by the gap in Fig. 1(d). In contrast to the undoped sample, under PH_3 the dome structure is stable up to 10^4 nm^3. If the composition is assumed to be uniform for that dome size adopting a model proposed earlier,[15] one finds an average Ge fractional concentration of 0.95. There are no islands with $10^4<\text{volume}<10^5$ nm^3

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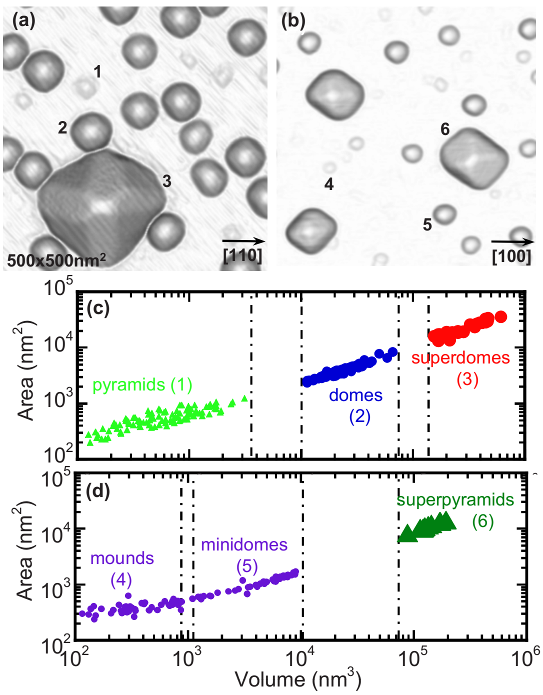

FIG. 1. (Color online) AFM images of samples (a) U and (b) D showing the different island morphologies obtained after the deposition of 11.2 eq-ML of pure Ge at 600 °C on a Si(001) substrate. The color scale corresponds to the slope. Surface area (nm^2)×volume (nm^3) island statistics for the different morphologies found on samples (c) U and (d) D: (1) pyramid, (2) dome, (3) superdome, (4) mound, (5) minidome, and (6) superpyramid.

(corresponding to the average domes in sample U). This indicates that the minidomes in sample D are richer in Ge than the domes found in sample U. For volumes larger than 10^5 nm^3, superpyramids prevail. These nanocrystals, only seen in doped layers,[12] have well defined facets[13] and are analogous to the superdomes found in U. The composition of superdomes has been investigated in a recent study,[16] showing significant intermixing in these dislocated islands. However, the effect of PH_3 in the Ge/Si intermixing in dislocated islands is not known.

Carrying out selective etching experiments for both samples may help to sort out these issues. The AFM image of sample U after etching reveals that the islands were partially attacked [Fig. 2(a)], showing that for all three shapes there is a composition gradient. In contrast, for sample D all islands

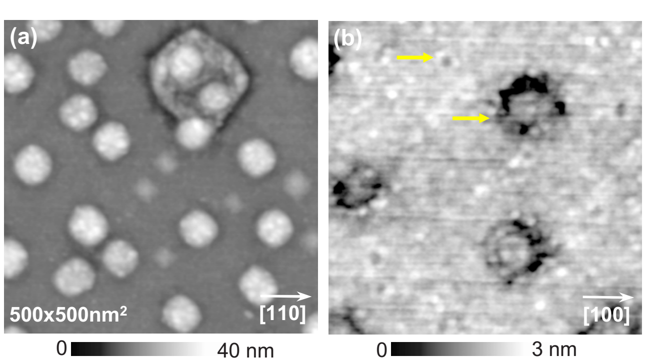

FIG. 2. (Color online) AFM images of samples (a) U and (b) D after the chemical etching with 30% H_2O_2 for 2 min at room temperature. While the islands were partially attacked in U, all the material is removed for sample D, independent of the island morphology. The arrows indicate the footprints left by one minidome and one superpyramid after the chemical etching.

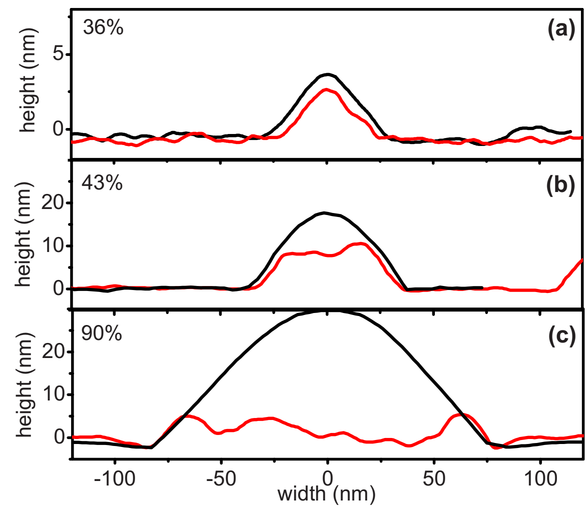

FIG. 3. (Color online) Line scans along the [110] direction of one representative (a) pyramid, (b) dome, and (c) superdome of sample U taken before (black lines) and after (red lines) the chemical etching with 31% H_2O_2. The percentages indicate the volume of material removed by the etching for each island shape.

were completely removed, as shown in Fig. 2(b), suggesting that they contain a Ge_x-Si_{1-x} alloy richer than 0.65 in Ge. The minidome and superpyramid footprints left by the etching (indicated by arrows) show that the initial Ge cluster has remained intact (i.e., nonalloyed) upon island growth.

The growth under a PH_3H_2 flux suppresses Si and Ge atom exchange. The phosphine environment selectively impedes the Si diffusion at the substrate surface during the Ge deposition as the P–Si bond is stronger than P–Ge bond.[3] As a consequence, island growth in a phosphine atmosphere has distinct kinetics, producing different composition profiles.

Figure 3 shows line scans before and after etching for representative islands with three different morphologies found for sample U. For the pyramid [Fig. 3(a)], only the island shell was removed by the etching solution. The remaining 64% of the volume of the islands is formed by a Ge_x-Si_{1-x} alloy with $x<0.65$. In Fig. 3(b), the dome top was removed (~43% of the island volume), leaving behind a Si rich nanocrystal core. The line scans of the superdome before and after the chemical etching [see Fig. 3(c)] show that ~90% of the material in the dislocated islands was removed, leaving an irregular topography, suggestive of dome coalescence [as shown by the AFM image in Fig. 2(a)]. Thus, as the island family size increases, more material is removed by the selective etching, indicating that the larger islands, independent of their families, are richer in Ge. In fact, dislocated islands can accommodate a much higher Ge content due to partial strain relief caused by dislocations.[16] Additionally, the role of intermixing during Ostwald ripening has not been fully investigated, but it is expected to be important for a system with low enthalpy for alloy formation such as Ge–Si.[17]

The line scans of representative minidomes and superpyramids before and after the chemical etching are shown in Figs. 4(a) and 4(b).[18] Upon further inspection of the island footprints given by these line scans, it is found that the intermixing process reaches 0.4 and 1.6 nm deep below the reference surface for minidomes and superpyramids, respectively (corresponding to a Ge–Si alloy with $x>0.65$). The depressions observed can be better understood by the process

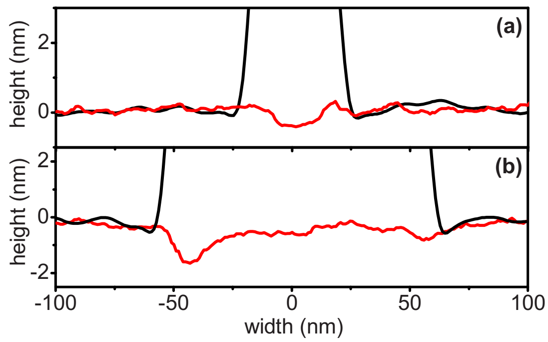

FIG. 4. (Color online) Line scans along the [100] direction of one representative (a) minidome and (b) superpyramid of sample D taken before (black lines) and after (red lines) the chemical etching with 31% H_2O_2. The height scale was selected to better show the depressions at the island base, revealed by the selective etching, as a result of the Ge/Si exchange that takes place at the island base during the material deposition.

depicted in Fig. 5. The Ge and P atoms are initially randomly distributed at the substrate surface [Fig. 5(a)]. As more material is deposited, the islands nucleate in regions where there are enough Ge atoms to form a stable cluster, as shown in Fig. 5(b). Simultaneously, Ge and Si atoms start to exchange in the surrounding surface (wetting layer). The island formation takes place with a Ge rich core that coarsens upon deposition [Fig. 5(c)]. The observed footprints (depressions) are consistent with Ge atoms forming the initial clusters being prevented from intermixing, which would require bulk interdiffusion. In contrast, the wetting layer intermixes with Si due to surface diffusion. Consequently, the island is completely etched and the wetting layer is not. In addition to this complex intermixing process, PH_3 changes the island surface energy, concurrently altering the overall energetic balance. It is surprising that the islands remain Ge rich, independent of their size or shape, despite energetic and entropic considerations which would lead to a Ge–Si alloy.[4,6]

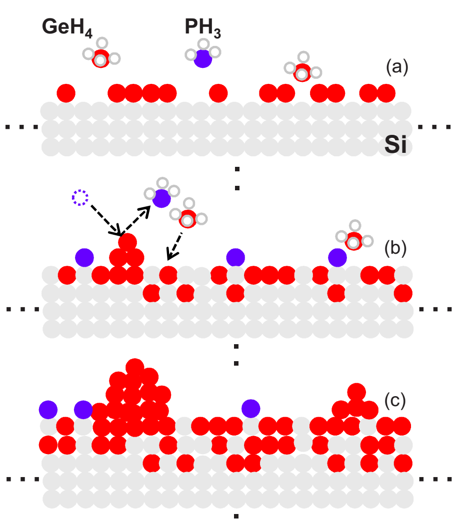

FIG. 5. (Color online) Simplified model describing the intermixing processes which takes place for sample D. (a) Ge and P atoms arrive randomly at the Si substrate. (b) After the first layer of atoms is deposited at the Si surface, the Ge atoms will preferentially bond to other Ge atoms, as the competing Si–P bonds are more energetically favorable (Ref. 3). Si and Ge atom exchange happens primarily at the top layers. An island starts to nucleate after a stable cluster of Ge is formed. (c) During the Ge deposition (and island growth) Ge/Si exchange may occur at the island base and in regions of the wetting layer that are covered by Ge. After the material deposition, the final islands are richer in Ge compared to the undoped ones.

Summarizing, a controlled experiment was performed in which the Ge/Si intermixing in islands was suppressed. For regular Ge:Si(001) nanocrystals the volume increase led to an enhancement of the Ge content within the islands. However, under a PH_3/H_2 flux, the islands grew with a modified surface energy, resulting in smaller islands richer in Ge, compared to undoped islands, independent of their shape.

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[1]E. P. McDaniel, Q. Jiang, P. A. Crozier, J. Drucker, and D. J. Smith, Appl. Phys. Lett. **87**, 223101 (2005).
[2]G. Katsaros, G. Costantini, M. Stoffel, R. Esteban, A. M. Bittner, A. Rastelli, U. Denker, O. G. Schmidt, and K. Kern, Phys. Rev. B **72**, 195320 (2005).
[3]M. S. Leite, G. Medeiros-Ribeiro, T. I. Kamins, and R. Stanley Williams, Phys. Rev. Lett. **98**, 165901 (2007).
[4]G. Medeiros-Ribeiro and R. Stanley Williams, Nano Lett. **7**, 223 (2007).
[5]Y. Tu and J. Tersoff, Phys. Rev. Lett. **98**, 096103 (2007).
[6]M. S. Leite, A. Malachias, S. W. Kycia, T. I. Kamins, R. Stanley Williams, and G. Medeiros-Ribeiro, Phys. Rev. Lett. **100**, 226101 (2008).
[7]M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[8]M. Copel, M. C. Reuter, M. Horn von Hoegen, and R. M. Tromp, Phys. Rev. B **42**, 11682 (1990).
[9]A. Portavoce, M. Kammler, R. Hull, M. C. Reuter, M. Copel, and F. M. Ross, Phys. Rev. B **70**, 195306 (2004).
[10]M. Katayama, T. Nakayama, M. Aono, and C. F. McConville, Phys. Rev. B **54**, 8600 (1996).
[11]N. Paul, S. Filimonov, V. Cherepanov, M. Çakmak, and B. Voigtländer, Phys. Rev. Lett. **98**, 166104 (2007).
[12]T. I. Kamins, D. A. A. Ohlberg, and R. Stanley Williams, Appl. Phys. Lett. **78**, 2220 (2001).
[13]T. I. Kamins, G. Medeiros-Ribeiro, D. A. A. Ohlberg, and R. Stanley Williams, J. Appl. Phys. **94**, 4215 (2003).
[14]O. A. Schmidt, U. Denker, S. Christiansen, and F. Ernst, Appl. Phys. Lett. **81**, 2614 (2002).
[15]A. Rastelli, M. Kummer, and H. von Kanel, Phys. Rev. Lett. **87**, 256101 (2001).
[16]T. Merdzhanova, S. Kiravittaya, A. Rastelli, M. Stoffel, U. Denker, and O. G. Schmidt, Phys. Rev. Lett. **96**, 226103 (2006).
[17]M. S. Leite, T. I. Kamins, and G. Medeiros-Ribeiro (unpublished).
[18]Since the mounds are in the same scale as the AFM measurement noise it was not possible to infer their line scans after the etching.