Effect Of Phosphorus On Ge/Si(001) Island Formation

Theodore I. Kamins, Gilberto Medeiros-Ribeiro[1], Douglas A. A. Ohlberg,
and R. Stanley Williams
Hewlett-Packard Laboratories, Quantum Science Research, Palo Alto CA 94304
[1]Also Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil

ABSTRACT

When Ge is deposited epitaxially on Si, the strain energy from the lattice mismatch causes the Ge in layers thicker than about four monolayers to form distinctive, three-dimensional islands. The shape of the islands is determined by the energies of the surface facets, facet edges, and interfaces. When phosphorus is added during the deposition, the surface energy changes, modifying the island shapes and sizes, as well as the deposition process. When phosphine is introduced to the germane/hydrogen ambient during Ge deposition, the deposition rate decreases because of competitive adsorption. The steady-state deposition rate is not reached for thin layers. The deposited, doped layers contain three different island shapes, as do undoped layers; however, the island size for each shape is smaller for the doped layers than for the corresponding undoped layers. The intermediate-size islands are the most relevant. The intermediate-size doped islands are of the same family as the undoped, multifaceted "dome" structures, but are considerably smaller. The largest doped islands appear to be related to the defective "superdomes" discussed for undoped islands. The distribution between the different island shapes depends on the phosphine partial pressure. At higher partial pressures, the smaller structures are absent. Phosphorus appears to act as a mild surfactant, suppressing small islands.

INTRODUCTION

When Ge is deposited epitaxially on Si, the strain energy from the lattice mismatch causes the Ge in layers thicker than about three monolayers to form distinctive, three-dimensional islands. The thermodynamically stable shape of the islands is determined by the energies of the surface facets, facet edges, and interfaces [1-2]. To control the size and shape of the island, these energies can be modified, possibly by introducing additional species onto the growing surface [3-5].

In a previous study, Cl was added to the surface in an attempt to control the island shape [6]. Although the surface Cl reduced the surface diffusion needed to form the thermodynamically stable islands, it did not appear to significantly change the island shapes. At the thickness corresponding to transition between two different island shapes, adding gaseous HCl during the deposition (while keeping the deposition rate constant), favored retaining the low-thickness island shape and retarded formation of the shape favored at the higher thickness. Thus, adding Cl during the deposition influenced the kinetics, rather than the thermodynamics.

However, when phosphorus is added, the surface energy changes, modifying the steady-state island shapes and sizes. The deposition kinetics are also changed. When phosphine is added to

the germane/hydrogen ambient during Ge deposition, the deposition rate decreases because of competitive adsorption. The steady-state deposition rate is not reached for thin layers. This paper will describe the basic behavior of the islands and show that three island types are formed, as for undoped islands, but that the size and shapes are quite different for the doped islands than for the undoped islands.

EXPERIMENTAL METHOD

The Ge layers were deposited on lightly doped, *p*-type, 150-mm diameter, Si(001) Si substrates by chemical vapor deposition (CVD) in a commercially available (Applied Materials Centura) reactor. In this reactor, the wafer is placed on a support plate of moderate thermal mass, and the main gas flow is approximately parallel to the wafer surface. The main carrier gas is hydrogen; germane (GeH_4) is the germanium source, and phosphine (PH_3) (100 ppm diluted in hydrogen) is added as the phosphorus source.

The reaction chamber is connected to a nitrogen-purged transfer chamber, through which the wafers are moved from wafer cassettes in the load lock into the reaction chamber. Thus, the reaction chamber is not exposed to air during normal operation.

After the wafer is loaded, it is heated to approximately 1150°C for 2 minutes to remove native oxide and to order the surface. It is cooled to approximately 1080°C, and a silicon buffer layer about 400 nm thick is grown using SiH_2Cl_2 as the silicon source. (This Si buffer layer is sometimes omitted with no discernible change in the subsequently grown Ge layer, but was used in these experiments.) The temperature is then further reduced to the Ge deposition temperature of 600°C. The GeH_4 and PH_3 are metered through mass flow controllers into a manifold separate from the main H_2 carrier gas, so that they are well mixed by the time the mixture in the manifold is introduced into the main H_2 carrier gas. Typical deposition rates (for undoped layers) are 3-6 eq-ML/min (1 equivalent monolayer [eq-ML] = 6.3×10^{14} Ge atoms cm^{-2}); PH_3/GeH_4 ratios of 0.025 to 0.25 were investigated. After the desired Ge deposition, the gases in the manifold are removed from the process chamber, and the wafer is quickly cooled to about 500°C in hydrogen and then removed into the nitrogen ambient in the process chamber.

The Ge island morphology was examined primarily by atomic-force microscopy using Digital Instruments atomic-force microscopes. The island shapes were observed directly, and statistical information about the island heights and volumes was obtained from detailed computer analysis of the data. The thicknesses of the Ge layers were measured using Rutherford Backscattering Spectroscopy (RBS). Additional thick layers were deposited so that the phosphorus concentration could be determined by secondary ion mass spectrometry (SIMS).

EXPERIMENTAL RESULTS AND DISCUSSION

Deposition rate

During deposition of silicon from silane, adding large amounts of phosphine is known to decrease the silicon deposition rate [7]. The phosphine is apparently more firmly adsorbed on the growing surface than is silane, limiting the number of adsorption sites available for silane adsorption, and hence reducing the deposition rate. Germane is more active than silane, so the suppression of the deposition rate is expected to be less for Ge deposition from germane than from silicon deposition from island.

For Ge layers about 11 eq-ML thick formed using the deposition conditions cited above, little decrease of the deposition rate is found for PH_3/GeH_4 ratios less than approximately 0.05; for a ratio of 0.25, the deposition rate decreases about 30%. At the lower PH_3/GeH_4 ratios of 0.03-0.06, used for most of the experiments to be described below, the deposition rate does not appreciably decrease below the undoped rate for layers about 11~eq-ML thick. However, for very thick layers (>100~eq-ML) thick, the deposition rate is about 30% lower for doped layers than for undoped layers. This behavior suggests that the phosphorus concentration on the surface increases gradually as more Ge is deposited and that the P/Ge ratio does not reach its steady-state value for the thinner layers, which are the subject of this study.

Island types

Undoped Ge islands on Si(001) have been studied extensively [1-2]. Three island types can be present, with the dominant type depending on the amount of Ge on the surface. The intial five monolayers of deposited Ge form a uniform wetting layer; the generally accepted wetting layer thickness is about three monolayers, but kinetic limitations on island formation allow the wetting layer to exceed its steady-state value by a moderate amount under the deposition conditions used here. With six monolayers of Ge deposited on the surface, characteristic square pyramids form; these pyramids are bounded by {105} facets. Figure 1a shows a detailed view of the pyramids obtained by depositing Ge by physical vapor deposition and imaging in-situ using scanning tunneling microscopy [1-2]. These pyramids are the dominant island type until about 8 eq-ML of Ge is deposited. Above this transition thickness of 8 eq-ML, a more complex, multi-faced structure forms (Figure 1b); this structure is the dominant island type for 11 eq-ML of Ge. Islands of this "dome" type have a narrower size distribution than do the pyramids that dominate for lower amounts of deposited Ge; a significant amount of energy is needed to add further atoms to a Ge dome, so they do not grow appreciably larger. Above about 14 eq-ML, a larger defective island structure forms; these "superdomes" can continue growing without an energy barrier than constrains their size.

For phosphorus-doped islands, three island types again appear [8], as shown in Figure 2a. However, these islands are markedly different than the undoped islands shown in Figure 1 and Figure 2b. The wetting layer thickness is approximately the same or very slightly lower than for undoped islands. Above this thickness, small islands form; because of their low height, their size is difficult to quantify statistically, but they appear to be about 2.5 nm high. More significant are

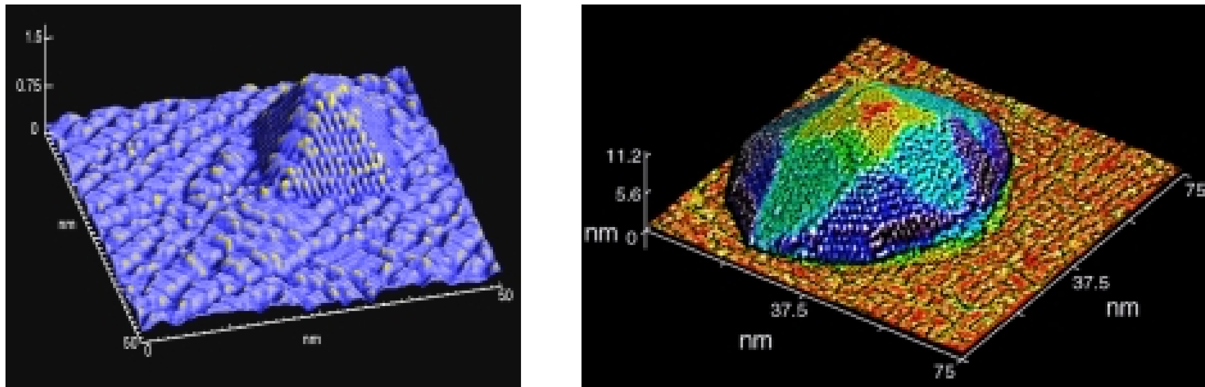

Figure 1: Scanning tunneling micrographs of Ge (a) pyramids and (b) domes deposited by physical vapor deposition and imaged in-situ to preserve the atomic-scale features. The islands deposited by CVD are similar, but the atomic features are obscured by air exposure before imaging.

the second type of islands that form. These islands start appearing when slightly less than 6 eq-ML of Ge is deposited and are about 10 nm high. Analysis of the height and surface area *vs.* volume shows that these second type of doped islands are of the same family as the “dome” structure of undoped islands, but are about 30% shorter and contain about 1/3 the volume. The surface area and volume of each island are obtained by computer analysis of the imaged data. On a scatter plot of surface area *vs.* volume, points corresponding to a given structure should fall on the same straight line with a slope of 2/3. Figure 3 shows that the data points corresponding to domes of the undoped layers and the second doped island type fall on the same straight line,

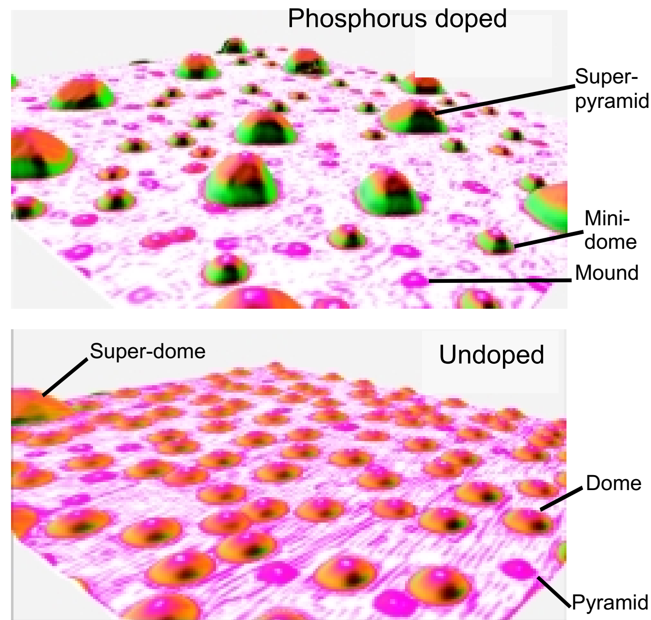

Figure 2: Atomic-force micrograph perspective views of (top) phosphorus-doped islands and (bottom) undoped islands, showing different island types for each situation.

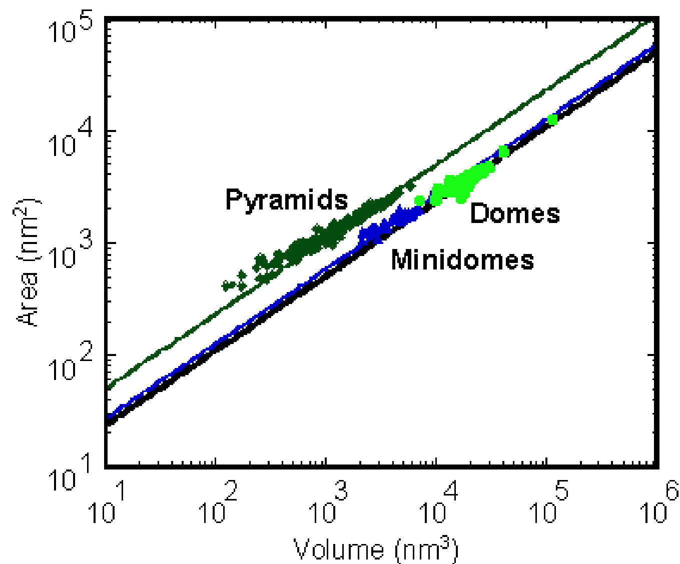

Figure 3: Scatter plot of pyramids and domes of undoped layer and second island type of doped layer, showing that the domes and doped islands are of the same family.

indicating that they belong to the same family. Because of the similar shape and smaller size, we call these doped islands "mini-domes." As for the undoped domes, the height of the doped mini-domes does not change significantly over the thickness range where they are the dominant island type.

For greater amounts of deposited Ge, a third island type appears [9]. Unlike the defective "super-domes" found for undoped layers, this third doped structure is pyramidal, but with its base edges along [110] directions, unlike the [100] directions of the small, undoped pyramids. The sides are also much steeper than those of the undoped islands and appear to be {111} planes near the base and {113} planes near the top.

A practical method of increasing the PH_3/GeH_4 ratio is to decrease the GeH_4 partial pressure while keeping the PH_3 partial pressure constant. For undoped layers deposited over a substantial range of GeH_4 partial pressures, the structure is not significantly affected by the rate at which the Ge is deposited when the deposition time is changed inversely with the GeH_4 partial pressure. (At very high rates, however, the thermodynamically favored structures do not have time to form, and for 11 eq-ML films, dome-shaped islands are not as dominant as at normal rates. At very low rates, some coarsening of the islands can occur, but over a significant range of deposition rates, the distribution is only minimally affected by the rate.) For doped islands, the analysis is further complicated by the dependence of the deposition rate on the PH_3/GeH_4 ratio because of competitive adsorption, with the rate decreasing significantly at higher PH_3/GeH_4 ratios, as discussed above. Within these limitations, however, decreasing the GeH_4 partial pressure allows extending the range of the experimental space that can be investigated.

For undoped layers 11 eq-ML thick, pyramids and domes co-exist at the highest rate, but domes dominate for all the other rates investigated. The average dome height remains constant

at 14 nm for most of the rates studied, but increases to 17 nm at the lowest rate. For doped islands deposited under similar conditions, however, all three structures are seen at the highest rate. At the lowest ratio, only the large pyramidal structures are seen, the mini-domes and smaller structures are suppressed by the high PH_3/GeH_4 ratio. In addition, the average height of the large pyramids increases from 24 nm at the lowest ratio to 42 nm at the highest ratio. The layers deposited at the higher PH_3/GeH_4 ratios are somewhat thinner than the less heavily doped layers, as discussed earlier.

For thinner doped layers formed under conditions that produce 6 eq-ML of undoped Ge, islands are suppressed at higher PH_3/GeH_4 ratios, both by the effect of phosphorus on the structure, and also by the decreasing thickness of the layer. At the highest ratio, the thickness is likely to be below the thickness of the wetting layer.

Figure 4 shows the distributions of island volumes for both undoped and doped layers of two different thicknesses. For layers 6 eq-ML thick, no dome-like structures are seen for undoped layers, but mini-domes are found in doped layers. For thicker (11 eq-ML) layers, dome-like structures are found for both undoped and doped layers, but the average dome volume is markedly smaller for the doped layers. Thus, some control over the size distribution can be obtained by introducing additional species to the gaseous ambient during deposition. This behavior suggests that the added species modify the energies involved, thermodynamically favoring smaller volumes for the dome-shaped islands.

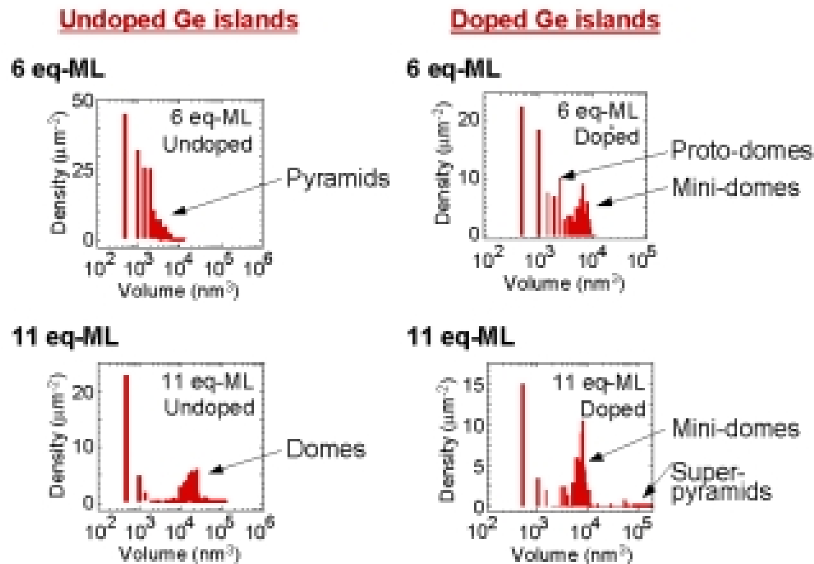

Figure 4. Distributions of island volumes for undoped and phosphorus-doped layers with two different amounts of Ge deposited.

SUMMARY

Adding phosphorus during deposition of Ge islands on Si(001) decreases the deposition rate as the PH_3/GeH_4 ratio increases and also as the thickness increases, suggesting competitive adsorption of PH_3 decreases the access of the incident GeH_4 to the surface. Three island types are formed in doped layers as in undoped layers, but the island types are different. Dome-like islands are seen in both undoped and doped layers, but the size of the dome-shaped islands is markedly smaller for the doped layers, indicating that phosphorus on the surface changes the surface energy and thus the size at which a give structure forms. As the PH_3/GeH_4 ratio and the surface phosphorus increase, the smaller islands are suppressed.

REFERENCES

[1] R. Stanley Williams, *et al.,* Acc. Chem. Res. **32,** 42 (1999).
[2] G. Medeiros-Ribeiro, A. M. Bratkovski, T. I. Kamins, D. A. A. Ohlberg, and R. Stanley Williams, Science **279,** 353 (1998).
[3] H. Hibino, N. Shimizu, K. Sumitomo, Y. Shinoda, T. Nishioka, and T. Ogino, J. Vac. Sci. Technol. A **12,** 23 (1994).
[4] D. J. Eaglesham, F. C. Unterwald, and D. C. Jacobson, Phys. Rev. Lett. **70,** 966 (1993).
[5] D. J. Bottomley, M. Iwami, Y. Uehara, and S. Ushioda, J. Vac. Sci. Technol. A **17,** 698 (1999).
[6] T. I. Kamins, G. A. D. Briggs and R. Stanley Williams, Appl. Phys. Lett. 73, 1862 (1998).
[7] T. Kikuchi, *et al,* Proc. First Int'l Symp. on ULSI Process Integration (ed. C. L. Claeys, et al, Electrochemical Society, 1999) Proc. Vol. PV99-18, p. 147.
[8] T. I. Kamins, G. Medeiros-Ribeiro, D. A. A. Ohlberg, and R. Stanley Williams, Physica E **13**, 974 (2002)
[9] T. I. Kamins, D. A. A. Ohlberg, and R. Stanley Williams, Appl. Phys. Lett. **78,** 2220 (2001).