



## Are bare surfaces detrimental in epitaxial growth?

M. Copel and R. M. Tromp

Citation: Applied Physics Letters **58**, 2648 (1991); doi: 10.1063/1.104796 View online: http://dx.doi.org/10.1063/1.104796 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/58/23?ver=pdfcov Published by the AIP Publishing

### Articles you may be interested in

Topography of epitaxial GaAs surfaces for growth J. Vac. Sci. Technol. B **27**, 1072 (2009); 10.1116/1.3119684

Epitaxial growth of ZnS on bare and arsenic-passivated vicinal Si(100) surfaces J. Appl. Phys. **82**, 2251 (1997); 10.1063/1.366031

Epitaxial growth and surface structure of (0001) Be on (111) Si Appl. Phys. Lett. **64**, 31 (1994); 10.1063/1.110911

Rate equation models of epitaxial growth on stepped surfaces J. Vac. Sci. Technol. A **9**, 1551 (1991); 10.1116/1.577660

Thermal Accommodation Coefficient of Helium on a Bare Tungsten Surface J. Chem. Phys. **23**, 861 (1955); 10.1063/1.1742136



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 141.212.109.170 On: Thu, 11 Dec 2014 14:50:43

# Are bare surfaces detrimental in epitaxial growth?

M. Copel<sup>a)</sup> and R. M. Tromp IBM Research Division, T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598

(Received 2 January 1991; accepted for publication 15 March 1991).

For growth of epitaxial silicon-germanium structures by hydride chemical vapor deposition (CVD), the growth front is hydrogen-stabilized. Using medium energy ion scattering to examine the abruptness of an embedded Ge film in a Si(001) host, intermixing can be directly assessed. We have explored CVD films grown with varying hydrogen coverages, and find that adsorbed hydrogen serves a beneficial role in maintaining the abruptness of the interface. Embedded layers grown by molecular beam epitaxy are also more abrupt when the surface is stabilized, in this case by an adsorbed passivant such as Sb or As. Growth in the presence of a surface active agent (surfactant)-results in greater control of constituents with no loss of epitaxial quality.

A long-standing challenge in materials research has been to control the fabrication of epitaxial films. Competing growth techniques such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) offer various advantages, but are difficult to compare directly, and may lead to films with differing physical and electronic properties. One significant difference is that with silicon MBE, as traditionally practiced, the crystal growth front is an atomically clean surface, terminated with dangling bonds. Low-temperature growth from chemical sources usually occurs with the surface saturated with reaction byproducts and/or precursor molecules.<sup>1,2</sup> To elucidate the role of adsorbed species during growth, we have prepared similar structures by both MBE and CVD, with and without an adsorbed surface layer. Analysis of the samples by the medium energy ion scattering (MEIS) reveals a strong correlation between the presence of an adsorbed surface species during growth and an abrupt silicon-germanium interface. Interfaces prepared by growth with an adsorbate present, be it hydrogen or a dopant species, remain sharper at a higher growth temperature than interfaces prepared by growth on a bare surface.

Previous studies on the effect of adsorbed As and Sb on growth of Ge/Si(001) and Si/Ge/Si(001) detailed the change in growth modes from island formation to layerby-layer growth.<sup>3,4</sup> The samples were grown with saturation coverages of the surfactant, which occurs at near 1 monolayer (ML) for As/Si(001) (1 ML =  $6.78 \times 10^{14}$ / cm<sup>2</sup>). But for hydrogen, maintaining monolayer coverage at the growth temperature of interest, 550 °C, is not experimentally feasible on a Ge film, since the desorption temperature is  $\simeq 350$  °C.<sup>6</sup> Lowering the temperature to keep a saturation coverage would have the side effect of altering the Ge mobility, greatly complicating the interpretation of results. Thus, the present study focuses on intermixing between\_Si and Ge, rather than islanding of Ge/Si(001). (We note that for samples where there is pronounced intermixing, surface germanium may increase the rate of hydrogen desorption.<sup>6</sup>) As a benchmark structure, a film of Ge several ML thick was deposited on Si(001). Subsequently, a capping layer of Si was deposited. Studies of similar structures grown by MBE demonstrated a pronounced intermixing between the embedded Ge and the Si capping layer.<sup>7</sup> The intermixing takes place *during* growth. For Ge<sub>x</sub>Si<sub>1-x</sub> layers embedded in silicon<sup>8</sup> surface Ga during growth improved the interface characteristics.

Atomically clean Si(001) samples were prepared by a lengthy degassing at 600 °C followed by light sputtering. A 40 s flash to 1040 °C removed the native oxide, leaving no traces of oxygen or carbon visible by x-ray photoemission. The cleaning and analysis were conducted in a stainlesssteel ultrahigh-vacuum system with a base pressure in the  $10^{-11}$  Torr regime. The chamber was connected to a turbopumped, cold-walled stainless-steel CVD cell, with a base pressure of  $6 \times 10^{-10}$  Torr. High-purity disilane was introduced to the system through a quartz capillary array a few centimeters from the sample, with the ion gauge filament off. After dosing, the sample was directly transferred back into the analysis chamber, without exposure to air at any stage. The samples were free of oxygen, and showed a  $(1 \times 2)$  low-energy electron diffraction pattern characteristic of the reconstructed Si(001) surface. Ge marker layers were prepared either by in situ MBE, or by decomposition of germane, with no significant differences found in samples prepared by the two methods. Growth temperatures were measured by an infrared pyrometer.

The samples were analyzed by high-resolution (MEIS), a technique that has been described in great detail elsewhere.<sup>9</sup> For channeling spectra, the [111] axis of the sample was aligned to a beam of 200 keV He<sup>+</sup>. Random spectra were obtained by rotating the samples azimuthally by 12°, along with a polar rotation of 4°. Backscattered ions were energy analyzed with a toroidal electrostatic analyzer with an energy resolution of  $\Delta E/E = 1.2 \times 10^{-3}$ . Spectra were integrated for an angular range of  $\pm 1.6^{\circ}$  about the chosen scattering angle, 51.4°.

Due to the well-characterized nature of our experimental technique, interpretation of our data is straightforward. With the sample aligned to a random incidence geometry, ions are backscattered from the sample with a known Rutherford cross section. This can be used to determine the

2648 Appl. Phys. Lett. 58 (23), 10 June 1991 0003-6951/91/232648-03\$02.00 (© 1991 American Institute of Physics 2648 This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:

<sup>&</sup>lt;sup>a)</sup>Present address: IBM General Technology Division, East Fishkill Facility, Hopewell Junction, NY 12533.

![](_page_2_Figure_0.jpeg)

FIG. 1. Ion backscattering spectra for Ge films embedded in Si(001) grown by chemical vapor deposition. The Ge film has been buried underneath a capping layer of 40 Å of Si. (a) At 520 °C, a narrow Ge peak can be seen in the random spectrum, with no Ge visible in the channeling spectrum. (b) At 560 °C, the Ge peak has broadened, and (c) at 590 °C, the Ge leading edge extends as far as the surface of the sample.

coverage *in situ*. Furthermore, the ions slow down while traversing the sample, allowing the use of fabulated stopping powers to assign an accurate depth scale to the energy spectra. In a channeling geometry, atoms that occupy lattice sites within the crystal are shadowed from the incident ions by atoms that are closer to the surface. Thus, an embedded epitaxial film will be nearly invisible in a channeling spectrum. Combining information from channeling and random spectra gives a detailed picture of the depth distribution, areal density, and crystal quality of a film.

A series of samples with Ge films of  $\simeq 1.5$  ML thickness were capped with CVD Si. The samples were given isothermal exposures at constant pressure, with growth temperatures ( $T_{g}$ ) varying from 520 to 625 °C and disilane pressures at the sample position between 0.2 and 2 mTorr. Backscattering spectra showed a significant change in Ge depth distribution over the temperature range examined (Fig. 1). For  $T_g = 520$  °C, a narrow Ge peak appears in the random spectrum, with little or no Ge visible in the channeling spectrum. At a slightly higher  $T_g$ , an asymmetric broadening of the Ge peak can be seen, indicating interdiffusion into the Si capping layer. Finally, for  $T_g$ = 590 °C, not only is the Ge peak noticeably broader, but significant quantities of surface Ge can be seen. At high temperatures there is an increase in the background of the channeling spectra, characteristic of poor epitaxy. The difference in the crystal quality is not due to variations in the growth rate, since the pressure was adjusted to give identical growth rates (0.2 ML/s) for the samples in Figs. 1(b) and 1(c). Indeed, one would expect better crystal quality

at *higher* temperatures. Ultimately, at the highest temperatures examined, 625 °C, the Ge peak broadens towards lower energies, suggesting that the morphology of the capping layer was degraded.

Structures grown by MBE were prepared *ex situ*, transferred in air, and analyzed using MEIF. The samples were prepared with growth rates of 0.1 ML/s, which is slightly lower than the growth rates of the CVD films. The data has been reported earlier,<sup>7</sup> and indicate that abrupt interfaces can only be obtained for  $T_g \leq 250$  °C. For  $T_g = 350$  °C, the Ge profile broadened to resemble spectra as shown in Fig. 1(b), prepared by CVD at 560 °C.

To prepare abrupt structures at temperatures above 520 °C, one must terminate the surface with an adsorbate that does not desorb as readily as hydrogen. Consequently, we use antimony as a surfactant. A sample was prepared using the same cleaning process as the CVD samples, but followed with deposition of 1 ML layer of Sb at 625 °C. The sample was then exposed to disilane at 625 °C, and a thin Si capping layer of 20 ML was deposited. The sample exhibited a sharp Ge peak, especially surprising considering the relatively high  $T_g$ . Since hydrogen has an extremely short surface residence time of 625 °C, the lack of intermixing must be attributed to the presence of Sb, rather than the influence of surface hydrogen. Indeed, samples prepared with silicon MBE using a monolayer of arsenic as a surfactant at 550 °C have abrupt profiles as well.<sup>3</sup>

It is instructive to compare the temperature dependence of the Ge intermixing for films grown using different techniques. To this end, the lineshapes from Fig. 1 were analyzed assuming that the Ge concentration exponentially decays towards the surface. The depth distribution was convolved with the detector resolution and ion energy straggling before comparing with the data. On a physical level, the decay constant can be derived from a model where for every ML of deposited Si, there is a constant probability that the surface Ge will "float" along the growth front  $(P_{\text{float}})$ . Thus, the concentration in a given layer is proportional to the concentration in the next deepest layer. A minor inadequacy in this model concerns diffusion when growing Si on a Ge film more than 1 ML thick. No provision is made for differences in  $P_{\text{float}}$  between the first layer and subsurface Ge. Nonetheless, the data could be fit quite well with this model. Due to limits in the depth resolution of MEIS, the measurement is most accurate for samples with  $P_{\text{float}} \ge 0.7$ .

The behavior of  $P_{\text{float}}$  shows drastically different temperature dependencies for the crystal growth methods examined (Fig. 2). First, let us examine the data for MBE films. Between 250 and 350 °C,  $P_{\text{float}}$  increases to about 0.9 with some small increase at higher  $T_{g}$ . In the presence of a free surface, Ge atoms must become highly mobile at relatively low temperatures. Since the dechanneling of ions is quite large for films grown at 250 °C, these films are not good enough crystals for most practical purposes.

Films prepared with CVD retain a low  $P_{\text{float}}$  at much higher temperatures than MBE films. There is a steep increase in  $P_{\text{float}}$  between 520 and 625 °C. This temperature span overlaps the hydrogen desorption temperature from

![](_page_3_Figure_0.jpeg)

FIG. 2. Temperature dependence of the probability of Ge floating to the surface during growth. Data is shown for MBE, CVD, and surfactant grown samples. A low value of the floating probability ( $P_{\rm float}$ ) indicates a more abrupt interface. Simulated ion scattering spectra for various values of  $P_{\rm float}$  are included to indicate the sensitivity of the experimental probe.

Si(001). The trend from growth on hydrogen-rich to bare surfaces was exaggerated in the data by the choice of disilane pressure, which was selected so that samples prepared at higher temperatures were grown at lower pressures. This was done to reduce the variation in growth rates for the different samples. To sort out the influence of hydrogen coverage ( $\theta_{\rm H}$ ) as opposed to growth rate, it was necessary to model the hydrogen coverage. The model was based on published values of the desorption rate  $(R_{desorp})$  from Si(001) in a reactor environment.<sup>2</sup> Assuming that the  $\theta_{\rm H}$  is constant during growth, desorption must be balanced by the rate of incoming hydrogen, which is proportional to the growth rate. We can assume that relatively little hydrogen incorporates into the film, since a substantial hydrogen content would have disrupted the lattice, and resulted in dechanneling of ions. Thus, for first-order desorption kinetics.

$$\frac{d\theta_{\rm H}}{dt} = kR_{\rm growth} - 2\theta_{\rm H}R_{\rm desorr}$$

#### $\theta_{\rm H} = (kR_{\rm growth})/(2R_{\rm desorb}),$

where  $R_{\text{growth}}$  is the growth rate, and the constant k is the amount of surface hydrogen donated by each adsorbed disilane molecule. Using an activation energy of 47 kcal/mol, and a constant of  $2.9 \times 10^{11}$ /s for  $R_{\text{desorp}}^2$  and assuming that k is of order unity, we can approximate  $\theta_{\rm H}$  for any combination of temperature and pressure. (This model neglects any increase in  $R_{\text{desorp}}$  due to surface Ge.) The absence of surface hydrogen correlates with high values of  $P_{\text{float}}$ , plotted in Fig. 3. Therefore, we conclude that the dominant factor in determining interface abruptness in CVD growth is the quantity of surface hydrogen during growth.

![](_page_3_Figure_6.jpeg)

FIG. 3. Probability of Ge floating towards the surface during growth  $(P_{\text{float}})$  as a function of surface hydrogen concentration. The surface hydrogen concentration was modeled from the observed growth rate and the hydrogen desorption rate.

The microscopic basis for the intermixing observed in samples grown with bare surfaces is fairly well understood. Current models of  $\text{Ge}_x\text{Si}_{1-x}$  surfaces predict that a Ge termination is the most stable, which may drive segregation during growth.<sup>10</sup> Furthermore, strain could enhance the segregation. The role of adsorbed species during growth is less clear. Substantial quantities of surface hydrogen are required to effectively suppress Ge segregation. Thus, it would seem unlikely that the mechanism involves decoration of defect sites or steps. It is more plausible that mobility of surface atoms is curtailed in the presence of an adsorbate, decreasing intermixing at the growth front.<sup>11</sup>

The present study has highlighted the importance of the crystal surface in the synthesis of silicon germanium structures. A free, unterminated surface permits intermixing during growth. But if the surface is terminated with either a dopant, or hydrogen, a far more precise control can be maintained.

We wish to thank S. S. Iyer for providing *ex situ* MBE samples. In addition, M. C. Reuter, M. Horn von Hoegen, M. Liehr, and B. Meyerson provided helpful advice.

- <sup>1</sup>B. S. Meyerson, Appl. Phys. Lett. 48, 797 (1986).
- <sup>2</sup>M. Liehr, C. M. Greenlief, S. R. Kasi, and M. Offenberg, Appl. Phys. Lett. 56, 629 (1990).
- <sup>3</sup>M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. 63, 632 (1989).
- <sup>4</sup>F. K. LeGoues, M. Copel, and R. M. Tromp. Phys. Rev. Lett. 63, 1826 (1989).
- <sup>5</sup>L. Surnev and M. Tikhov, Surf. Sci. 138, 40 (1984).-
- <sup>6</sup>B. S. Meyerson, K. J. Uram, and F. K. LeGoues, Appl. Phys. Lett. 53, 2555 (1988).
- <sup>7</sup>S. S. Iyer, J. C. Tsang, M. W. Copel, P. R. Pukite, and R. M. Tromp, Appl. Phys. Lett. 54, 219 (1989).
- <sup>8</sup>P. C. Zalm, G. F. van de Walle, D. J. Gravesteijn, and A. A. van Gorkum, Appl. Phys. Lett. 55, 2520 (1989).
- <sup>9</sup>J. F. van der Veen, Surf. Sci. Reports 5, 199 (1985).
- <sup>10</sup> P. C. Kelires and J. Tersoff, Phys. Rev. Lett. 63, 1164 (1989).
- <sup>11</sup> M. Copel, M. C. Reuter, M. Horn-von Hoegen, and R. M. Tromp, Phys. Rev. B 42, 11682 (1990).

#### M. Copel and R. M. Tromp 2650

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 141.212.109.170 On: Thu. 11 Dec 2014 14:50:43