Note: This is a preprint of a paper submitted for publication. Contents of this paper should not be quoted or referred to without permission of the author(s).

To be presented at the Spring Meeting of the Materials Research Society, San Francisco, California, April 17-21, 1995 and published in *Strained Layer Epitaxy—Materials, Processing, and Device Applications*, ed. by J. Bean, E. Fitzgerald, J. Hoyt, and K.-Y. Cheng
Materials Research Society, Pittsburgh, Pennsylvania

Triangular Step Instability and 2D/3D Transition During the Growth of Strained Ge Films on Si(100)

K. M. Chen, D. E. Jesson, S. J. Pennycook, M. Mostoller, and T. Kaplan

Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6030

T. Thundat and R. J. Warmack

Health Sciences Research Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6123

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
under
Contract No. DE-AC05-84OR21400
with the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee

April 1995

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TRIANGULAR STEP INSTABILITY AND 2D/3D TRANSITION DURING THE GROWTH OF STRAINED Ge FILMS ON Si(100)

K. M. CHEN*, D. E. JESSON*, S. J. PENNYCOOK*, M. MOSTOLLER*, T. KAPLAN*, T. THUNDAT**, AND R. J. WARMACK**

* Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6031;

** Health Sciences Research Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

ABSTRACT

We show that an activation energy barrier exists to the formation of wavy step edges due to stress-driven 2D instability. The barrier height and the barrier width depend sensitively on the surface stress anisotropy and step free energy. The large misfit strain of Ge films significantly reduces the barrier by lowering the S_B step energy, inducing S_A steps to undergo a triangular instability even during low temperature growth of Ge on Si(100). The step instability results in a novel arrangement of stress domains, and the interaction between the domains causes a spatial variation of surface strain with a surprisingly large influence on the energy barrier for island nucleation. Calculations indicate a dramatic enhancement in the nucleation of 3D islands at the apex regions of triangular steps, in good agreement with our experimental measurements.

INTRODUCTION

Thermodynamically, the stability of step structure is determined by the subtle interplay between surface free energy contributions from step (creation) energy and elastic energy arising from surface stress. Any change in surface stress and/or step free energy may effect this balance in surface energy, and consequently induce step instability. For example, step edges were predicted¹ to undergo a phase transition, from straight steps to long-wavelength sinusoidal step instabilities when the terrace width is larger than a characteristic length.² The driving force for the step edge undulations is to lower long range surface stress at the expense of increasing step energy. However, such instability is not observed on the Si(100) surface in most cases,³ except after extremely high temperature (1250°C) annealing.⁴ Therefore, further investigation is necessary to fully understand the stress-driven wavy step instability.

For the Ge(100) strained film, the surface is not only subject to the intrinsic surface stress arising from dimerization, but also the large misfit stress. In this paper, we report a remarkable effect of misfit strain on the 2D step instability. Using atomic force microscopy (AFM), we have observed a new triangular step instability which occurs even *during* low temperature growth of strained Ge film on a slightly miscut Si(100) surface. Based on surface energy calculations, we demonstrate the existence of an activation energy barrier to the initial step instability. The barrier height is sensitively dependent on the step free energy and surface stress anisotropy. Our molecular dynamics simulations show that a compressive misfit stress has a striking effect in lowering of S_B step energy, and consequently reduces the activation barrier for S_A step instability. A novel, triangular S_A step instability evolves at or near step flow, while S_B steps remain straight. We also show that the instability causes a spatial variation in surface stress, which yields a surprisingly large influence on 3D island nucleation.

EXPERIMENTAL OBSERVATIONS

The growth of the Ge thin film was carried out in a custom-design MBE system. Substrates were nominally flat Si(100) wafers, with an actual vicinal angle, determined by x-ray diffraction, of 0.06° towards $\langle 011 \rangle$. A well ordered (2x1) Si(100) surface was prepared before the Ge thin film was deposited on the surface at 430°C. The surface of Ge film displayed a weak (2x8) reflection high energy electron diffraction (RHEED) reconstruction. RHEED intensity oscillation measurements indicated that the growth was near step flow. The sample was quenched to room

temperature immediately after deposition and then taken out of chamber for AFM measurements. AFM images were acquired using tapping-mode AFM in a dry, helium-filled glove box.

Figure 1 shows typical AFM images of an 8 ML thick Ge(100) film grown on Si(100). The major new feature of our observations is the long-wavelength (about 1800 Å), triangular S_A step configuration (microscopically it consists of kinks with both S_B and S_A step segments). These steps alternate with straight S_B steps. There is a pronounced tendency for a spatial out-of-phase relationship between steps such that the peaks of a triangular S_A step are close to the valleys of the next closest S_A step. It is well known that the monoatomic height steps also serve as domain boundaries of (dimerization-induced) surface stress. This spatial "phase" relationship between the stress domains provides strong evidence for a stress driven instability of steps. Based on the following calculations, we demonstrate that the triangular step morphology is induced by misfit stress, rather than kinetic-induced step instabilities arising for example from "kissing sites",⁶ or "diffusion bias".⁷

In Figure 1, at least half of the macro-islands are preferentially nucleated on the apex regions of the triangular undulations, while 30% of islands are located near step edges and the remaining 20% are on terrace away from step edge. Taking into account the fact that the apex regions only take a small fraction ($\sim 1/1000$) of the total surface area, we estimate that the nucleation rate at apex regions is about 2500 times larger than that on terrace regions.

Fig. 1 AFM image of a Ge/Si(100) surface showing a triangular step instability, macro-islands. Scan size: 1600x1600 nm². Two types of steps (triangular S_A steps and straight S_B steps) can be seen. Macro-islands appear as bright square-like dots.

Fig. 2 Surface pattern of equally spaced straight steps S_B alternating with triangular S_A steps. Step spacing L , wavelength λ , and amplitude A are indicated. The thin dashed lines show the average position of S_A steps prior to step instability. The surface is actually composed of surface units (marked out with thick dashed lines) of dimensions λ and L . Shaded and non-shaded regions correspond to $N \times 2$ and $2 \times N$ stress domains, respectively.

THEORETICAL ANALYSIS

Surface Energy Calculations of Step Instabilities

The continuum elastic theory has been shown^{1,2} to be appropriate for the treatment of stressed surfaces whose stress domain sizes are very large compared to atomic dimensions. Here we use the similar approach of an elastic Green's function treatment to calculate the elastic energy of the steps. We only consider the "force monopole", i. e. the force resulting from interaction of

surface stress domains. The force density $f_i(R) = \partial_j \sigma_{ij}(R)$, here σ_{ij} is the two-dimensional intrinsic surface stress tensor, R is the position vector on the surface. The force acting at domain boundary thus would cause the surface displacement $u_\alpha(R)$ (α donated as x , or y directions), which can be written in terms of an elastic surface Green's function $\chi_{ij}(R, 0)$:

$$u_\alpha(x) = \int dR' \chi_{\alpha j}(R-R', 0) f_j(R') \quad (1)$$

and the elastic energy of the steps is

$$E_{el} = -1/2 \int dR dR' \chi_{ij}(R-R', 0) f_i(R) f_j(R') \quad (2)$$

In order to simplify the calculation, we treat the surface as an ideally periodic structure of stress domains, bounded by equally spaced triangular and straight steps as shown in fig.2. The calculation of E_{el} can be more easily carried out in reciprocal space:

$$E_{el} = -1/2 \sum_G |f_i(G)| \chi_{ij}(G) |f_j(G)| \quad (3)$$

if we assume that the elastic medium is isotropic, then the Fourier transforms of both the elastic Green's function and the force density can be performed analytically. Thus, the elastic energy contribution (per unit area) of wavy steps can be further written as:

$$\Delta E_{el} = -[F_0^2(1-\nu)/\pi\mu L] E'(\lambda, A) \quad (4)$$

where μ and ν are the shear modulus and Poisson's ratio of the medium, respectively. a is the surface lattice constant. $F_0 = \sigma_{//} - \sigma_{\perp}$, characterizes the anisotropy of surface stress tensor along ($\sigma_{//}$) and normal ($\sigma_{\perp}$) to the dimer. $E'(\lambda, A)$ is a dimensionless function of step undulation wavelength λ and amplitude A , reflecting the contribution of triangular step waviness to the elastic energy. The quantity E' can be calculated numerically through reciprocal space summation and is given by $\text{Ln}(L/2\pi a)$ when the steps are straight.²

The waviness of one type of step would require the creation of kinks of the other type (with creation energy ϵ_k per unit length), as well as "corners" (with energy C per corner). The energy cost (per unit area) for the step waviness from straight steps is thus:

$$\Delta E_{step} = (2A/\lambda L) \epsilon \quad (5)$$

Here step free energy or line tension $\epsilon = \epsilon_k + nC - \epsilon_l(T)$. n is the number of corners per unit length along the wavy steps and $\epsilon_l(T)$ is the thermal or entropic contribution⁴ to step free energy per unit length, which depends on surface temperature T . The step waviness contribution to surface energy (per unit area) is therefore;

$$\Delta E = \Delta E_{el} + \Delta E_{step} = -[F_0^2(1-\nu)/\pi\mu L] [E'(\lambda, A) - \text{Ln}(L/2\pi a)] + (2A/\lambda L) \epsilon \quad (6)$$

Eq. 6 is our principal result defining the stability of surface steps. If $\Delta E < 0$, the decrease in strain energy outweighs the cost of increasing step length and the straight step would be unstable to step undulation; otherwise, for $\Delta E > 0$ the steps remain straight. Fig.3 shows a typical plot of contours of constant energy ΔE as a function of the wavelength λ and amplitude A for the triangular undulations. Contours with $\Delta E < 0$ are shown as dotted lines, so straight steps are unstable over the entire region of A and λ .

We emphasize that an energy barrier region exists to the formation of step undulations, as shown in fig.3. The barrier can be physically understood in that the surface elastic energy gained from initial small undulations is not sufficient to compensate the increase of step free energy. The barrier height or width is sensitively dependent on the anisotropy of surface stress (F_0) and step free energy (ϵ). For surface with larger surface stress anisotropy and/or lower step free energy, the barrier height drops dramatically until it vanishes. However, with smaller F_0 and larger ϵ , the barrier height will increase until the instability is completely suppressed.

Fig. 3 Contours of constant surface energy contribution ΔE per surface area, as a function of wavelength λ and amplitude A . $L=2800$ Å, $F_0=0.20$ eV/Å², $\epsilon=4.2$ meV/Å. Contours with $\Delta E < 0$ are shown as dashed lines. Successive contours of dashed lines differ in energy by 0.003 meV/Å², while the energy values are indicated for contours of solid lines in units of 10^{-4} meV/Å².

Molecular Dynamics Calculations of Step Energies

Since step free energy is a key factor characterizing step formation and step instability, it is essential to evaluate the step energies and their behavior under misfit strain. We carried out molecular dynamics simulations with the Stillinger-Weber potential⁸ to determine the step energies for Si(100) and strained Ge/Si(100) surfaces. The step energy is defined as the energy difference between a surface with and without a step. In Fig. 4, we plot the step energies for the S_A and S_B steps as a function of terrace width on a Si(100) surface, and a strained Ge(100) film surface. The calculated step energies for Si(100) is consistent with previous reports⁹. It can be seen that the Ge(100) S_B is reduced significantly compared to that of Si(100) surface, while the change of S_A step energy is very small (< 7 meV/a). The energy differences between S_B surface steps of Si(100) and strained Ge(100) are as large as 100 meV/a, which can not be explained only by the difference of bulk bond strengths between Ge-Ge and Si-Si. We believe that the lowering of S_B step energy on strained Ge(100) results from the large compressive misfit strain, which partially cancels the inherent tensile strain of rebonded S_B step edges. By contrast, S_A steps do not contain any rebonded pairs of atoms with large tensile strain, so that the step energy remains essentially unaffected by misfit strain. These results are consistent with experimental measurements of kink energies by STM⁵, and are also in agreement with recent calculations by Xie et al.¹⁰

Fig. 4 Step energy vs. terrace width for S_B steps and S_A steps on the Si(100) surface, and a strained Ge/Si(100) film surface. a is the surface lattice constant. Note that the S_B step energy of strained Ge surface is much lower than that of Si(100) surface, S_A step energies remain essentially the same for both surfaces.

Step Instability on Si(100) and Strained Ge(100) Surface

We are now in the position to investigate the instability behavior of steps on strained Ge(100) and Si(100) surfaces. For the Si(100) surface, F_0 has been calculated¹¹ to be $0.26 \text{ eV}/\text{\AA}^2$; We estimate the free energy $\mathcal{E}$ to be about $8.0 \text{ meV}/\text{\AA}$ for S_B steps, and $23 \text{ meV}/\text{\AA}$ for S_A steps at 430°C , based on our calculations above and the experimental measurements in reference 12. Inserting these values in Eq. (6), we plot out ΔE as function of undulation amplitude A in Fig. 5. For a typical wavelength of $1800 \text{\AA}$, we find that S_A steps are stable, while for S_B steps there exists an energy barrier of 5.4 eV per triangle, which is much larger than the available thermal energy of 60 meV . This demonstrates that the instability is kinetically suppressed for both steps at low temperatures. However, the free energies for S_A and S_B steps are reduced dramatically due to the increasing entropic contribution at higher temperatures until both vanish simultaneously at about 1230°C ¹³. Consequently the step instability is essentially barrierless at high temperatures, and the sinuous step instabilities could occur for both S_A and S_B steps, as observed by Tromp et al.⁴ Similar behavior is observed for all other wavelengths.

Fig. 5 Contribution of step waviness to surface energy per unit area (ΔE) as a function of amplitude (A) for S_A and S_B steps on Si(100) and Ge(100) at different temperatures. For a wavelength of $1800 \text{\AA}$ and a terrace width of $2800 \text{\AA}$ both steps are unstable at high temperature (1230°C denoted by HT). At low temperature (430°C denoted by LT), a significant activation barrier suppresses step waviness on Si(100), while on the strained Ge film the barrier for S_A steps is greatly reduced.

In the case of the Ge/Si(100) film surface with the (2×8) reconstruction, we find that the surface stress anisotropy $F_0 = 0.20 \text{ eV}/\text{\AA}^2$, which is similar to that of Si(100). However, the creation energy for S_B kinks is drastically reduced due to the large misfit stress, as shown in fig. 4. This leads to a dramatic change in S_A step stability. We can estimate $\mathcal{E}$ from the Si step energies and the above calculated difference in step energies between strained Ge and Si surface, that $\mathcal{E}$ is about $3.0 \text{ meV}/\text{\AA}$ for the S_A step, and $8.0 \text{ meV}/\text{\AA}$ for the S_B step of a strained Ge(100) surface. Eq. (6) then yields the plots shown in fig. 5. Clearly, the barrier for the S_A step instability is only 0.5 eV per triangle, which is comparable to the thermal energy. Hence S_A step instabilities can readily occur even during low temperature growth. However, for S_B steps, the instability is kinetically suppressed at the growth temperature of 430°C . This explains why the S_A step is unstable to triangular undulation whereas the S_B step is straight. It appears therefore that the large misfit strain can destabilize surface steps, even during far from equilibrium growth.

3D Island Nucleation

Finally, we examine strain fluctuations resulting from the triangular step instability, and the consequence for 3D island nucleation. Considering the mosaic of surface stress domains as shown in fig. 2, the displacement $u_\alpha(R)$ from Eq. 1 can be written in reciprocal space:

$$u_\alpha(G) = f_j(G) \chi_{\alpha j}(G) \quad (7)$$

To the first order approximation, the strain field $\Delta \epsilon_{\alpha\alpha}$ of the medium, i. e. the surface

strain fluctuation resulting from the interaction is:

$$\Delta\epsilon_{\alpha\alpha}(\mathbf{R}) = \partial u_{\alpha}(\mathbf{R}) / \partial R_{\alpha} = \partial / \partial R_{\alpha} \left[\sum_G u_{\alpha}(G) \exp(iG\mathbf{R}) \right] \quad (8)$$

From equations (7) and (8), we have calculated the spatial variation of the strain field $\Delta\epsilon_{\alpha\alpha}$ arising from the interaction of (2x8) stress domains which have stress tensors $\sigma_{||}=0$, and $\sigma_{\perp}=0.20$ eV/Å². We find¹⁴ that the apex regions are the most strained areas, while the most relaxed regions occurs at valley.

Small spatial variations in strain can dramatically effect the 3D island nucleation. Since the nucleation rate of 3D islands is exponentially dependent on its activation barrier height, any change of the barrier would have a large influence on the island nucleation. The activation barrier E_a and critical island size are sensitive functions of local surface stress, being proportional to σ_L^{-4} and σ_L^{-6} respectively.¹⁵ Apex regions with enhanced compressive strain can therefore dramatically reduce the activation barrier. Far from a step, the barrier is calculated to be 2.4 eV, which is reduced to 1.92 eV close to the apex regions of the triangle. The island nucleation rate at apex regions is therefore enhanced by a factor of $\exp(\Delta E_a/kT) \sim 3 \times 10^3$. This explains the dramatic enhancement of 3D islands at the apex regions as observed in Fig. 1.

CONCLUSIONS

In conclusion, we have demonstrated the existence of an activation barrier to a stress-driven step instability. A compressive misfit strain is found to significantly reduce the S_B step energy and consequently induce a triangular S_A step instability, even during low temperature growth under (or near) step flow conditions. The monatomic height step undulations can lead to stress concentrations, which trigger the 2D to 3D transition. Our work provides a natural link between the 2D step instability and 3D surface morphology instability.

ACKNOWLEDGMENTS

This research was sponsored by the Division of Material Science, U. S. department of Energy under contract number DE-AC05-84OR21400 with Martin Marietta Energy System, Inc., and in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Program administrated by Oak Ridge Institute for Science and Education.

REFERENCES

1. J. Tersoff and E. Pehlke, Phys. Rev. Lett. **68**, 816 (1992).
2. O. A. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).
3. see for example, Y.-W. Mo, et. al, J. Vac. Sci. Technol. **A8**, 201 (1990).
4. R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **68**, 820 (1992).
5. Fang Wu, X. Chen, Z. Zhang and M. G. Lagally, Phys. Rev. Lett. **74**, 574 (1995).
6. B. S. Swartzentruber, Y. W. Mo, and M. G. Lagally, Appl. Phys. Lett. **58**, 822 (1991).
7. G. S. Bales and A. Zhangwill, Phys. Rev. B **41**, 5500 (1990)
8. F. Stillinger and T. Weber, Phys. Rev. B **31**, 5262 (1985)
9. Tze W. Poon, S. Yip, P. S. Ho and F. F. Abraham, Phys. Rev. Lett. **65**, 2161 (1990)
10. Y. H. Xie et al., Phys. Rev. Lett. **73**, 3006 (1994)
11. M.C. Payne, N. Roberts, R. T. Needs, M. Needels and J. D. Joannopoulos. Surf. Sci. **211/212**, 1 (1989).
12. B. S. Swartzentruber, Y. -W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. **65**, 1913 (1990).
13. N.C. Bartelt, R. M. Tromp and E.D. Williams. Phys. Rev. Lett. **73**, 1656 (1994).
14. K. M. Chen, et al. Phys. Rev. Lett., to be published.
15. J. Tersoff and F. K. LeGoues, Phys. Rev. Lett. **72**, 3570 (1994).