

# Temperature dependent Mechanisms of Ge-Si epitaxial growth mediated by Surfactants

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## Abstract and Motivation:

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It is seen that surfactant mediated growth (SMG) of Si(1-x) Ge(x) promotes two-dimensional (2D) nucleation regime and increases the critical thickness of the 2D-3D transition at 350 °C. At this temperature, thick defect free flat Ge layers can be epitaxied on 1 monolayer Sb-Si(001) without formation of Ge islands. At higher temperature ~550 °C, Ge islands nucleate after the growth of several 2D monolayers; SMG induces a dramatic reduction of the islands lateral size on both Si(111) and Si(001). The different SMG effects obtained at 350 and 550 °C are explained in terms of thermodynamic and kinetic effects. First, the increase of 2D-3D transition critical thickness by the reduction of Sb induced surface energy is explained. This surface energy reduction has a stabilizing effect of flat Si(1-x)Ge(x) layers against island growth. Second, at the higher temperature, the dramatic reduction of islands size is attributed to a lower Ge diffusion length on Sb rich surface.

Ge on Sb(SMG)- Si(001) can be used for the growth of flat layers and the self-assembling of ultra-small, dense and homogeneous Ge dots. The flat layers formed due to suppression of the 3D islanding aid in making smooth films suitable for the fabrication of microelectronic devices. At a higher temperature, formation of ultra-small dense islands is essential for fabrication of quantum devices that require highly homogeneous islands of small lateral sizes. In general, used for optoelectronic applications such as quantum dots for lasers and LEDs.

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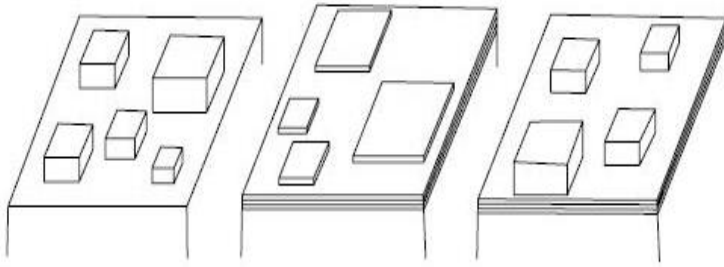
Studies report the effects of introducing Sb for SMG of Si(1-x)Ge(x) on Si. It is reported that:

- i) coherent strained flat Ge layers can be grown up to higher critical thickness without relaxation by misfit dislocations
- ii) dynamic Ge segregation during growth is reduced and Si/Ge intermixing is suppressed
- iii) Si<sub>1-x</sub>Ge<sub>x</sub> relaxed buffer layers of better crystalline quality can be obtained (lower density of dislocations and lower surface roughness).

Surfactant are usually classified into two categories: (i) elements decreasing surface diffusion (As, Sb, Bi, Te) and promoting flat surface and (ii) elements increasing surface diffusion (Sn, Pb, Ga, In) and promoting island formation. Several theoretical and experimental works have been devoted to the microscopic exchange process of Ge—surfactant rather than to the explanation of the SMG mechanism. Kandel and Kaxiras have shown that surfactants of column V induce a complete passivation of Si. SMG effect is then explained by the different adsorption energies on the terraces and along the step edges. Ab-initio density functional theory calculations has given thermodynamic evidence of the surfactant aided layer-by-layer growth. The analysis of energetic data of surface free energy as a function of chemical potential was shown to provide a general theoretical signature of the growth mode.

In this experiment, Si and Ge layers were grown on Si(001) and Si(111) substrates in a Molecular Beam Epitaxy system, with a base pressure < 10<sup>-11</sup> Torr. Si flux was obtained from an electron beam evaporator. Ge and Sb were evaporated from effusion Knudsen cells. Si wafers of nominal orientation were ex situ cleaned and protected by an oxide layer as a final step. This oxide layer was subsequently removed into the growth chamber by flashing the substrate at 900 °C before performing growth. Si and Ge were deposited at a rate about 0.3 Å/s and 0.063 Å/s, respectively, directly on the substrate or after the deposition on the surface of a sub-monolayer coverage of Sb. The morphology of the surface was qualitatively determined during growth by RHEED. Growth regimes were deduced from the RHEED specular beam

intensity variations during growth. After growth, atomic force microscopy (AFM) was used for morphological and structural characterization of the deposited layers.



**Fig 1: Three mechanisms of epitaxial growth** (a) Volmer–Weber (VW) mechanism or island growth (b) Frank–van der Merwe (FM) mechanism or layer-by-layer growth and (c) Stranski–Krastanov (SK) mechanism or layer-by-layer growth followed by the formation of isolated 3D islands.

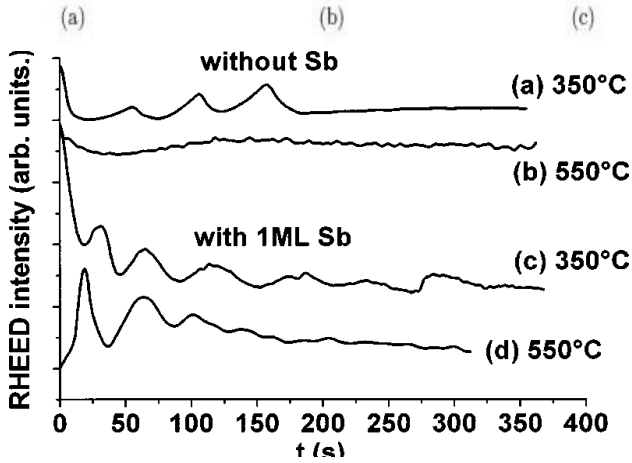


Figure 2: Variations of the RHEED intensity during the growth of Ge/Si(111) (a), (b) and Ge/1 ML Sb-Si(111) (c), (d)

	350 °C	550 °C
Ge/Si	2D rough layer r.m.s. ~ 1 nm	3D islands $h = 10$ nm, $\varnothing = 1500$ nm, $d \sim 2.10^7/\text{cm}^2$
Ge/Sb-Si	2D layer r.m.s. ~ 0.2 nm	3D islands $h = 5$ nm, $\varnothing = 80$ nm, $d \sim 9.10^9/\text{cm}^2$

TABLE I. Typical features of Ge surface morphologies obtained at 350 and 500 °C on Si and Sb-Si surfaces. r.m.s. represents the root mean square roughness of the 2D layers.  $h$ ,  $\varnothing$ , and  $d$  represent the height, diameter, and density of the 3D islands.

## Discussion (Mechanisms)

Evidences of different effects of Sb SMG depending on the temperature are: at low temperature, delay of the 2D-3D growth transition and inhibition of the step-flow growth regime; at high temperature, a dramatic reduction of Ge island size accompanied by an increase of their density and by a modification of island shape (with the absence of visible facets). We suggest that these effects can be interpreted as the combination of two driving forces: i) thermodynamic: the decrease of surface energy induced by Sb sub-monolayer coverages which promotes 2D growth and ii) kinetic, the decreases of adatoms diffusion length due to the competition between surface diffusion and exchange with Sb atoms of the subsurface which reduces the island size.

## Thermodynamic Effects of Surfactants:

The critical thickness of 2D-3D transition ( $h_c$ ) corresponds to the minimisation of the total free energy of the system ( $E$ ). By approximation, if  $E$  only consists of two terms, surface energy ( $g$ ) and elastic energy ( $E_{el}$ ), then  $h_c$  corresponds to the thickness at which the reduction of elastic energy induced by relaxation at step edges in the islands becomes larger than the excess surface energy induced by the larger surface developed by the islands. In both cases (with or without Sb surfactant) at 2D-3D transition, the total critical free energy ( $E_c$ ) is same in both cases [ $\Delta E_c(h_c) = 0$ ]. We can write at constant temperature:

Ge / Si(111)

Ge / Sb-Si(111)

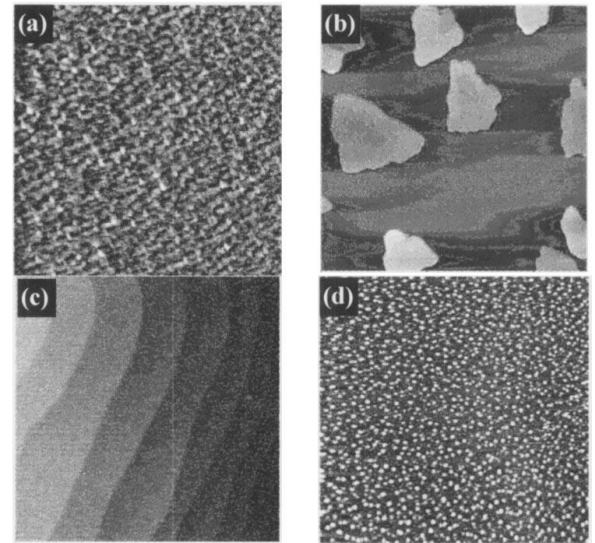


Figure 3: AFM images of the surface after deposition of Ge/Si(111) at  $T_G = 350$  °C (a) and  $T_G = 550$  °C (b) and Ge/1 ML Sb-Si(111) at  $T_G = 350$  °C (c) and  $T_G = 550$  °C (d). At 350 °C 2D layers are obtained (scan of the image is  $2 \times 2 \mu\text{m}^2$ ) while at 550 °C islands have formed (scan size of the images is  $4 \times 4 \mu\text{m}^2$ )

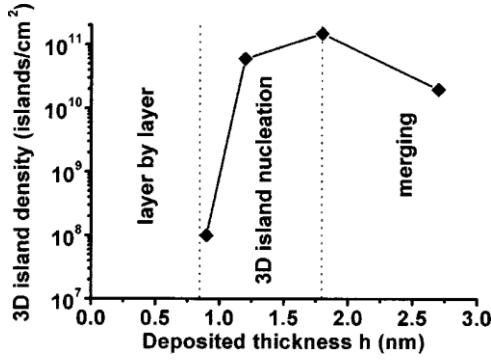


Figure 4 : Evolution of the 3D islands density with the deposited thickness for growth at 550 °C on 1 ML Sb-Si(001)

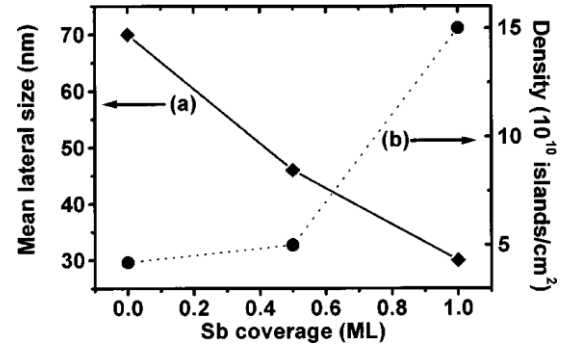


Figure 5: Evolution of the mean lateral size of islands (a) and of their surface density (b) with Sb coverage

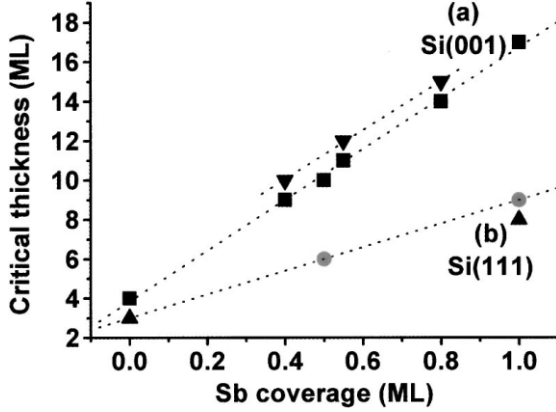


FIG. 6. Evolution of the critical thickness of the 2D-3D growth transition with Sb coverage on Si(001) (a) and on Si(111) (b). Up and down triangles represent experimental values.

Increase of the critical thickness for the 2D-3D transition observed experimentally at low temperature during Sb SMG.

$$\Delta \gamma(\theta) + \Delta E_{el}(h_c) = 0$$

Here, the first term refers to surface energy, while 2<sup>nd</sup> term corresponds to the elastic energy differences between Ge/Si and Sb:Ge/Si structures. The variations of the volume and of the chemical potential of the crystal are neglected in Eq. (1) as the silicon substrate can be considered as semi-infinite. Neglecting the possible changes of the microscopic surface state (surface reconstruction, roughness, etc.) it is reasonable to assume that the surface energy follows a Vegard's law with Sb coverage ( $\theta$ )

$$\gamma(\theta) = \theta \gamma^{Sb} + (1 - \theta) \gamma^{Ge}$$

The elastic energy ( $E_{el}$ ) stored in the flat Ge layer epitaxied on the Si substrate is calculated using the classical equation where  $\mu$  and  $\nu$  are the shear modulus and the Poisson's ratio of Ge;  $\varepsilon$  is the lattice misfit between Ge and Si;  $E_{el}(h) = 2\mu \frac{1+\nu}{1-\nu} \varepsilon^2 V$  with  $V = Sh$   $V$  is the volume of

the Ge layer and  $S$  the surface area of the crystal. At low temperature, when there is no Sb desorption, the experimental  $h_c$  is in good agreement with the calculated values. At higher temperature, the smaller  $h_c$  measured experimentally is explained by Sb partial desorption. The linear increase of surface energy with Sb desorption as described in the equation with  $\gamma$  above, promotes island formation. We can say that above a critical Sb coverage, the Ge layer relaxes strain directly by nucleating dislocations without formation of 3D islands at low temperatures. This interpretation is based on purely macroscopic thermodynamic arguments. Thus, the surfactants suppress the thermodynamic driving force for 3D islanding by "locking" the crystal atoms into bulk-like positions. A surfactant is thermodynamically effective when it adsorbs more strongly to the film rather than to the substrate, i.e.  $E_{SA} > E_{SB}$ .

### Kinetic Effects of Surfactants:

The coefficient of diffusion ( $D$ ) for a cubic lattice can be written as:

$Z$ ,  $a$ ,  $n$ ,  $E$ ,  $k$ , and  $T$  are the number of neighbour sites, the distance between neighbour sites, the Debye frequency, the activation energy, the Boltzmann constant, and the temperature, respectively.

The mean surface diffusion coefficient (DSD) of Ge adatoms can be expressed as:

where  $E_{SD}^{Sb}$  and  $E_{SD}^{Ge}$  are the activation energies of the Ge adatom diffusion on a Sb and a Ge surface, respectively

$$D_{SD} = a^2 Z_s \nu_s \left\{ \theta \exp\left(\frac{-E_{SD}^{Sb}}{kT}\right) + (1 - \theta) \exp\left(\frac{-E_{SD}^{Ge}}{kT}\right) \right\}$$

Because of dynamic segregation of Sb during growth, another mechanism should be considered: the two sites exchange between adatoms and Sb atoms located in the subsurface layer. Hence, when an atom is deposited on the surface, it can either diffuse, or exchange with Sb subsurface atoms.

The exchange rate can be defined as

$$\Gamma_{\text{ex}} = \theta \nu_{\nu} \exp\left(-\frac{E_{\text{ex}}}{kT}\right)$$

Considering that the phonon vibrations at the surface are generally twice the value as in bulk, the diffusion time of Ge adatoms before to exchange with Sb subsurface atoms is then

$$\tau = \frac{1}{\Gamma_{\text{ex}}} = \frac{2}{\theta \nu_s} \exp\left(\frac{E_{\text{ex}}}{kT}\right)$$

The Ge adatom diffusion length on the surface can be expressed as

$$\lambda = a \sqrt{2Z_s} \left[ \exp\left(\frac{E_{\text{ex}} - E_{SD}^{\text{Sb}}}{kT}\right) + \frac{(1-\theta)}{\theta} \exp\left(\frac{E_{\text{ex}} - E_{SD}^{\text{Ge}}}{kT}\right) \right]^{1/2}$$

At  $\theta=1$ , it becomes

$$\lambda = a \sqrt{2Z_s} \left[ \exp\left(\frac{E_{\text{ex}} - E_{SD}^{\text{Sb}}}{kT}\right) \right]^{1/2}$$

The evolution of  $\lambda$  in equation above explains the reduction of Ge island size when Sb coverage increases when  $\theta$  decreases, the diffusion length increases (the second term of  $\lambda$  increases). At  $\theta=1$ , the diffusion length is directly related to  $E_{\text{ex}} - E_{SD}^{\text{Sb}}$  (equation above). Hence, lower is the activation energy of exchange, lower is  $\lambda$  and consequently lower is the island size. In conclusion, considering equilibrium thermodynamics or kinetics, the island formation at 550 °C is explained by the partial desorption of Sb during growth. In absence of a surfactant the atoms arriving at the crystal surface diffuse on it, join pre-existing steps or islands, or give rise to new islands. At sufficiently high temperatures the diffusivity of the atoms on the terraces is high and they reach the pre-existing steps before meeting with each other. At low temperatures and in turn low diffusivity, the atoms meet with each other before reaching the steps and give rise to 2D nuclei on the terraces. Kandel and Kaxiras (2000) reached the same conclusion by kinetic Monte Carlo calculations.

## Conclusions:

We find that the driving force of Sb SMG effect comes from the conjunction of thermodynamics (surface energy/elastic energy) and kinetics (surface diffusion/surface segregation) phenomena. We see that pre-deposition of a sub-monolayer of Sb before Ge MBE growth permits (i) at low temperature ~350 °C, increase the critical thickness of the 2D-3D growth transition and (ii) at higher temperature ~550 °C, to control Ge island size, shape and density (reduction of islands size, increase of surface density and modification of shape). We can explain these two effects by the decrease of both the surface energy and the surface diffusion length during Sb SMG of Ge. We see that both equilibrium and kinetic considerations can explain island formation at 550 °C by the partial desorption of Sb. The Sb:Ge SMG process developed in this study can be used for applications like the growth of highly concentrated Si(1-x)Ge(x) flat layers in epitaxy on Si and the self-assembling of very small Ge dots with a high surface density.

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