# Interfacial Energies Providing a Driving Force for Ge/Si Heteroepitaxy

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Epitaxy of Ge on Si(001) from undersaturated solutions demonstrates a novel principle: minimization of interfacial energy between solution and solid in a system provides the driving force for heteroepitaxy. Growth according to this principle leads to sharp heterointerfaces and Ge layers free of nucleation sites for dislocations. The relations of interfacial and strain energy vary on the system's pathway towards self-termination of growth and determine the layer morphology.

Every crystallization process requires a driving force. This driving force results from a difference in Gibbs free energy $\Delta G < 0$ between the feeding and the crystalline phases of the system. Following Bauer [1], $\Delta G$ is composed of two terms. The first term expresses the difference in chemical potential $\Delta\mu = \mu - \mu_0$ between a crystalline phase and a feeding phase of potentials $\mu$ and $\mu_0$, respectively. In the case of homoepitaxy $\Delta\mu < 0$ forms the driving force. The second term is attributed to the formation of new phase boundaries and the strain at these boundaries. Heteroepitaxy is strongly influenced by this term, due to the different element-specific surface free energies $\gamma$. Early work of Bauer showed how different values of $\gamma$ relative to vacuum of the epitaxial layer and the substrate strongly influence the growth *mode* of the system: an epitaxial layer may grow monolayer by monolayer if each added layer lowers $\gamma$ [1]. As a consequence, such growth must be possible even under conditions of undersaturation ($\Delta\mu > 0$). More recent theoretical work shows that this two-dimensional (2D) epitaxy, as modeled by Bauer, actually requires undersaturation [2]. These conditions, however, have thus far been very difficult to realize in vacuum. Undersaturation can be obtained, however, when the feeding phase is a solution. Interfacial energies $\gamma_{ls}$ between solution and solid replace $\gamma$ in this case. Studies of heteroepitaxial growth where $\Delta\mu > 0$ are, therefore, significant for the understanding of growth modes and the role of free energies in heteroepitaxy.

In this Letter, we show that a driving force due to a minimization of a system's interfacial energies promotes heteroepitaxy, *even under conditions of undersaturation.* We further show that the magnitude of $\Delta G$ influences the mechanism of strain energy relief and that the nucleation of facets of low interfacial energy, *combined* with strain energy relief causes coherent island formation. "Interfacial energy epitaxy" (IEE), a novel method in Ge/Si heteroepitaxy, yields these results [3]. This method advances the advantages of liquid phase epitaxy (LPE), like low defect densities. The crystal perfection of the IEE layers, which are grown closer to equilibrium than is usual

for LPE layers, is sufficiently high to suppress any nucleation of dislocations.

The epitaxy experiments are done under hydrogen atmosphere (1 bar) in a step motor controlled tiltable slider graphite boat, designed for growth times down to 0.6 s. A 10-zone microprocessor controlled furnace is employed. The 4 cm$^2$ Si substrate and source wafers, the metal solvent (typically 10 g of purity 99.999%) together with the solute Ge, are loaded into different boat chambers. After an *in situ* oxide evaporation at 940 °C, the saturation temperature $T_{sat}$ is adjusted and the liquid metal–Ge solution is brought into contact with the Si source wafer, part of which dissolves. The amount of Ge $m_{Ge}$ is chosen to completely dissolve at $T_{sat}$. Thermodynamic equilibrium is established between the metal-Ge-Si solution and a solid GeSi phase (of composition determined by $T_{sat}$ and $m_{Ge}$) [4], which is isothermally regrown on the Si saturation wafer, analogous with results for the liquid-InGaAs/solid-GaAs system [5]. Then the solution and the saturation wafer are separated. In contrast to conventional LPE experiments [6], the temperature is *increased* after the saturation to a constant growth temperature $T_g$, which should be *higher* than $T_{sat}$ and lower than the melting point of Ge, 937 °C. An *undersaturated* solution is thus obtained. This undersaturated solution is brought into contact with the Si substrate and Ge(Si) growth takes place at constant $T_g$ provided conditions discussed in this Letter. After this IEE growth, the solution and the substrate are separated at $T_g$. The thermal stability of the layers is tested by postgrowth annealing at 920 °C. The samples are characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), and by Auger electron spectroscopy (AES). A new high-resolution TEM (HRTEM) technique [7] provides chemical information on an atomic scale.

Pure Ge layers of different growth time $t_g$ were grown by IEE on Si(001) with Bi as solvent. The growth temperature $T_g = 920.0$ °C and the superheating $\Delta T = T_{sat} - T_g = -140$ °C were kept constant to guarantee conditions of 4% and 20% undersaturation relative to Si and Ge, respectively, according to the Bi-Ge-Si phase diagram [4].
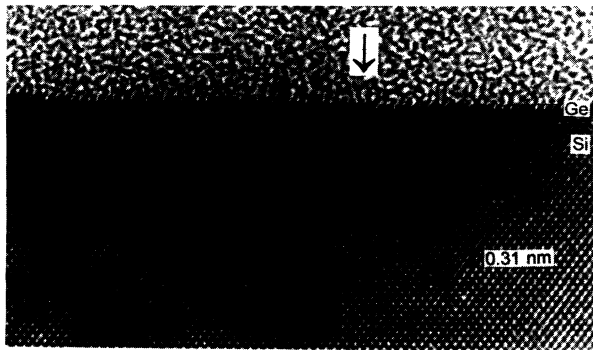
FIG. 1. HRTEM cross-sectional image providing chemical information of the Ge interface to Si(001). The contrast reversal shows that the Ge to Si transition takes place on a lattice plane scale. A step, marked by the arrow, on the substrate surface is reproduced at the layer surface. The layer was grown at 920 °C by IEE under conditions of undersaturation ($\Delta T = -140$ °C), using Bi as solvent. This growth is driven by interfacial energy minimization.
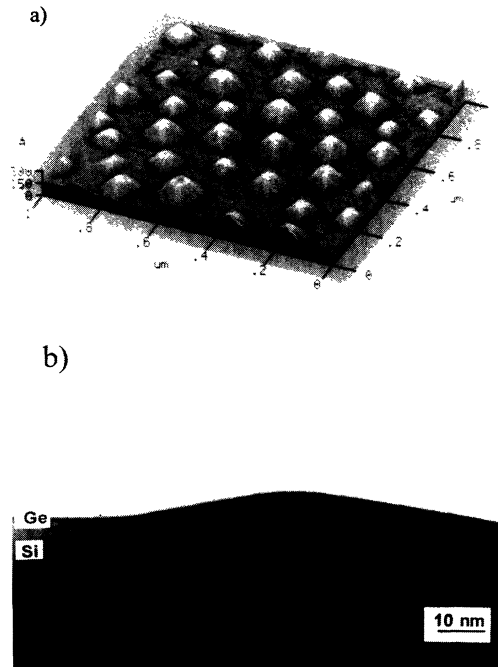


FIG. 2. Microfaceting in the second growth stage (0.3 ML/s). (a) Pyramidal islands along $\langle 110 \rangle$ with a periodicity of 160 nm appears. The AFM plot shows a 1 $\mu m^2$ area with an expanded vertical scale. (b) The pyramids are {115} faceted. A clear Ge material contrast can be seen in the $\langle 110 \rangle$ TEM cross section.

A 2D Ge layer is formed after 2 s of growth. The thickness $h$ is 4 monolayers (ML), as shown in the cross-section HRTEM image in Fig. 1 and verified by Auger electron intensity relations [8]. The abrupt reversal from tunnel to column image contrast [7] shows that the Si to Ge transition takes place within a lattice plane distance. Monatomic steps at the former Si substrate surface are reproduced at the Ge layer surface. Annealing at 920 °C does not influence the interface or surface morphology, indicating that the layers are thermally stable up to this temperature. The dark contrast spots on every second {111} plane of the Ge surface are possibly due to Bi dimers in $\langle 110 \rangle$ directions.

Microfaceting follows the 2D growth, as shown in the (1 $\mu m^2$) AFM plot of Fig. 2(a). The facets define pyramidal islands aligned along the $\langle 110 \rangle$ directions. The average width $w$ of the pyramids is 160 nm and the relation between 2D and island area is 1:1. Inspection by TEM [Fig. 2(b)] reveals a clear Ge material contrast and a uniform {115} faceting on the 4 ML 2D layer. The average growth rate, given by the pyramid volume divided by area and growth time, decreases to 0.3 ML/s at this stage of growth.

A transition to {111} macrofaceting takes place after extended growth times. The islands attain the shape of truncated pyramids, whose four sides are {111} facets, as shown in the multibeam cross section in Fig. 3. The bases of the islands have the same width $w = 160$ nm as the {115} islands in Figs. 2(a) and 2(b) and the 1:1 island/ (4 ML)2D ratio is preserved. When the {111} facets initially form, the growth rate increases to 20 ML/s. In a final stage of the {111} faceting, the growth terminates by itself, which shows that the equilibrium state is reached. The islands reach a final thickness above 100 nm and consist of Ge, according to AES measurements [8].

Figures 1 to 3 and the sharpness of the Ge/Si interfaces imply continuing growth. Therefore, substantial Ge solid diffusion into the Si can be excluded, in contrary to experimental results for the GaAlAs/GaAs system where the formation of a heteroepitaxial solid at $\Delta \mu > 0$ has been ascribed to solid diffusion at high rate [9].

Dislocation-related contrast is *not* observed in any cross-sectional or plane-view micrograph of IEE layers. Figure 4 shows islands in the final growth stage, imaged in dark field and plane view. Only whitish strain related contrast with a maximum at the intersection of {111} planes at the bases of the islands is seen. So far, none of the IEE experiments produced any dislocated material, although the thickness of the pseudomorphic islands exceeds by more than a factor of 3 the critical thickness for dislocation formation in islands of identical geometry, grown under the same conditions by LPE, but at a larger supersaturation ($\Delta \mu < 0$) [6]. The supersaturation thus influences the strain relaxation mechanism: the crystal perfection of the IEE layers is remarkably improved to an absence of nucleation sites for dislocation formation.

Growth of Ge layers from Bi solution on Si takes place even if a driving force for dissolution is applied by undersaturating the solution. Considering the ternary phase diagram solubility data alone [4], this undersaturated Bi-Ge-Si solution would catastrophically dissolve a Si (before establishment of the equilibrium GeSi solid phase)
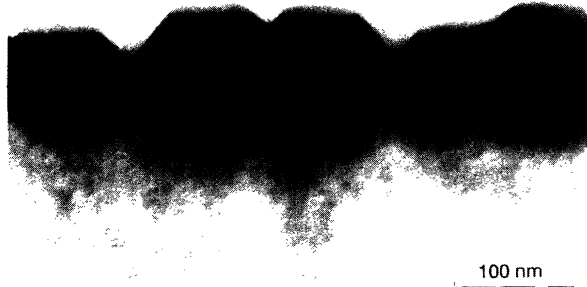
FIG. 3.　Macrofaceting in the third state of growth (20 ML/s): truncated pyramids bound by four {111} side faces. The islands have the same width and interisland distance 160 nm as the microfacets in Figs. 2(a) and 2(b) and are up to 80 nm thick. TEM ⟨110⟩ cross section under multibeam conditions.
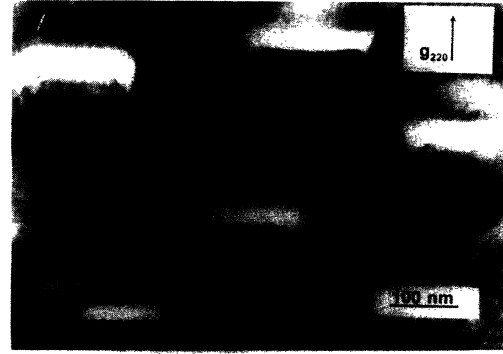


FIG. 4.　Plane-view TEM image in dark field showing coherent Ge islands in the final IEE growth stage. The broad whitish contrast as the bases of the islands is strain related and has a maximum at the intersection of {111} planes. Growth self-terminate at equilibrium without dislocation nucleation.

or a Ge substrate.　The observed growth on Si substrates can only be understood by considering the complete energy balance of the Bi-Ge/Si system.　The surface free energy $\gamma_l$ of liquid Bi in hydrogen atmosphere has been experimentally determined [10] to be $0.34 \ \mathrm{J\,m^{-2}}$ at 920 °C and the surface free energies $\gamma$ of Ge and Si(001) faces have been calculated to be 1.14 and 1.70 $\mathrm{J\,m^{-2}}$, respectively [11].　The liquid-solid interfacial energy $\gamma_{ls}$ is given by $\gamma_{ls} = \gamma - \gamma_l$, when $\gamma_l < \gamma$, i.e., when complete wetting takes place [2].　The dangling bonds of the substrate surface are most likely saturated by the solvent atoms. We, therefore, neglect reconstruction effects on $\gamma$.　In a first approximation, only the interfacial energies $\gamma_{ls}$ of the Bi-Ge/Si system are considered: $\gamma_{ls} = \gamma_{Si} - \gamma_l = 1.36 \ \mathrm{J\,m^{-2}}$ before growth at 920 °C.　The surface free energy of the system is approximately that of liquid Bi: $\gamma_l = 0.34 \ \mathrm{J\,m^{-2}}$.　Then a Ge-Bi interface is created.　The system surface free energy remains constant but the interfacial energy changes: $\gamma_{ls} = \gamma_{Ge} - \gamma_l = 0.80 \ \mathrm{J\,m^{-2}}$.　By binding Ge atoms which diffuse close to the Si-Bi interface the system gains (neglecting strain effects) the difference in interfacial free energy, $\Delta\gamma_{int} = (\gamma_{Ge} - \gamma_l) - (\gamma_{Si} - \gamma_l) = -0.56 \ \mathrm{J\,m^{-2}}$.　This corresponds to the surface free energy difference between unreconstructed Ge and Si.　The interfacial energy difference acts as driving force for epitaxy.

The thermally induced difference in chemical potential $\Delta\mu = \mu - \mu_0$ between a solid surface of potential $\mu$ and a solution of potential $\mu_0$ can be calculated by standard thermodynamic relations, $\Delta\mu$ is proportional to $\Delta T/T_{sat}$ [12].　When homoepitaxial growth takes place $\Delta\mu$ is always smaller than zero.　The difference of chemical potential (per unit area) $\Delta\mu$ for our IEE system can be adjusted to *positive* values and is 0.1 $\mathrm{J\,m^{-2}}$ for the considered Bi-Ge/Si system.　This potential difference acts as a driving force for dissolution of the solid Ge.

Inserting $\Delta\mu$ in the energy balance gives a total [13] energy difference of $\Delta G = \gamma_{int} + \Delta\mu = -0.46 \ \mathrm{J\,m^{-2}}$,

which allows growth as observed under conditions of undersaturation.　It also determines the initial rate of 2 ML/s.　The growth rate can be set by adjusting $\Delta T$. Germanium layers can, therefore, be grown with monolayer precision from a solution.

The Ge adatoms no longer directly interact with the Si substrate after deposition of the initial 4 ML and the initial driving force for epitaxy caused by $\Delta\gamma_{int}$ must decrease.　Interfacial strain energy $E_{ls}$ simultaneously builds up due to the 4% lattice mismatch to Si.　The growth rate decreases by a factor of 7 at this stage, which indicates that the system, at least locally on the layer surface, approaches a near-equilibrium state where $\Delta G$ is out balanced by $E_{ls}$.　The condition under which the initial heteroepitaxial growth takes place becomes

$$\Delta G = \Delta\gamma_{int} + \Delta\mu + E_{ls} + \gamma_{ss} < 0, \qquad (1)$$

where $\Delta\mu_{int}$ is the interfacial, $\Delta\mu$ the thermal deviation from equilibrium as defined above, $E_{ls}$ the strain energy of the liquid-solid interface, and $\gamma_{ss}$ the solid-solid interfacial energy [13] between the solid layer and substrate [14].

After the initial 2D growth, $\Delta G$ is small.　The diffusion lengths at the solution-surface boundary thus become larger, and the adatoms may only adhere at locally favorable sites.　Further growth under conditions of undersaturation is only possible if the system may gain energy by local faceting.　We compare the energy total of a 2D layer with that of the same layer with coherent islands on top to obtain the criterion for near-equilibrium facet growth:

$$\gamma_{ls}^{I} + E_{ls}^{I} \le \gamma_{ls}^{2D} + E_{ls}^{2D}, \qquad (2)$$

where $I$ denotes island, 2D layer (or substrate).　The interfacial energy $\gamma_{ls}^{I}$ is given by

$$\gamma_{ls}^{I} = \sum_{hkl} \left[ (\gamma^{hkl} - \gamma_l) A^{hkl} \right], \qquad (3)$$

where $\gamma^{hkl}$ represents the surface free energy of the observed facet orientations and $A^{hkl}$ the corresponding facet area. Finite-element calculations indicate that the Ge lattice constant has increased to the bulk value at the surface of the (111) faceted island [15], in agreement with previous results for the InGaAs/GaAs system [16]. Conditions for homoepitaxy are approached at the island surface and growth terminates, before completion of the pyramids, due to the undersaturation. Inserting the values of $\gamma_{ls}^l$ for different facet orientations [11] in Eq. (2), assuming the observed morphology with $E_{ls}^l \approx 0$ and $E_{ls}^{2D}(4\ \mathrm{ML}) = (0.2\ \mathrm{J\,m}^{-2})A^{hkl}$ according to standard elasticity theory, shows that this criterion is fulfilled and the total energy is minimized for pyramids with {111} faces, as experimentally observed. Islands bound by other low-index faces (e.g., {001}) would increase the total and not fulfill Eq. (2). Thus, not the strain energy reduction alone, but also the *lowering* of the interfacial (and surface free) energy promotes the facet growth.

We have shown that a reduction of interfacial energies between a liquid solution and a solid surface provides a driving force for heteroepitaxy, even under conditions of undersaturation. We employ this driving force for heteroepitaxy, partly out balanced by a driving force for dissolution, for Ge/Si heteroeptiaxy very close to equilibrium. Germanium layers of excellent crystal quality, free of sites for dislocation nucleation, result. The relations of interfacial and strain energy vary on the system's pathway to equilibrium and determine the layer morphology, e.g., coherent facets.

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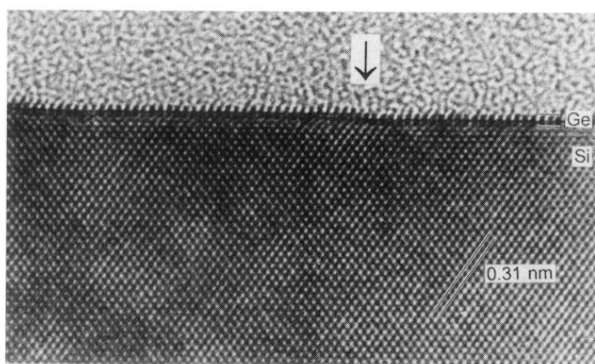
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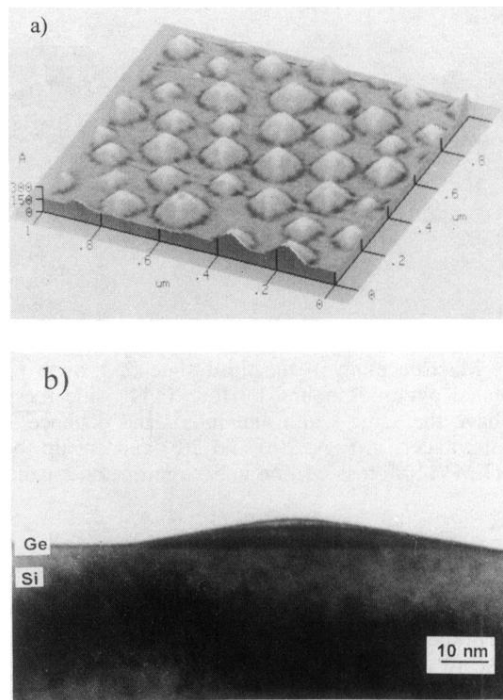
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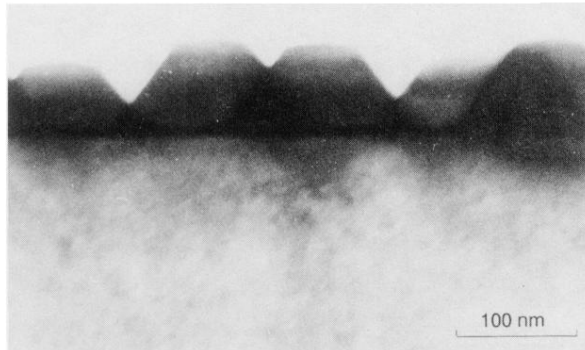
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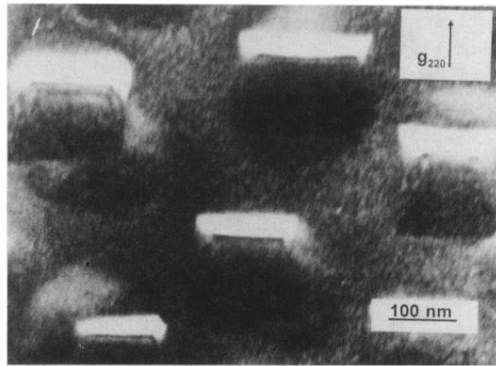
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