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To cite this article: A. Antons *et al* 2003 *EPL* **62** 547

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Strain-induced surface structures on Sb-covered Ge(111): Epitaxial Ge films on Si(111):Sb

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(received 24 October 2002; accepted in final form 10 March 2003)

PACS. 68.43.Bc – *Ab initio* calculations of adsorbate structure and reactions.

PACS. 68.37.Ef – Scanning tunneling microscopy (including chemistry induced with STM).

PACS. 81.15.-z – Methods of deposition of films and coatings; film growth and epitaxy.

Abstract. – STM images of surface structures of an Sb-covered Ge film growing on Si(111):Sb are presented, showing the $(\sqrt{3} \times \sqrt{3})$ structure on Si(111):Sb, a $(6\sqrt{3} \times 6\sqrt{3})$ structure consisting of hexagons with a size of 40 Å with triangular subunits of (1×1) structure for the three-monolayer Ge film, and a (2×1) Sb-structure for the thick relaxed Ge film. Using an *ab initio* total energy and force method, we have investigated the stability of the different structures of Ge(111):Sb(1 ML) as a function of the lateral lattice constant. We find that the (2×1) chain-reconstruction of Ge(111):Sb has a range of stability between about 5.5% compression and 1% expansion. For larger dilatations the (1×1) structure becomes stable, for larger compressions the T_4 $(\sqrt{3} \times \sqrt{3})$ structure does. The observed (1×1) structure on top of the hexagons can be explained by an 8% dilatation of the surface (compared to Si bulk) due to the stress exerted by the Sb atoms on the Ge film and at the rim of the finite hexagons.

In the past years, there has been a concentrated effort to produce artificial heterostructures of semiconductors. However, a number of problems appear: Lattice mismatch between the substrate and the overlayers leads to the creation of defects; interdiffusion at the interface; polarity effects introduce carriers or long-range imperfections. These problems can make the semiconductor devices useless for applications.

It is possible to improve the growth in certain systems with the proper choice of a “surfactant”, *i.e.* by depositing a (sub-)monolayer of foreign atoms on the surface of the growing crystal. An important example of growth modification by surfactants is the suppression of normally occurring three-dimensional (3D) island growth (Stranski-Krastanov growth [1]) in Ge epitaxy on Si. Several groups [2–5] have shown that a monolayer (ML) coverage of group-V atoms (As, Sb or Bi) turns the growth mode of Ge on Si(111) or Si(001) to layer-by-layer

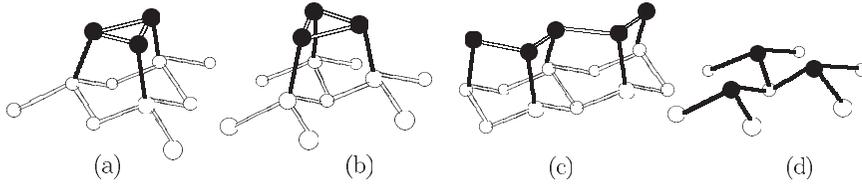


Fig. 1 – Geometries for group-V adsorbate layers: (a) H_3 -trimer centered above a hexagon composed of first- and second-layer substrate atoms, (b) T_4 -trimer centered above a second-layer substrate atom, (c) chain, and (d) substitutional (adsorbate atoms black, substrate atoms open spheres). The unlike-atom (adsorbate-substrate) bonds are shown in black, to distinguish them from like-atom (adsorbate-adsorbate or substrate-substrate) bonds.

(Frank-van der Merwe) growth [6]. Especially, Sb has been successfully applied, and a MOSFET with an active p -doped Ge layer on a Si(111) substrate has been built recently [7]. It is known from experimental and theoretical studies that group-V elements form short-period units of bonded adsorbate atoms on Si and Ge(111) surfaces. The substitutional (1×1) geometry (fig. 1(d)) is found for As-covered Si(111) and Ge(111) [8]. The T_4 -trimer ($\sqrt{3} \times \sqrt{3}$) structure (fig. 1(b)) is found for (Bi, Sb)-covered Si(111) [5, 9], and the (2×1) chain structure (fig. 1(c)) for Sb-covered Ge(111) [10]. The H_3 -trimer (fig. 1(a)) has not been found as an equilibrium structure. First-principles density-functional calculations yield lowest-energy geometries consistent with the experimental observations [11, 12]. All arrangements satisfy the bonding requirements: Every Si or Ge atom has four covalent bonds, and every group-V atom has three covalent bonds and one lone pair of non-bonding electrons. This yields a low surface energy. In three structures (fig. 1(a-c)) the surfactant atoms sit on top of a full substrate double layer (DL), whereas in the substitutional geometry, fig. 1(d), the adsorbate atoms replace the substrate atoms in the upper half of a DL.

For geometrical reasons, an atomically flat Ge film growing on Si(111):Sb has to change the surface structure from layer to layer: For an even number of Ge layers the Sb atoms sit on top of a full DL (*e.g.* on Si(111)), for an uneven number the Sb atoms have to be incorporated into a Ge DL, *e.g.* on substitutional sites, fig. 1(d). Such changes of the surface structures are manifested for Si homoepitaxy [13, 14] as well as for Ge heteroepitaxy [10, 15] on Si(111):Sb. From the different results for Sb-covered surfaces one can suspect that an interplay between bond strengths, atom sizes, lattice constants and surface strain determines the actual structures. Horn-von Hoegen [16] has analyzed the structures and the strain of a growing and relaxing Ge film on Sb-covered Si(111) using electron scattering. However, this technique cannot reveal the real-space structure of the surface directly. We have performed a detailed STM analysis of the real-space surface structure of the growing Ge film. Both studies agree that growth of Ge on Si(111):Sb proceeds in several steps (see fig. 2): i) The Sb layer on Si(111) shows the ($\sqrt{3} \times \sqrt{3}$) T_4 -trimer structure, fig. 2(a). ii) After deposition of three MLs of Ge (1 ML = 7.8×10^{14} atoms cm^{-2}) in a wide temperature range a homogeneous wetting layer develops which shows 1 ML deep trenches. At high temperatures ($\approx 660^\circ\text{C}$) a long-range ordered hexagonal ($6\sqrt{3} \times 6\sqrt{3}$) structure appears, fig. 2(b). A similar structure was found for P adsorption on Si(111) [17]. The hexagons are separated by micro-ditches and consist of triangular sections with the (1×1) structure where the Sb atoms sit on substitutional sites, fig. 2(c). iii) Growth proceeds with a roughness of less than 3 layers until iv) the Ge film largely relaxes by the formation of misfit dislocations at the Ge/Si interface when 10-12 Ge layers are deposited. v) Further growth proceeds on the relaxed Sb-covered Ge film which shows the (2×1) surface structure, fig. 2(d).

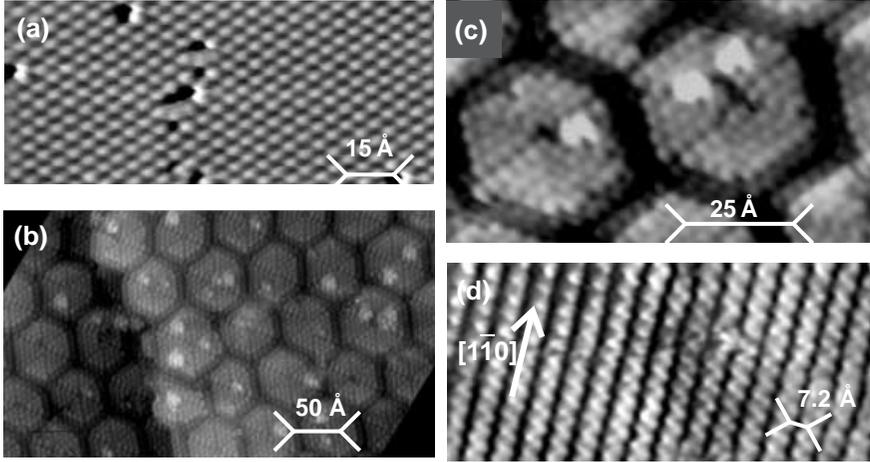


Fig. 2 – STM images of the surface structures of the growing Sb-covered Ge film on Si(111):Sb as a function of film thickness. (a) On clean Si(111) the $(\sqrt{3} \times \sqrt{3})$ T_4 -trimer structure is found. (b) For 3 ML Ge long-range-ordered flat hexagons in a $(6\sqrt{3} \times 6\sqrt{3})$ arrangement are found, which consist of triangles showing the (1×1) structure. (c) The atomically resolved triangular (1×1) subunits are visible in a magnified image. (d) For thick (> 10 ML) relaxed Ge films the (2×1) chain structure is found.

In order to understand the structures of the growing and relaxing Sb-covered Ge film deposited on Si(111), we have investigated the surface energies for the four structures in fig. 1 as a function of lateral lattice constant a . Previous investigations of Kaxiras [18,19] suggested that the Sb-covered Ge DL on Si(111) at the Si lattice constant shows the (2×1) chain structure, and the Sb-covered Ge(111) substrate at the equilibrium lattice constant of Ge shows the substitutional (1×1) geometry. However, in the experiments (fig. 2(d) and [10]) only the (2×1) chain geometry has been observed on relaxed Ge(111).

We have carried out first-principle calculations with the EStCoMPP code [20]. The surfaces are modeled by slabs which are periodically repeated in the direction perpendicular to the surface. The slabs consist of 10 atomic Ge(111) layers for the substitutional geometry and 8 for the chain and trimer geometries in an inversion symmetric arrangement, and a Sb ML covering each side of the slab. Opposing Sb layers from different unit cells are separated by a vacuum region equivalent to 4 DL of Si/Ge substrate, *i.e.* of at least 12 \AA thickness. We checked that no electronic charge overlap across the vacuum was possible. Thus, interactions between surface layers can be neglected. We used a plane-wave basis set with a cutoff energy of 13.69 Ry, which yields well-converged results. Furthermore, for reliable energy comparisons of structures with different periodicities, a k -point sampling of all systems with identical distributions in the reciprocal lattice is essential. We chose a set of 2×2 k -points in the surface Brillouin zone for the 3×3 unit cell used for the H_3 - and T_4 -trimer structures, and correspondingly larger sets for the structures with smaller periodicity. All k -point sets correspond to a set of 6×6 k -points in the surface Brillouin zone of the (1×1) unit cell. To establish minimum energy configurations the forces acting on the atoms are relaxed to less than 0.1 mRy/a.u.

For the calculation of the surface energy of Sb-covered Ge we need reference energies for Ge and Sb atoms. The choice of these energies depends on the physical process one has in mind for the formation of the surface. We consider the following process: a Ge bulk crystal, which is strained laterally to a given lattice constant and tetragonally distorted in (111) -direction to minimize the energy, is cut in the (111) plane to create a surface. Sb atoms from Sb_4 -

molecules in the gas phase are deposited on top of the bulk-terminated tetragonally distorted, but otherwise unrelaxed Ge surface in one of the structures shown in fig. 1. The entire system is relaxed to the minimum energy configuration for fixed lateral lattice constant, and the energy per area of a (1×1) -unit is compared to the energy of equal numbers of atoms in the starting configuration (strained Ge bulk and isolated Sb_4 -molecules). We thus have performed calculations of E_{at} (bulk Ge) for laterally strained Ge bulk and of $E(\text{Sb}_4)$ for Sb_4 -molecules, using the same k -point density as for the slab calculations. This is important in order to avoid spurious errors. The surface energies, E_s , per (1×1) surface unit cell, or equivalently the binding energies per Sb atom, are defined by

$$E_s(\text{struct}) = [E_{\text{tot}}(\text{struct}) - E_{\text{ref}}]/N_s$$

for the 4 structures (struct = $H_3, T_4, \text{chain}, \text{subst.}$) defined above in fig. 1. Here, N_s is the number of (1×1) -surface unit cells used in the slab, and the reference energy is

$$E_{\text{ref}} = N_{\text{Ge}}E_{\text{at}}(\text{bulk Ge}) + \frac{N_{\text{Sb}}}{4}E(\text{Sb}_4)$$

with N_{Ge} and N_{Sb} the number of Ge and Sb atoms, respectively, in the slab.

The calculated surface energies E_s are shown in fig. 3 as a function of the lateral lattice constant. We first discuss the stable structure of the relaxed Ge film at the equilibrium lattice constant. We find that the (2×1) chain geometry has the lowest energy and is thus the most stable structure, in agreement with experimental observations (fig. 2(d) and [10]), but different from Kaxiras's proposal [18, 19]. The substitutional geometry found to be stable by Kaxiras [18] is slightly higher in energy than the chain at $a_{\text{th}}(\text{Ge})$ ($= 5.632 \text{ \AA}$ obtained with the universal binding energy relation [21] from bulk Ge calculations), $\Delta E = 22 \text{ meV}$, or $a_{\text{exp}}(\text{Ge})$ ($= 5.657 \text{ \AA}$ taken from [22]), $\Delta E = 12 \text{ meV}$. The H_3 -trimer configuration is the highest-energy structure compared with the other structures at $a_{\text{th}}(\text{Ge})$ or $a_{\text{exp}}(\text{Ge})$, as also found by Kaxiras [18]. The different theoretical results might be due to different basis sets used in the two calculations. As mentioned above, we have carefully chosen identical k -point sets for all systems, and we used a higher cut-off energy than Kaxiras one (13.69 Ry *vs.* 10 Ry).

We find that the (2×1) chain reconstruction of Ge(111):Sb is stable in the entire range from the Si lattice constant (determined by our method to be 5.403 \AA) to the Ge lattice constant. It is also stable for slightly dilated Ge films ($< 1\%$); for larger dilatations the (1×1) substitutional structure becomes stable. For highly compressed Ge films, the $(\sqrt{3} \times \sqrt{3}) T_4$ -structure (found experimentally on Si(111):Sb) becomes competitive. We find it stable for lattice constants compressed more than 5.5%.

The variation of the energies for the four structures is worth analyzing in some detail. There are two opposing contributions to the total energy: stronger bonds stabilize the structure, strain reduces the stability. Both contributions depend on bond partners, bond lengths and bond angles which are different in the structures considered. For the substitutional geometry, the only degree of freedom is an (outward) relaxation of the Sb layer which yields a distortion of the tetrahedral bond angles at the Ge atoms. Apparently, the appropriate Sb-Ge bond length (larger than the Ge-Ge bond) can better be accommodated with smaller bond angle distortion if the Ge layer is dilated. The surface energy in this structure decreases with increasing lateral lattice constant. The minimum is found for a Ge film at $a_0^{\text{subst}} = 5.692 \text{ \AA}$, dilated 1.1% from a_{th} .

For the three on-top structures additional Sb-Sb bonds exist which lead to a completely different behavior, as seen in fig. 3: The surface energies decrease with decreasing lattice constant, and the minima are found for compressed films ($a_0^{H_3} = 5.332 \text{ \AA}$ compressed 5.3%

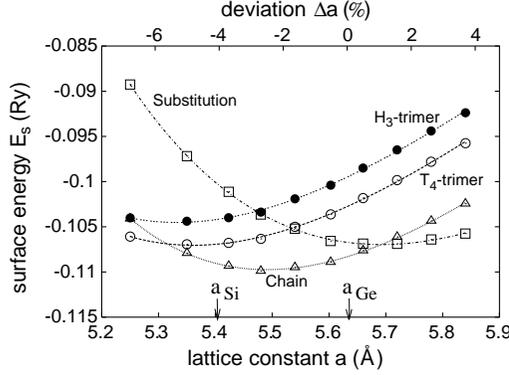


Fig. 3

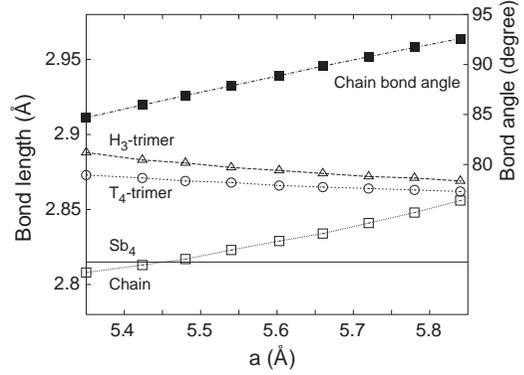


Fig. 4

Fig. 3 – Surface energies E_s per Sb atom deposited on Ge(111), plotted against lateral lattice constant a for different structures. The filled circles, empty circles, triangles, and squares represent the H_3 -trimer, T_4 -trimer, chain, and substitutional geometries, respectively. The arrows indicate the theoretical Si and Ge lattice constants.

Fig. 4 – Sb-Sb bond lengths (open symbols) and bond angles (filled squares) between adsorbed Sb atoms plotted against substrate lattice constant a in the H_3 -trimer (triangles), T_4 -trimer (circles) and chain (squares) geometries on a Ge(111) substrate. The horizontal line indicates the calculated bond lengths of the relaxed Sb_4 -molecule and unsupported Sb double chain.

from a_{th} for H_3 -trimer, $a_0^{T_4} = 5.361$ Å compressed 4.8% for T_4 -trimer, and $a_0^{chain} = 5.491$ Å compressed 2.5% for chain, respectively). The main difference between the chain structure and the trimer structures is the Sb-Sb bond angle. While for the chain structure the Sb-Sb bond angle varies around 90° for the entire range of substrate lattice constants considered (see fig. 4), in the Sb trimers the Sb-Sb bond angle is fixed to 60° . Since also in other stable Sb structures (bulk, Sb_4 -molecule) bond angles are close to 90° or larger, we suggest that this is the reason for the lower energy of the chain structure. We have checked this hypothesis by relaxing an unsupported Sb double chain and an unsupported Sb double trimer. The energy per Sb atom is always lower for the double chain than for the double trimer, irrespective of the (externally fixed) bond length. In all on-top structures the Sb-Ge bond length (height above the Ge DL) can rather freely adjust, but the Sb-Sb bond length and bond angle adjustments require a distortion of the tetrahedral angle at the Ge atoms in the upper layer. We find two different trends for the Sb-Sb bond lengths with varying lateral lattice constant (see fig. 4).

In the chain geometry, the Sb-Sb bond length decreases with decreasing lateral lattice constant, and at $a_0^{chain} = 5.491$ Å is approximately equal to that in the relaxed Sb_4 molecule and unsupported Sb double chain (where $d_{Sb-Sb} = 2.82$ Å, obtained from our calculations). This indicates that only the chemical interactions of adsorbate Sb atoms within the chains are important, and interactions between the chains can be neglected.

However, in both (H_3 and T_4) trimer structures, the Sb-Sb bond lengths within the trimers slightly increase with decreasing lattice constant; they closely approach the shortest bond length of bulk Sb ($d_{Sb-Sb} = 2.90$ Å from our calculations) at their equilibrium lattice constants. This indicates that the chemical interactions between adsorbate Sb atoms in different trimers become more and more important with decreasing lattice constant. Indeed, we find that at $a = 5.84$ Å the electron densities of different trimers are well separated from each other, but at $a = 5.35$ Å they are overlapping. These emerging interactions between adsorbate Sb atoms

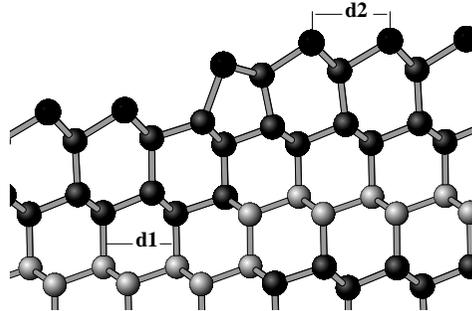


Fig. 5 – Calculated structure of narrow terraces on Sb-covered 3 ML Ge film grown on Si(111) (Sb: dark, Ge gray, Si light). Note that at the step edge Sb atoms are bound to Ge atoms of the upper and lower terrace. The pulling of these atoms aids the dilatation due to the stress exerted by the Sb atom in the top layer. This results in an over-relaxation of the Sb-Ge layer. The in-plane lattice constant of the top layers (Sb-Sb or Ge-Ge distance; $d2$) is $\approx 8\%$ larger than the Si lattice constant, although the Si layer in the middle of the slab is fixed at the Si lattice constant ($d1$).

in different trimers lead to the slight increase of the Sb-Sb bond lengths in the trimers. To prove this further, we have relaxed an isolated T_4 -trimer on the Ge(111) substrate at two different lateral lattice constants ($a = 5.84 \text{ \AA}$ and 5.35 \AA). The obtained Sb-Sb bond length in the isolated trimer ($d_{\text{Sb-Sb}} = 2.850 \text{ \AA}$) does not depend on the lattice constant. In view of the subtle interplay of bond strengths, bond angles and strain, it is not surprising that Sb on Ge(111) behaves differently than on Si(111), where Kaxiras [18] found all bond lengths for chain and trimer geometries to be close to the value of bulk Sb.

From the results for the surface energies one would expect the (1×1) structure on a growing Ge film on Si(111) if the lattice constant were *dilated* for some reason. This cannot be realized for a full Ge layer on Si(111), but in the experiments finite-size hexagons separated by trenches are found as the equilibrium structure for a Sb-covered 3 ML Ge film grown on Si(111) (see fig. 2(b) and (c)). We have simulated one of the triangular subunits by considering the structure of a narrow terrace (width 5 nearest-neighbor distances) terminated by a double-layer step as found experimentally for the hexagons. We used an inversion symmetric slab containing one DL of Si in the middle (kept fixed at the Si lattice constant) plus 3 ML Ge and one ML Sb covering the surface on each side. The steps of $(11\bar{2})$ -orientation were periodically arranged. An Sb atom was placed overhanging the terrace edge. The Sb and Ge atoms were allowed to relax freely by the method described above. The resulting minimum energy configuration is shown in fig. 5. We find an over-relaxation of the Sb-covered Ge film, whose lateral lattice constant is about 8% larger than the lattice constant of Si bulk. This coincides very well with the measured lattice constant on top of the hexagons found in our STM studies for the 3 ML Ge film on Si(111), and earlier by Voigtländer and Zinner [15]. We suggest that the tensile stress due to the substitutional Sb in the surface layer can relax due to the finite terrace width, aided by the pull of the step edge Sb atom. In contrast to the full layer the (1×1) structure can thus be stabilized. A similar mechanism operates on the finite hexagons.

In conclusion, we have performed STM-experiments to study the surface structures of a growing and relaxing Ge film on Si(111):Sb (1 ML), showing the $(\sqrt{3} \times \sqrt{3})$ structure on Si(111):Sb, the (1×1) structure on triangular subunits of hexagons establishing a $(6\sqrt{3} \times 6\sqrt{3})$ structure for the 3 ML Ge film, and a (2×1) Sb structure for the thick relaxed Ge film. We

have carried out *ab initio* calculations to investigate the stability of different Sb structures on Ge(111) as a function of the lateral lattice constant. We find that the chain geometry of reconstructed Ge(111):Sb(2×1), experimentally observed at the equilibrium lattice constant of Ge, is stable between 5% compression and 1% dilatation, which covers the entire range between the lattice constants of Si and Ge. For larger dilatations the substitutional structure becomes stable, and for larger than 5.5% compression the T_4 -trimer structure does. For each surface structure, the equilibrium lattice constant is different from bulk Ge. This means that all structures experience surface stress. Our results show that the evolving surface stress can fully explain the structure evolution for pseudomorphic Ge growth on Si(111) using Sb as a surfactant. Especially the (1×1) substitutional structure found for the Sb-covered 3 ML Ge film on Si(111) can be understood in terms of a surface dilatation of the finite-size hexagons.

* * *

We would like to thank R. O. JONES for helpful discussions. The calculations were performed on Cray computers of the Forschungszentrum Jülich, Germany.

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