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Interplay of Strain and Chemical Bonding in Surfactant Monolayers.

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Abstract. – We investigate the effects of competition between strength of chemical bonds and strain induced on the substrate for monolayers of group-V adsorbates on Si(111). A large number of structural configurations for three different group-V adsorbates were considered and analyzed from first-principles total-energy calculations. The comparisons provide insight into the stability of possible structural arrangements and the ability of these structures to promote pseudomorphic growth of heterostructures.

Growth of artificial heterostructures is one of the most intensely pursued activities in surface physics, reflecting the intrinsic interest in growth of dissimilar materials, as well as the hope for technological breakthroughs. In this effort, chemical reactions on the surface and the strain conditions imposed by the crystalline substrate have to be delicately balanced. A recent advance relies on surfactants which alter both the surface energy and the surface stress, thus allowing the formation of structures which would be otherwise *thermodynamically forbidden*. A striking example is the pseudomorphic growth of Ge on Si(100) beyond the thermodynamically allowed thickness, using a monolayer of As as a surfactant [1]. What constitutes a successful surfactant is at present a difficult question. To answer this question one needs to have detailed knowledge of adsorbate-surface interactions both for equilibrium and kinetically allowed configurations.

The purpose of this letter is to investigate the balance between the strength of chemical bonds and surface strain in surfactant monolayers, and to provide some insight into the process of pseudomorphic heteroepitaxial growth. These issues will be addressed by considering three different adsorbates on a semiconductor surface, and studying the relative stability of a range of possible structures through first-principles total-energy calculations. We will concentrate on Si(111) which is a representative and one of the most widely studied semiconductor surfaces. As far as pseudomorphic growth is concerned, we will consider Si/Ge superstructures, which have been the subject of much recent experimental work [2]. We will consider Si/Ge superstructures at a few selected compositions and examine the effects of the different adsorbates. Our choice of adsorbates consists of three group-V elements, P, As and Sb. The interplay of strain and chemical bonding is manifested by the differences in the equilibrium structure that the adsorbates assume, even though in all cases we are dealing with a tetravalent substrate and pentavalent adsorbates. The choice of adsorbates was motivated by two considerations: first, by analogy with the Si(100) case, where As was

proven to act as a successful surfactant [1]. Because of differences in bonding arrangements and topology between Si(111) and Si(100), it is by no means trivially obvious that the same adsorbates will be effective for the two surfaces. (In fact our calculations indicate that As is *not* a good surfactant for Si(111), but Sb is.) Secondly, it is known that group-V elements form units of strongly bonded adsorbate atoms on (111) semiconductor surfaces, which, we will argue below, is an essential feature for successful surfactant behavior.

The different structures considered involve bonding arrangements of the group-V adsorbates that render the surface chemically passive. This is by forming structures in which every Si atom has four covalent bonds and every group-V atom has three covalent bonds and one lone pair of non-bonding electrons. Four structures that satisfy these requirements are shown in fig. 1. The simplest one (fig. 1*a*)) consists in replacing the surface Si atoms of an ideal, bulk-terminated plane by group-V atoms. In this case, the group-V adsorbate substitutes what was a threefold bonded Si atom, that involved an unsaturated electronic orbital (dangling bond). Due to the higher valence of the adsorbate, the Si dangling bond is replaced by a low-energy, filled group-V orbital, producing an inert surface (this has been demonstrated for Si(111):As) [3]. Two other geometries involve triangular units (trimers) of group-V atoms. The trimer units can be placed in two inequivalent positions on the surface, the H_3 position (above an open hexagon of Si atoms, fig. 1*b*)) and the T_4 position (with the center of the triangle directly above a second-layer Si atom, fig. 1*c*)). It has been established from theoretical and experimental studies that the trimer units stabilize the Si(111) $\sqrt{3} \times \sqrt{3}$: Sb reconstruction [4] and the GaAs(111) 2×2 surface reconstructions under As-rich conditions [5, 6]. Finally, the last geometry consists of zig-zag chains, in which every group-V atom is bonded to two other group-V atoms and to one surface Si atom (see fig. 1*d*)). This geometry is similar to the reconstruction of (110) surfaces of III-V semiconductors, although in that situation both group-III and group-V atoms are involved in the chain [7]. It also resembles closely the 2×1 chain reconstruction of Si(111); in that situation the structure is stabilized by π-bonding interactions between the dangling bonds of the Si atoms that form the chains [8]. The substitutional geometry gives a 1×1 periodicity, the two trimer geometries give a $\sqrt{3} \times \sqrt{3}$ periodicity and the chain structure gives a 2×1 periodicity.

In order to determine which of these structures is energetically preferred for each

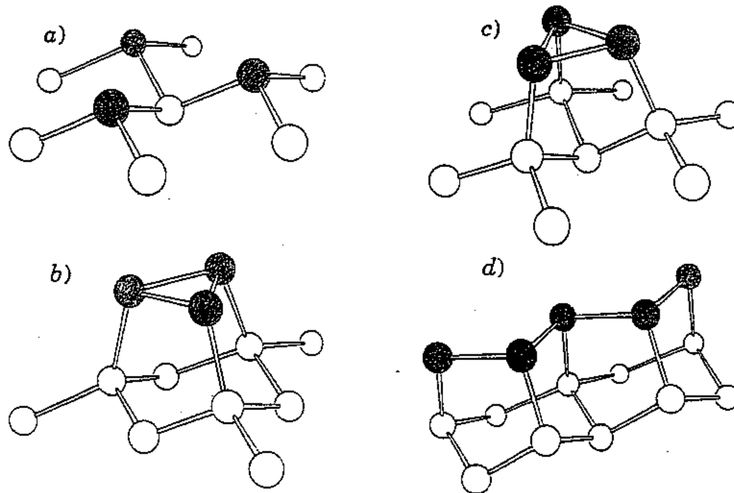

Fig. 1. – Geometries for the group-V adsorbates: *a*) substitutional, *b*) trimer in H_3 position, *c*) trimer in T_4 position, *d*) chain. The surface bilayer and adsorbate layer are shown with substrate atoms as open circles and group-V atoms shaded.

adsorbate, we have calculated their relative energies using the Local Density Functional approach [9], and norm-conserving pseudopotentials to represents the atomic cores [10]. The surface was modeled by repeated Si slabs 10-layer thick, separated by vacuum regions of 20 Å, prior to addition of the adsorbates. Inversion symmetry (with adsorbate layers covering both sides of each slab) was used to ensure proper cancellation of spurious vacuum fields: the extra layer of pentavalent atoms on the surface would give rise to a spurious field in the vacuum region, which can adversely affect the relaxation, if inversion symmetry were *not* present in the slab. The different valence of the adsorbates can also, in principle, result in charged layers by partial electron transfer to the substrate. However, the threefold bonded geometries for the group-V atoms eliminate such charge transfer in the structures considered here, by allowing the adsorbate atoms to retain a lone pair of electrons thus preserving their neutral-charge state [11]. Fully relaxed atomic geometries were obtained by minimizing the calculated Hellmann-Feynman forces using steepest descent. A basis which includes plane waves with kinetic energy up to 10 Ry was used. Since we are dealing with structures of different periodicity, a well-converged sampling of surface Brillouin zone (SBZ) points is essential for reciprocal-space integrals. We find that a set of at least 16 points in the full SBZ is needed for the larger-periodicity $\sqrt{3} \times \sqrt{3}$ structures, with correspondingly larger sets for the structures of smaller periodicity ([1]). Convergence studies indicate that the error bar in relative energy comparisons is 5 meV/adatom (we refer here to adsorbate atoms as «adatoms»; all structures considered contain the *same* number of adsorbate atoms per surface unit area).

The results of the relative energy comparisons are shown in fig. 2. The energy comparisons implicitly include the full effect of surface strain, which is a direct consequence of the relaxation. The H_3 trimer configuration is the highest-energy structure for all three adsorbates. The two positions of the trimer are closest in energy for Sb trimers. The P and As lowest-energy structure is by far the substitutional one (see fig. 1*a*)). This geometry is not as favorable for Sb. Finally, the chain geometry has high relative energy for P and somewhat lower energy for As and Sb, but is never the overall preferred structure. Based on these comparisons, we conclude that for As and P the equilibrium configuration is the substitutional one, whereas for Sb the equilibrium structure is the trimer at the T_4 position. These conclusions are in agreement with experimental observations for the three systems [3, 4, 12].

It is worth analyzing these results in some detail. The very low energy of the substitutional geometry for P and As reflects the matching of bond length distances so that no substrate strain is produced, and the relative strength of As-Si and P-Si chemical bonds compared to As-As and P-P bonds. The latter type of bonds does not exist in the substitutional geometry, but it exists in all the other structures for each adsorbate in a ratio of 1:1 group-V–group-V to group-V–Si bonds. The larger bond length of Sb, and the concomitant larger tensile stress induced on the substrate, make the substitutional geometry unfavorable for this element. In all three cases, the T_4 position of the trimer is preferred over the H_3 position, as might be expected by analogy with the behavior of group-III adsorbates (Al, Ga, In) which also exhibit a preference for the T_4 site [13]. (In those cases a single group-III adatom takes the place of the group-V trimer.) The chain geometry gives different bonds between group-V adsorbates than the trimer geometry. A comparison of the bond length between group-V atoms in the chain and trimer geometries, and the covalent bond of the three elements in their ground-state bulk structure [14], sheds light on the energy

([1]) The calculation of relaxation is particularly sensitive to convergence with reciprocal-space sampling and much less sensitive to the energy cut-off for the plane-wave basis. Our convergence studies indicate that the calculated forces are well converged (to better than 0.005 Ry/a.u.) with the 10 Ry plane-wave cut-off and the k-point sets described in the text.

TABLE I. – *Comparison of bond lengths between group-V atoms in the bulk and in the T_4-trimer and chain geometries on* Si(111), *and corresponding relative energies, for three adsorbates. Bonds in* Å, *energies in* meV/adatom.

Adsorbate	Bulk bond ([a])	Trimer bond	Chain bond	$E_{chain} - E_{trimer}$
P	2.18	2.23	2.34	60
As	2.51	2.43	2.49	– 60
Sb	2.87	2.81	2.79	10

(*a*) From ref. [14].

ordering (see table I). Notice that the trimer and chain bond lengths are *determined* by the balance of chemical interactions of adsorbate atoms with one another and with the substrate Si atoms. This balance gives too long a bond in the chain geometry for P, making it unfavorable; it gives just the right bond length in the chain geometry for As, making it preferred over the trimer; and it gives almost equal bond lengths for the trimer and the chain structures for Sb, making them close in energy (the trimer is preferred by 10 meV/adatom).

The overwhelmingly lower energy of the substitutional geometry for P and As has important implications for the ability of these elements to act as surfactants. A key element in this process is the ease with which the surfactant layer can be separated from the substrate and float on top of the growing material [1, 2]. In the substitutional geometry each adsorbate has three bonds to the substrate, all of which need to be severed if these atoms are to act as surfactants during growth. This indicates that the substitutional geometry is ill suited for promoting growth, and consequently, P and As are unlikely to act as surfactants on Si(111). The case of Si(100):As, where As does act as a successful promoter of Ge pseudomorphic growth [1], is *qualitatively* different: in that situation, the equilibrium structure contains strongly bonded adsorbate units in the form of As dimers. This comparison suggests that the presence of such strongly bonded adsorbate units is an essential feature of successful surfactants. These units can separate from the substrate with relative ease, *i.e.* by breaking two bonds per adsorbate atom, as opposed to three bonds, which is required to separate the substitutional geometry from the Si(111) substrate. Moreover, the dimers retain much of their cohesion when separated from the substrate, since the intradimer bond is not broken. The same arguments apply to the trimer and chain geometries on the Si(111) substrate. In this case the separation from the substrate is relatively easier, since only one bond per adsorbate atom needs to be broken, and the intratrimer and intrachain bonds remain unbroken. These arguments are based on equilibrium energy comparisons, and do not address the important problem of kinetics (we elaborate on this below). The trimer and chain geometries are energetically preferred only for Sb (see fig. 2), making this element the only reasonable choice for a group-V surfactant on Si(111), which is consistent with experimental findings (see ref. [2]).

The evolution of pseudomorphic growth using Sb as a surfactant will depend on whether Sb trimers, present in the equilibrium structure of Si(111):Sb, maintain their cohesion or transform into a different configuration during growth. Both the relative energy of competing structures, and kinetic barriers for transformations between such structures, will play an important role. We have investigated the first of these issues by comparing three different situations, involving an Sb adsorbate layer and mixtures of Si and Ge in the substrate. The first case is the pure Si substrate, discussed above. In this case our model of the surface consists of 10 Si layers and 2 Sb layers, covering the two sides of the slab. The second case consists of a slab with 6 Si layers, 4 Ge layers and 2 Sb adsorbate layers. In this case,

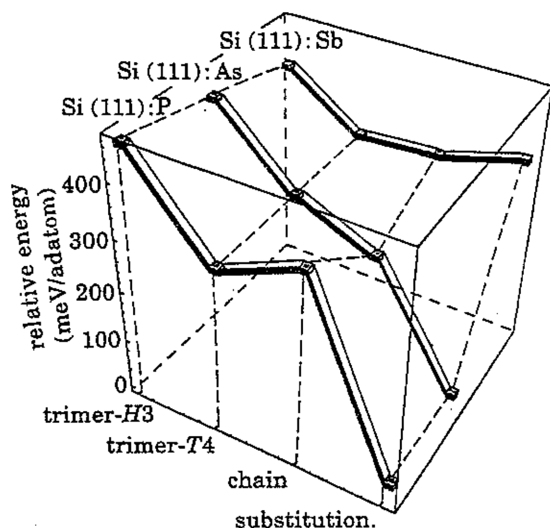

Fig. 2.

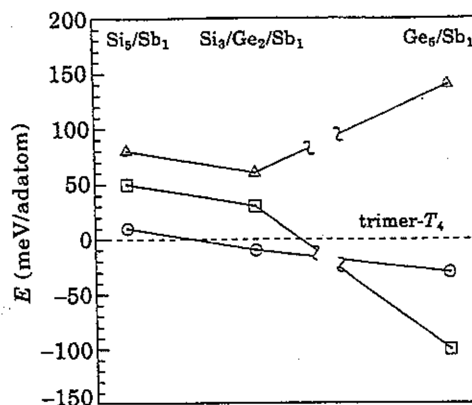

Fig. 3.

Fig. 2. – Relative energies in meV/adatom for the different geometries of fig. 1, and for the three different group-V adsorbates. The relative energy with respect to the T_4-trimer geometry (arbitrary energy value) is given in each case. Structures of the same adsorbate are joined by thick solid lines. Structures of the same geometry but different adsorbates are joined by dashed lines.

Fig. 3. – Relative energy of different geometries for the Sb adsorbate, in three different compositions: Si_5/Sb_1, $Si_3/Ge_2/Sb_1$, and Ge_5/Sb_1 (see text). The relative energy with respect to the T_4-trimer geometry is given in each case. The lines are guides to the eye. The break in the solid lines indicates a change in the lateral lattice constant from that of bulk Si (to the left of the break) to that of bulk Ge (to the right). △ trimer H_3, ○ chain (2 × 1), □ substitutional.

Ge forms one bilayer near each surface, below the Sb layer. The lateral lattice constant for these two cases was fixed to that of bulk Si. The third case consists of a 10 layer Ge slab, covered on either side by Sb adsorbate layers. The lateral lattice constant for this case was chosen to be that of bulk Ge. Figure 3 displays the relative energy for the different structures in these three cases. Interestingly, the trimer-T_4 structure is the lowest-energy geometry *only* in the first case, that is the pure Si substrate. When the Ge bilayer is included in the system, between the Si substrate and the Sb layer, the energetically preferred geometry is the chain. Finally, in the other extreme of a pure Ge substrate, the lowest-energy structure is the substitutional one: apparently, the larger lattice constant of Ge (4% larger than Si) accommodates Sb in the substitutional geometry without introducing significant substrate strain.

The comparison of total energies discussed so far does not address the issue of kinetic barriers. Specifically, the transformation from trimers to chains may be inhibited by a large activation energy, allowing the trimer units to survive as the preferred structure beyond the point suggested by the results of fig. 3. Calculation of all relevant activation barriers is not currently feasible, due to the very large number of possibilities and degrees of freedom in the problem. At first glance, it would appear that all trimer bonds need to be broken in order to form the chains, suggesting such a large activation energy. However, we have identified a possible pathway for the trimer-to-chain transformation, which involves a single-bond exchange between trimer units within a larger surface unit cell. The larger unit cell contains one T_4 and one H_3 trimer at nearest-neighbor positions. The energy difference between the two trimer positions is the smallest for Sb atoms on Si(111) (see fig. 2) and decreases with

addition of a Ge bilayer (see fig. 3), making their simultaneous presence more likely. The possibility of such a pathway suggests that the trimer-to-chain transformation may *not* be inhibited by kinetics. If this is indeed the case, we expect the Sb-chain geometry to be stable after deposition of the first Ge bilayer as fig. 3 shows. Further theoretical investigation is necessary to determine the validity of this argument.

Summarizing the above discussion, we find that P and As are unsuitable as growth-promoting surfactants on Si(111) because the lowest-energy structure for both elements involves strong bonding of each adsorbate atom to three substrate atoms. Sb, on the other hand, is likely to promote pseudomorphic growth on Si(111) because the energetically preferred structure consists of trimer units which should be easily removable from the substrate. How far the pseudomorphic growth can proceed will depend on the specifics of the system. We find that Ge can grow in this mode for at least a bilayer, at which point the chain structure becomes energetically preferred. A possible pathway of low-activation barrier was mentioned, which suggests that the trimer-to-chain transformation is not inhibited by kinetics. Whether further pseudomorphic growth can be sustained depends on the viability of the chain as a low-energy structure, and its ability to separate easily from the surface. In the limit of thick Ge overlayers, with the lateral lattice constant equal to that of bulk Ge, the substitutional-Sb geometry is preferred. When this geometry becomes energetically stable, it will tend to inhibit further pseudomorphic growth of Ge.

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