Absence of surface stress change during pentacene thin film growth on the Si(111)-(7 × 7) surface: a buried reconstruction interface

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Abstract. We use high-resolution surface stress measurements to monitor the surface stress during the growth of pentacene (C₂₂H₁₄) on the (7 × 7) reconstructed silicon (111) surface. No significant change in the surface stress is observed during the pentacene growth. Compared to the changes in the surface stress observed for Si and Ge deposition on the Si(111)-(7 × 7) surface, the insignificant change in the surface stress observed for the pentacene growth suggests that the pentacene molecules of the first adsorbate layer, although forming strong covalent bonds with the Si adatoms, do not alter the structure of the (7 × 7) reconstruction. The (7 × 7) reconstruction remains intact and, with subsequent deposition of pentacene, eventually becomes buried under the growing film. This failure of the pentacene to affect the structure of the reconstruction may represent a fundamental difference between the growth of organic thin films and that of inorganic thin films on semiconductor surfaces.

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Atomically clean surfaces are produced—sometimes literally—by the cleaving of crystals. This process creates dangling bonds and thus an energetically unfavorable configuration at the surface. Newly created, bulk-terminated semiconductor surfaces, therefore, will undergo an ordering rearrangement of the topmost atoms, which results in a so-called reconstruction [1], in order to minimize the total surface free energy. Except for the trivial case of weakly interacting adsorbates that only passivate dangling bonds with a limited saturation coverage, the general belief is that an alteration of fundamental structural components of a semiconductor reconstruction will occur as a result of chemisorption [2, 3]. It is only in rare instances that adsorption would leave a semiconductor reconstruction structurally intact. For example, based on x-ray diffraction (XRD) measurements, it has been suggested that the (7×7) reconstruction of the Si(111) surface could remain structurally intact upon the deposition of Si [4]–[7] and Ge [8] at room temperature (RT) and certain metals [9, 10] at low temperatures.

The interplay of structural transitions and stress on the Si(111)-(7×7) reconstruction is still a subject of active research [11]–[13], even though 20 years have passed since the structure of the (7×7) was first understood [14, 15]. The complex arrangement of dimers and adatoms and the stacking fault of the Si(111)-(7×7) reconstruction produce a high intrinsic tensile stress of nearly 3.0 N m⁻¹ [16]. Although the surface stress of the bulk-terminated (1×1) surface is much lower than this value [17], the complicated rearrangement of surface atoms in the (7×7) reduces the total surface energy due to the saturation of dangling bonds. It is the stability of (7×7)’s structure, which is believed to originate from partial compensation of the positive and negative stresses between different layers [18, 19], that led to the assertion [4]–[10] that this reconstruction might remain structurally intact during adsorption processes.

We have investigated the effect of thin film growth on a surface reconstruction by monitoring the surface stress. The observation of the surface stress during deposition yields reliable, but implicit, information on the structural integrity of a surface reconstruction. We apply our method of experimentally measuring the surface stress during the deposition of pentacene on the Si(111)-(7×7) surface. We demonstrate that the adsorbing pentacene molecules do not affect the structure of the (7×7) reconstruction and that a thin pentacene film covers the (7×7) in its initial, structurally unperturbed state.


2. Methodology

To experimentally verify the structural integrity of a surface during adsorption, surface stress turns out to be a reliable measurement. For physical processes near equilibrium, Kramer’s grand potential $\Omega$ must be minimized. The surface excess density of this potential is the surface free energy, $\gamma$. All physical processes occurring at surfaces, such as adsorption, film growth and the formation of reconstructions, are solely governed by the minimization of the surface free energy. Thus, $\gamma$ is an important quantity to be determined for a surface. A direct measurement of $\gamma$, however, is not possible. Fortunately, it is possible to measure the surface stress $\sigma_{ij}$. This is the change of the surface free energy $\gamma$ per deformation $\epsilon_{ij}$ as expressed by the Shuttleworth equation

$$\sigma_{ij} = \frac{1}{A} \left\{ \frac{\partial (\gamma A)}{\partial \epsilon_{ij}} \right\}_{\epsilon_{ij}=0} = \frac{\partial \gamma}{\partial \epsilon_{ij}} + \gamma \delta_{ij}. \quad (1)$$

If the surface free energy changes from $\gamma^{(1)}$ to $\gamma^{(2)}$ during an adsorption reaction, then the surface stress changes by

$$\Delta \sigma_{ij} = \left( \frac{\partial \gamma^{(2)}}{\partial \epsilon_{ij}} + \gamma^{(2)} \delta_{ij} \right) - \left( \frac{\partial \gamma^{(1)}}{\partial \epsilon_{ij}} + \gamma^{(1)} \delta_{ij} \right) = \frac{\partial \Delta \gamma}{\partial \epsilon_{ij}} + \Delta \gamma \delta_{ij}. \quad (2)$$

Any change $\Delta \gamma$ in the surface free energy $\gamma$ will thus be visible in the surface stress signal $\Delta \sigma_{ij}$, except for the case where $\frac{\partial \Delta \gamma}{\partial \epsilon_{ij}}$ exactly compensates $\Delta \gamma \delta_{ij}$ during a specific adsorption reaction.

Since $\frac{\partial \Delta \gamma}{\partial \epsilon_{ij}}$ can be interpreted as a force that attempts to drive the surface towards its equilibrium strain state [21], such an exact compensation is extremely unlikely since the change $\Delta \gamma \delta_{ij}$ in the surface free energy would have to be accompanied by the build-up of a driving force with the opposite sign but the same magnitude. Furthermore, this condition would have to hold not only at the beginning and end of the adsorption process, but also for all coverages during the deposition. Thus, in general, the stress of a surface is very sensitive to changes in its structure, with even slight total energy variations typically resulting in large variations of the surface stress [17]. Conversely, little or no observed change in the stress of a surface during adsorption would imply the absence of mismatch strain and any structural changes at the surface.

The surface stress is measured experimentally by detecting the bending of a thin sample [22]–[24]. The bending radius $R$ is a direct measure of the surface stress difference $\Delta \sigma$ between the front and back sides of the sample according to Stoney’s equation [25]. We used a novel experimental set-up which is capable of measuring surface stress, in situ during deposition, with a resolution of less than 0.01 N m$^{-1}$ ($\approx$0.6 meV Å$^{-2}$) [26]. The surface stress was monitored during pentacene ($C_{22}H_{14}$) deposition on Si(111) substrates at RT. The scanning tunneling microscopy (STM) images were produced in situ at RT in a separate UHV chamber equipped with an Omicron VT-STM. Atomic force microscopy (AFM) images were produced ex situ with a Veeco Dimension 3100, after the removal of the pentacene-covered substrates from UHV. Pentacene (Aldrich) was deposited by molecular beam epitaxy from a home-built evaporator [27] with a directly heated ceramic crucible after the typical purification of the evaporant under UHV conditions [28]. Ge and Si were evaporated from high-density graphite crucibles, heated with electron bombardment. The well-oriented, 150 µm thin Si(111)
substrates (Crystec) were degassed for several hours at 900 K and the protective oxide was removed by flash desorption in UHV prior to deposition. After a short annealing of the samples at 1100 K, this treatment yielded atomically clean silicon surfaces with a well-defined (7 × 7) reconstruction, as confirmed by high-resolution low energy electron diffraction and STM.

3. Results

The evolution of the surface stress during deposition of pentacene is shown by the red curve in figure 1. Upon adsorption of the first pentacene molecules, a change in the surface stress associated with a surprisingly small tensile stress of only 0.03 N m⁻¹ is observed (not visible with the scale used for figure 1). This surprisingly small value can be understood if the binding mechanism of pentacene on Si(111)-(7 × 7) is considered. Unlike some organic molecules that are bound to the surface via attractive van der Waals forces, pentacene binds covalently to the Si surface [30]–[32]. The middle ring of the pentacene molecule is the most reactive [33], and the molecule partially rehybridizes to an sp³ conformation [30]–[32] during the covalent adsorption. The first molecules arriving at the surface form a wetting layer of flat-lying molecules [28, 30, 34] that are bent in such a way that each end of the molecules is tilted slightly upward, like an inverted umbrella. This binding configuration is evident in figure 2. Figure 2(a) is an

4 In the case of the Si(111) surface with its threefold symmetry, the surface stress tensor \( \sigma_{ij} \) becomes isotropic, i.e. \( \sigma_{ij} = \sigma \delta_{ij} \). In contrast to the Si(001) surface with different stress components parallel and perpendicular to the dimer rows, there is only one surface stress value \( \sigma \) for the Si(111) surface.
Figure 2. (a) An STM image of the clean Si(111)-(7×7) surface before adsorption of pentacene. (b and c) STM images for RT pentacene growth on Si(111)-(7×7) at the coverages labeled B and C in figure 1. The STM images show (b) the alignment of an isolated molecule of the initial pentacene adsorption on the undisturbed (7×7) surface, and (c) the intact corner holes of the (7×7) structure at a pentacene coverage of roughly 0.1 monolayers, or 50% of the wetting layer saturation coverage. The right panel in (b) is the same STM image displayed in the left panel, but with a drawing of a pentacene molecule and circles highlighting the positions of the Si adatoms added to emphasize the binding geometry. (d) An AFM image produced at the coverage labeled D in figure 1. The AFM image shows the typical dendritic, monolayer-high islands [28] that form on top of the pentacene wetting layer.

STM image of the clean Si(111)-(7×7), and figure 2(b) is an STM image of an isolated pentacene molecule on the Si(111)-(7×7) produced at a pentacene coverage corresponding to that labeled B in figure 1. The left panel of figure 2(b) shows the STM image of the isolated molecule, and the right panel shows the same STM image with circles drawn to highlight the adatoms of the (7×7) reconstruction, a scale drawing of a pentacene molecule in the same orientation as the one in the STM image, and symbols representing an sp3 hybrid orbital and a resonant electron. It appears that one of the outer carbon atoms of the middle ring of the pentacene changes to an sp3 hybrid, and the molecule is connected to the surface with a single C–Si single bond to an adatom of the (7×7) unit cell. This adsorption geometry and rehybridization of the molecule is essentially the same as that recently proposed and calculated for pentacene on a single gold atom [35].

Due to the resonant stabilization of the created pentacene radical and the dimensions of the (7×7) reconstruction, no further bonding of the molecule to the substrate appears to be possible. A pentacene molecule can therefore rotate and align within the unit cell, but it is not
able to transmit any steric stress to the substrate, consistent with the very small stress change seen in figure 1.

With increasing coverage, the pentacene molecules occupy more adatom dangling bonds in geometries similar to that shown in figure 2(b). Shortly before the completion of the wetting layer, the sign of the surface stress changes to compressive stress. This change in the stress can be seen as the small inflection in the pentacene curve of figure 1 that takes place at an average film thickness of roughly 3 Å. Initially, one might be tempted to interpret this stress change as the relief of some of the tensile stress of the (7×7) reconstruction by removal of one of the adatoms of the (7×7). However, the magnitude of 0.1 N m\(^{-1}\) is much too small for this possibility. The removal of only one adatom of the 12 comprising the topmost layer of the (7×7) unit cell would be expected to yield a signal of \(\frac{1}{12} \times (42/49) \times 1.66 \text{eV}/(1 \times 1) \approx 0.15 \text{N m}^{-1}\) [16], which is already higher than the small measured amount of 0.1 N m\(^{-1}\).

Figure 2(c) shows an STM image at the higher pentacene coverage coinciding with the point labeled C in figure 1. The STM image indicates that none of the corner holes of the (7×7) are yet covered by pentacene. As expected [36, 37], the corner holes appear to be the least reactive sites of the (7×7) reconstruction. The other features in the STM image of figure 2(c) are due to the many pentacene molecules imaged in various adsorption geometries similar to that shown in the left panel of figure 2(b).

Further growth of pentacene proceeds with the formation of large crystallites on top of the wetting layer consisting of nearly upright standing molecules [28, 34]. Shown in figure 2(d) is an AFM image produced at the coverage labeled D in figure 1. The interaction of the deposited molecules with the chemisorbed wetting layer is of the relatively weak van der Waals type, and therefore only a small compressive film stress of 0.015 N m\(^{-1}\) per molecular layer builds up as the growth of the film progresses. The structure of the (7×7), during this gradual stress build-up, remains unchanged, as evidenced by the negligibly small change in the surface stress.

To put the surface stress behavior during the pentacene growth in its proper perspective, we have included in figure 1 the surface stress as a function of average film coverage for the growth of two atomic adsorbate films: (i) the RT homoepitaxial deposition of Si atoms on the Si(111)-(7×7), which produces thin amorphous Si films, and (ii) the high-temperature deposition of Ge on Si(111)-(7×7), a well-studied [38] classical heteroepitaxial system. The stress changes for the Si and Ge films are represented by the blue and green curves, respectively. In the latter, film stress is caused by the lattice mismatch of 4.2% between Ge and Si. This mismatch strain leads to a bi-axial compression in the Ge film, and to the build-up of the large associated compressive stress [38] as the film grows. The Ge surface stress curve of figure 1 illustrates the large stress build-up that occurs in thin film systems characterized by a large lattice mismatch and Stranski–Krastanov growth.

Due to the absence of mismatch strain in the Si homoepitaxial system, the initial steep decrease in the surface stress for the RT Si deposition and the large total decrease of about 2.2 N m\(^{-1}\) for the amount of Si deposited during the measurement shown in figure 1, can only be caused by the disordered rearrangement of structural elements of the (7×7) reconstruction. Figure 1 also displays two vertical rectangular bars, labeled adatoms and dimers. The combined vertical length of these bars represents the calculated amount of surface stress change that the surface would experience if the stress associated with all of the adatoms [16, 29], and all of the dimers [16] of the Si(111)-(7×7) reconstruction were released. Therefore, at the end of the Si deposition displayed in figure 1, only residual structural features of the Si(111)-(7×7) reconstruction, such as a few adatoms and dimers, the inert corner holes [36, 37] and
the persistent stacking fault [39], remain intact. A similarly dramatic altering of the \((7 \times 7)\) structure should be observed during the growth of organic molecules on the \((7 \times 7)\) if a C atom of the molecules should bond to the Si adatoms via a locally disordered sp\(^3\)-bond, similar to that formed by the deposited Si atoms in the case of amorphous Si film growth at RT. But, in contrast to the Si and Ge curves of figure 1, the change in the stress experienced by the surface during the pentacene adsorption is clearly insignificantly small, implying that, because of the sensitivity of the stress measurements to structural changes at the surface, no structural elements of the \((7 \times 7)\) have been altered as a result of the growth of the pentacene film.

4. Discussion

We are aware that we are not the first to report the observation of a buried, intact Si(111)-(7 \times 7) reconstruction. In XRD studies [40, 41], the observation of a residual 7-fold superstructure, apparent in the positions of the diffraction peaks, was interpreted as an intact Si(111)-(7 \times 7) reconstruction at the interface between grown amorphous Si thin films and the Si substrate. To resolve this clear contradiction between the XRD measurements and our stress results for Si/Si(111)-(7 \times 7), it is important to consider what exactly is meant by a structurally unperturbed, or intact, reconstruction. Since any entity arriving at a surface must modify the electronic structure of a surface for adsorption to occur, the concept of an intact reconstruction can only be defined as the absence of structural changes in a reconstruction after adsorption. It is reasonable to consider a reconstruction to be altered if, upon adsorption, bonds are broken or formed within the structure, if more than a negligible change\(^5\) of the atom positions within the structure occurs or if the bond nature, hybridization, bond configuration or conformation of any of the atoms of the reconstruction changes. If none of these conditions is fulfilled for a reconstruction after adsorption and subsequent film growth, then the only possible significant surface modification is the saturation of dangling bonds of the original reconstruction. If none of the structural elements of the initial reconstruction (such as the dimers, adatoms, stacking fault and corner hole in the case of the Si(111)-(7 \times 7)) are affected by adsorption, then the reconstruction remains intact and can be buried in such a state by the adsorbate film.

While a full kinematic XRD analysis of a buried interface would be the best experimental method for assessing the structural integrity of all of the elements of a reconstruction, providing access to structural information that is not available when monitoring surface stress, measurements of peak positions in XRD, alone, are not sufficient to determine whether the entire reconstruction or only residual parts remain intact. Our surface stress results for Si deposition are, however, sufficient to demonstrate that a significant amount of damage has been done to the \((7 \times 7)\) reconstruction. Coupled with the XRD data [40, 41], our surface stress observations for Si suggest that only part of the \((7 \times 7)\) reconstruction remains intact under the amorphous Si thin film. Most likely, at least the corner holes and stacking fault of the \((7 \times 7)\) remain, as evidenced by the \((7 \times 7)\) periodicity in the XRD [40, 41]. Thus, since the sevenfold periodicity of the interface is unchanged because of the lingering structural elements that are responsible

\(^5\) In the spirit of the Lindemann criterion [42], which estimates a change of 10% of a nearest-neighbor distance as the threshold for the melting of a crystal, we suggest a displacement of atoms by 1–2% of the nearest-neighbor distance as an upper boundary for a ‘negligible’ change of the atom position. We estimate from the tensile stress of 0.03 N m\(^{-1}\), attributed to the adatom relaxation, and from the elastic constants of bulk silicon that the pentacene molecules change the \((7 \times 7)\) adatom bond lengths by less than 1%.

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for the periodicity, a heavily damaged \((7 \times 7)\) reconstruction may appear in XRD measurements of spot positions, to be buried, completely intact, during deposition.

In order to illustrate the high sensitivity of the surface stress on subtle structural modifications, it is useful to consider the well-known covalent adsorption process of atomic H on Si(001). It is only possible to adsorb a saturation layer of H on Si; therefore, a thin film of H cannot be produced. Thus, even though the adsorption of H appears to only ‘saturate dangling bonds’, it turns out that even a single H atom adsorbed per \((2 \times 1)\) unit cell would influence the bond angles and the dimer buckling in such a way that the resulting surface stress would change by about twice as much \([43]\) as that observed here for the pentacene film on Si(111). Since the subtle structural change induced by adsorption of H on Si(001) would strongly affect the stress state of the surface and would thus be clearly visible in the surface stress signal, we conclude, by virtue of the very small change in surface stress we measured during pentacene deposition, that the Si(111)-(7 \times 7) remains intact.

5. Conclusion

The results we have presented for the deposition of Si and Ge are representative of all atomic adsorbates that we have deposited on the Si(111)-(7 \times 7) surface. Atomic adsorbates destroy, or heavily change, the initial semiconductor reconstruction. It can be hypothesized that the impact of less reactive entities, such as large organic molecules, on the structure of a semiconductor reconstruction should be much smaller than that produced by atoms. Such molecules do not carry dangling bonds which have to be saturated. They can, therefore, attach to the substrate via only a few bonds, thereby minimizing the structural impact on a reconstruction, despite the possibility that the bonding could be strongly covalent. Indeed, the insignificantly small surface stress change during the deposition of pentacene, a saturated organic molecule, indisputably establishes that the Si(111)-(7 \times 7) remains structurally unchanged and has been buried under the pentacene thin film. The specific, inverted-umbrella-like adsorption geometry of pentacene on the Si(111)-(7 \times 7) surface, which is apparent in our STM images, yields a maximum substrate passivation accompanied by a minimal adsorbate–substrate interaction, enabling the unobtrusive influence on the surface reconstruction.

The work presented herein demonstrates that the pentacene/Si(111)-(7 \times 7) system, characterized by covalent binding of the first adsorbate layer and the growth of high-quality thin adsorbate films, is the first such system that has been observed to maintain a structurally intact reconstruction at the interface. Certainly, there are other adsorbates that are known to leave a semiconductor reconstruction intact after adsorption. These materials, however, are adsorbed in a self-limiting manner, i.e. they interact with the surface and form a saturating layer. Multilayer growth for these adsorbates is typically not possible.

Earlier works have shown that the nucleation of pentacene films on top of the wetting layer follows the classical nucleation theory \([28, 34]\), implying that the conceptual framework of the formation of islands in homoepitaxial growth can be extended to heteroepitaxial organic/semiconductor systems. We demonstrate, in the present study, that the paradigmatic framework of interface formation for the two types of thin film systems is significantly different. We believe that this difference in the formation of interfaces may also apply to many other large organic molecules that are adsorbed on reconstructed semiconductor surfaces.
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