Interactions of Organic Molecules with Metal Passivated Semiconductor Surfaces Studied via STM
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Organic molecules offer a wide range of optical, electronic or chemical properties. Coupling them to silicon could pave way to novel applications and devices, however, a controlled molecular functionalization of silicon remains challenging due to the presence of highly reactive dangling bonds on its surfaces. We attempt to decrease the reactivity of low index silicon surfaces with an ultra-thin layer of a metal adsorbates and study their interaction with organic molecules via scanning tunneling microscopy.

In the first part we investigate the interaction of ethylene, a small unsaturated molecule, with tin and indium 1D chains grown on Si(001) – 2×1. The chains consist of dimers structurally analogous to the dimers of the underlying Si(001) – 2×1 surface. Aided by photoelectron spectroscopy we find that the Sn chains are less reactive than the Si(001) surface and that the absence of a π dimer bond renders indium chains inert.

In the second part we study the interaction of copper phthalocyanine, a small macrocyclic heteroaromatic compound, with the Si(111)/Sn – √3×√3 substrate. We find that despite the presence of dangling bonds on the tin atoms, the reactivity of the Sn layer is significantly decreased with respect to a bare Si(111) – 7×7. Substitutional defects, however, significantly increase the reactivity locally and strongly bind CuPc. Other Sn and In reconstructed Si(111) surfaces exhibit a similar trend, albeit the strength of the interaction at defect sites is noticeably weaker as CuPc can hop between defects.
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Part I

INTRODUCTION
INTRODUCTION

The role of silicon in the technological advances of the last century cannot be overstated. It is a semiconductor, the electronic properties of which can be greatly modified by doping with heteroatoms. Electronic properties of doping junctions have led to the fabrication of small and reliable integrated electronic components with low power consumption. Over time, advancing miniaturization and technology optimization have resulted nowadays powerful microprocessors or fast memory storage components.

The drawback of silicon over other semiconductor materials is that it does not have a direct bandgap. It therefore suffers from poor light absorption-emission performance [1]. The design of light emitting or harvesting devices such as lasers, LED’s or solar cells thus relies on direct bandgap semiconductors, e.g. gallium-arsenide [2]. Silicon nonetheless remains the most used semiconductor for the fabrication of electronic devices due to its other advantages such as the presence of a natural oxidation layer or well-established large-scale technology of crystal growth and doping.

Carbon, the lighter neighbour of silicon in group 14, stands out with its unparalleled ability to form extended chains and incorporate heteroatoms. It forms an extraordinarily diverse amount of molecules: from the small, lethal, gaseous carbon monoxide all the way to DNA elaborately storing building instructions of proteins catalyzing complex reactions in living organisms. Life, as we know it, would probably not be possible without the richness of carbon chemistry.

Organic compounds therefore offer a stupendous range of chemical and electronic properties which could be coupled to silicon and lead to novel hybrid applications and devices for sensing, light emission/harvesting, biocompatibility or exotic areas such as molecular electronics [3–5].

To successfully integrate molecular devices with silicon technology requires a good understanding and control of the processes at the molecule-semiconductor interface. This includes adsorption, self assembly, diffusion, electronic properties etc.

The silicon crystal consists of \( sp^3 \) bonded atoms arranged in diamond cubic lattice with lattice constant 5.43 Å, see figure 1.1. Cleaving the periodic bulk crystal to form a surface breaks the covalent bonds between the silicon atoms. As a result, the Si atoms on the surface contain unpaired electrons in highly localized electronic states, referred to as dangling bonds (DB). To decrease the surface free energy, the surface atoms rearrange and rebond giving rise to complex surface reconstructions. The (001) surface forms a
Figure 1.1: Crystalline structure of Si viewed along the [-110] direction. The (001) plane is on top, the (111) plane is marked in green. The unit cell is outlined in the bottom left corner.

Figure 1.2: Frozen view of the Si(001) – $2\times1$ reconstruction along the [-110] direction. The buckled dimers quickly flip-flop at RT.

$2\times1$ reconstruction at room temperature (RT), the most stable reconstruction of the (111) face is a large $7\times7$ unit, although other surface reconstructions such as $2\times1$ and the metastable $5\times5$ exist too [6].

$Si(001) – 2\times1$ surface

The $2\times1$ surface reconstruction of Si(001) consists of Si dimers stacked in a ladder-like fashion along the [-110] direction forming so called dimer rows. The orientation of the dimer rows changes by 90° on consecutive atomic terraces. The dimers are buckled, i.e. one atom goes up and the other atom down, see figure 1.2. The dimers flip at RT which results in the perceived $2\times1$ reconstruction. The flipping of dimers stops at low temperatures when the dimer tilt is frozen and alternates along the dimer row. This produces a
$p(2 \times 2)$ or $c(4 \times 2)$ reconstructions, depending if the tilts in the neighbouring dimer row is in phase or anti-phase \cite{7}.

Both atoms in the dimer are bound with a $\sigma$ and a $\pi$ bond, albeit the $\pi$ bond is weak due to the large distance between dimer atoms and the angle of the backbonds to the underlying atoms \cite{8}. The dimer tilt is accompanied with a charge transfer from the lower to the upper lying atom. The lower atom assumes a more $sp^2$ hybridized character, the upper atom a more $sp^3$ hybridized character. Due to the weakness of the $\pi$ bond and the charge transfer, the dimer can be seen partially as having unsaturated character, partially as a di-radical and partially as having a zwitterionic character, all of which account for a high reactivity of the surface.

\textit{Si(111)–7×7 surface}

The Si(111)–7×7 surface reconstruction is described by the dimer-adatom-stacking fault (DAS) model shown in figure 1.3 \cite{10}. The unit cell is split into two halves named faulted and unfaulted half unit cell (HUC) — depending whether a stacking fault of the rest atom layer against the bulk crystal is present or not. These HUC’s are surrounded with 9 dimers each. The formation of a surface reconstruction decreases the density of dangling bonds: While the unreconstructed Si(111)–1×1 surface would contain 49 dangling bonds in a 7×7 cell, the formation of the 7×7 reconstruction reduces their number to 19. In each HUC, the dangling bonds are located on six adatoms (corner atoms positioned in the corners of each triangular HUC, three centre adatoms in the centre of the sides) and three restatoms.

\footnote{The situation shown in figure 1.2 corresponds to the $p(2 \times 2)$ case.}
The remaining dangling bond is located on the atom in the hole on the corners of the whole unit cell.

Studies have shown that a significant charge redistribution occurs upon the formation of the reconstruction. The adatoms are positively charged while the restatoms and corner hole atoms are negatively charged [11]. The adatoms and restatoms can be regarded as forming charged pairs which, in addition to the complex structure of the unit cell, accounts for a complex adsorption behaviour exhibited by Si(111)–7×7 towards organic molecules.

1.1 REACTIONS ON SILICON SURFACES

Adsorption of an organic molecule on silicon surfaces can proceed in complex manner due to the complex nature of surface reconstructions. Often competing mechanisms are involved. In order to gain insight into the origin of the reactivity of silicon surfaces, it is useful to mention some types of adsorption mechanisms. Detailed reviews can be found in [4, 12, 13].

Pericyclic reactions

Pericyclic reactions proceed in a way that contains a transition state with a closed ring geometry. A major group of such reactions are cycloadditions, which are concerted (i.e. without intermediate states) ring closing reactions proceeding between unsaturated hydrocarbons. A typical example is the famous Diels-Alder reaction occurring between conjugated dienes and alkenes producing a six membered ring (e.g. 1,3-butadiene + ethylene → cyclohexene) which is denoted as a [4+2] cycloaddition: i.e. involving 4 and 2 π electrons respectively.

Nobel laureates R. B. Woodward and R. Hoffmann derived selection rules for allowed and forbidden types of cycloaddition reactions which are based on the symmetry of the frontier orbitals of the reactants. The [4+2] cycloaddition is symmetry allowed: the symmetry of the HOMO and LUMO orbitals of the reactants allows for a constructive overlap and two new σ bonds are formed while two π bonds are destroyed.

The [2+2] cycloaddition is according to these symmetry rules forbidden as there is a destructive overlap between the symmetry of the LUMO and HOMO orbitals. If it were not forbidden, ethylene would be unstable and react while producing cyclobutane. The [2+2] interaction may proceed, but requires electrons to be excited to higher levels of adequate symmetry, which can be achieved with electromagnetic radiation.

Interaction of ethylene with Si(001)–2×1, contrary to this rule, proceeds via [2+2] cycloaddition on top of the weakly π bonded Si dimers. The reaction proceeds surprisingly readily. While the reaction mechanism is
complex and proceeds via nonconcerted pathways, the end-result is a [2+2] bonded adduct.

This readiness of Si(001)−2×1 to bind alkenes via [2+2] cycloaddition poses a problem for the selectivity during the adsorption of 1,3-butadiene. According to the symmetry rules, the molecule adsorbs via a [4+2] cycloaddition on Si dimers, but a [2+2] bonded minority adsorption configurations coexist [14]. However, both of the end-products retain one double bond which could serve for additional functionalization of the surface [13].

The adsorption of benzene on Si(001)−2×1 results in several adsorption configurations which can be classified as di-σ bonded and tetra-σ bonded adducts on one or two dimers respectively [15]. In contrast, on Si(111)−7×7 benzene was found as a di-σ bonded adduct to adatom-restatom pairs [4]. This shows how the choice of different surface can affect the adsorption of a single molecule.

Nucleophilic/electrophilic reactions

Nucleophilic and electrophilic reactions are an important concept in organic chemistry [16]. They can be described as an interaction between a molecule that possesses a region with an increased electron density and a molecule with a region of decreased electron density.

The zwitterionic character of the buckled Si dimers (due to charge redistribution from the down towards the up atom) of Si(001)−2×1 or the adatom-restatoms pairs on Si(111)−7×7 satisfy the conditions for such bonding mechanisms to be involved.

Ethylene can therefore attack the more positively charged down Si atom in the dimers on Si(001)−2×1 and from a precursor to the final [2+2] bonded state as above [17]. This nonconcerted mechanism has been suggested to explain the readiness of the [2+2] cycloaddition on the Si(001) substrate.

Molecules containing electron lone pairs (nonbonding pairs) can form dative bonds by donating their lone pair to another species containing an incomplete shell. An example of this type of bonding would be the reaction between ammonia (NH₃) and boron trifluoride (BF₃). Nitrogen in ammonia contains a lone pair whereas boron has an incomplete shell. Boron can therefore accept the lone pair of nitrogen and form a covalent bond (H₃N: + BF₃→H₃N:BH₃).

Such dative bonding on Si(001)−2×1 has been shown to occur for trimethylamine N(CH₃)₃ [18].

Pyrazine, a six membered heteroaromatic molecule with two N atoms in para positions, shows how several mechanisms may compete during the interaction of a molecule with Si(001)−2×1. It was found to bind datively via its N atom to Si atoms as a lone molecule, but also in a double-dimer-bridge configuration where it is not datively bound via its lone pairs, but as a 1,4-di-
σ N-Si bonded product retaining its lone pairs while the aromatic character is lost [19]. In the double-dimer-bridge configuration, the nonreacted Si atoms of involved dimers have a stronger radical character and so can preferentially bind another pyrazine molecule which leads to 1D molecular chain growth perpendicular to the Si dimer rows. The assembly into 1D chains can be improved by deposition at higher temperatures where pyrazine can diffuse via the N-bonded precursor state [20].

**Dissociative bonding**

Adsorption of a molecule can also lead to its dissociation. An example of such dissociative bonding occurs during the adsorption of ammonia (NH$_3$) on Si(001)–2×1 which — despite having a lone pair — predominantly dissociates into Si—NH$_2$ and Si—H [21]. A similar reaction occurs for water on Si(001)–2×1 which dissociates into OH and H and is the origin of C-defects typical on Si(001)–2×1. The switching of their adsorption configuration has been observed in our group [22]. The adsorption of water breaks the π bonds of Si dimers, increases their radical character and so increases the local reactivity of the site which can serve as a nucleation centre for the growth of 1D adatom chains [23].

### 1.2 Modified Silicon Surfaces

Various interesting optical or electronic properties of conjugated molecules derive from the electronic structure of their delocalized π electron system. Upon adsorption on the bare Si surfaces these π electrons rebond with the dangling bonds and the π delocalized system is significantly altered [4]. Some applications therefore require reduced reactivity of silicon surfaces which can be achieved with hydrogen passivation [24]. In UHV conditions, the Si(001)–2×1 can be passivated with atomic hydrogen by dissociating H$_2$ on a hot tungsten filament [25]. To illustrate the effect of hydrogen passivation, pentacene chemisorbs on Si(001)–2×1 at room temperature and is thus immobile [26], while it remains very mobile at 5 K on the hydrogenated Si(001)–2×1 surface [27]. Despite the high mobility on the hydrogen passivated surface, pentacene is bound strongly to the substrate via dispersion forces [28]. On the hydrogen passivated vicinal Si(111) surface, copper phthalocyanine orders into lines in contrast to random distribution on the non-hydrogenated sample due to strong chemisorption [29].

The hydrogenated Si(001) surface can also be employed for nanolithography with STM [30]. Individual hydrogen atoms can be desorbed with the tip and such prepared dangling bonds can serve as anchoring sites for molecules [31]. Adsorption of selected molecules with the vinyl functional group (R—CH=CH$_2$) can lead to growth of 1D molecular chains by mechanism
described as a radical chain reaction: the molecule preferentially attaches to a loose dangling bond by cleaving the vinyl π bond and saturates the formed carbon radical by abstracting an adjacent hydrogen from the surface. This creates another dangling bond resulting in chain growth which can propagate parallel (styrene) [32] or perpendicular to the Si dimer rows (allyl mercaptan) [33].

Contrary to its relative feasibility on Si(001)−2×1, the passivation with atomic hydrogen of Si(111)−7×7 under UHV conditions is difficult due to etching of the surface [34], but can be easily achieved with wet methods by rinsing in NH₄F [24]. The chain radical reaction was also observed to occur on the hydrogenated Si(111)−7×7 surface, but was undirectional and resulted only in limited molecular islands [35].

1.3 Scope of this thesis

The rich spectrum of interactions involved during the adsorption of organic molecules poses opportunities as well as challenges for organic functionalization of silicon surfaces. It is therefore important to search for alternative ways of coupling organic molecules to silicon substrates. (Semi)metal adsorbates on silicon substrates can produce a broad range of surface reconstructions offering diverse spatial, electronic and chemical properties. It therefore presents an alternative way of modifying the properties of silicon substrates for adsorption of organic compounds.

In this thesis, we employ Si(001) and Si(111) substrates modified with tin and indium atoms and investigate how a small unsaturated molecule, ethylene, and a larger macrocyclic heteroaromatic molecule, copper phthalocyanine (CuPc), interact with the modified substrates. Indium and tin are neighbours in the 5th period of the periodic table: indium is a trivalent element, while tin is a tetravalent element and they are both capable of producing morphologically similar structures on Si(111) and Si(001) with different electronic properties.

The next section presents an overview of the research where organic molecules and metal modified Si(111), Si(001) and the analogous Ge(001) surfaces were employed.

1.4 Interaction of molecules with metal passivated silicon surfaces

The Si(111)/In−4×1 surface consists of conducting indium wires separated by silicon atoms which undergoes a phase transition to semiconducting 8×2 state at lower temperatures. The 1D nature of the indium wires could serve as a template for one-directional ordering of adsorbed molecules on Si(111) as an analogy to a linear radical chain growth absent on the hydrogen...
passivated Si(111). This has also been employed as a substrate for pentacene [36] which formed quasi 1D structures with its elongated axis oriented perpendicular to the direction of indium wires. Another molecule studied on this substrate was the popular perylene tetracarboxylic acid (PTCDA) [37]. The molecule forms titled structures held through hydrogen bonds on a number of substrates, but on Si(111)/In-4×1 was found to adsorb on Si atoms in-between the In wires with the long molecular axis oriented parallel to the wire direction.

Another possibility of reducing the reactivity of Si(111) is employing the Ag-√3×√3 layer. The layer consists of Ag trimers and has proved as an effective means of passivating Si(111) and facilitating the formation of ordered molecular structures: Co and Cu phthalocyanines deposited on Si(111)/Ag-√3×√3 were found to freely diffuse on the substrate until an ordered phase was formed at full layer coverage [38, 39]. Pentacene formed ordered layers on the substrate too [40]. It was employed as a substrate of choice (owing to its inert properties) for four-point probe conductance measurements of CoPc overlayers on Si(111) [41]. SRPES measurements revealed the formation of a dipole and counter-dipole at the silicon/Ag/molecule layer interface after depositing α-sexithiophene [42]. The Si(111)/Ag-√3×√3 also proved suitable for the formation of a 2D hydrogen-bonded molecular alloy between PTCDA and tetraaminobenzene [43].

PTCDA was also investigated on Si(111) surfaces terminated with other metals: It forms ordered layers on the Si(111)/Bi-√3×√3 substrate [44]. On the Si(111)/Sn-2√3×2√3 surface, PTCDA forms 1D molecular chains at submonolayer coverages [45], however it induces a new surface reconstruction at higher coverages accompanied with a charge transfer from the substrate to the molecule [36, 46]. Interaction of PTCDA was studied also with various Pb reconstructed Si(111) surfaces revealing a strong dependency of molecular ordering the underlying Pb reconstruction [47].

Similarly, the interaction of fullerenes (C_{60}) was studied with various Si(111) metal reconstructions: C_{60} deposited on Si(111)/In-3√3×3√3 are anchored on Si substitutional defects inducing a strain in the In layer allowing clustered C_{60} molecules to trap and fixate mobile vacancies [48]. C_{60} deposited on the more dense (and complex) In-3√3×7 and In-2×2 reconstructions displace In atoms within the layer which has been attributed to C_{60} forming stronger bonds with the underlying Si atoms. On In-4×1 they assemble into 1D ordered structures expelling underlying In surface atoms too [49]. Fullerenes on the Si(111)/Ag-3√3×3 also form a densely packed layer, but individual fullerenes were bound stronger to the substrate at sites of distorted Ag-trimer units of the layer [50]. Si(111)/Au-5×2 did not promote the formation of ordered C_{60} structures, but after adding a small amount of Tl atoms, ordered C_{60} structures appeared [51].
The same group also studied the influence of diverse metal-reconstructed Si(111) substrates on the mobility of adsorbed tryptanthrin: The clean Si(111)–$7\times7$ and Ag–$\sqrt{3}\times\sqrt{3}$ were two limiting cases of strong chemisorption and 2D molecular gas with In–$4\times1$ and Cu–$5.5\times5.5$’ presenting intermediate cases which has been discussed in terms of surface potential relief [52].

My colleagues employed a thallium 1×1 passivation layer on Si(111) as a substrate for copper phthalocyanine and copper perfluorophthalocyanine (F$_{16}$CuPc) and discovered that this layer facilitates the formation of ordered CuPc domains switchable with voltage pulses [53] and allowed them to observe the pair-correlation function of the F$_{16}$CuPc 2D molecular gas directly with STM in great agreement with kinetic Monte Carlo simulations [54, 55].

Unlike in the case of other adsorbate-reconstructed surfaces, where the modification of the Si substrate is achieved through the deposition of additional material, Si(111) can be passivated by its boron dopants. Upon annealing, boron atoms segregate in the subsurface layer and passivate the Si dangling bonds from within the bulk forming the deactivated Si(111)/B–$\sqrt{3}\times\sqrt{3}$ surface. ZnPc deposited onto this substrate was found to form densely packed molecular layers with upright molecular orientation [56]. Additional experiments with CuPc and CoPc revealed a strong role of the d-orbital occupancy of the central atom on the strength of the molecule-substrate interaction affecting the molecular orientation and packing at higher coverages [57].

Experiments probing the interaction of molecules with (semi)metal modified Si(001)–2×1 surfaces were very sparse: STM observation of CoPc and CuPc with bismuth lines grown on Si(001)–2×1 hinted at possible catalytic dissociation of the molecules on the Bi lines [58, 59]. In another study, the presence of indium 1D chains on Si(001)–2×1 resulted in improved growth of pyrazine 1D chains in the vicinity of In chains [60].

Some other experiments involving organic molecules were performed on the analogous Ge(001) surfaces reconstructed with noble metals: CuPc deposited onto Au-induced Ge nanowires on Ge(001) adsorbed on top a Ge wire or bridging two Ge wires [61]. The bridge configuration allowed to decouple the central Cu atom and charge it at voltages > 5 V [62]. The current through some of bridging configurations also exhibited a two-level fluctuations which was attributed to activation of vibrational modes due to electron injection into the LUMO+1 orbital [63]. The platinum modified Ge(001) surface was employed as a substrate for CuPc which exhibited mobility along Pt wires [64]. The substrate was also employed for octanethiol which could be controllably contacted by the scanning tip revealing rectifying character of the junction, the conductance of which could furthermore be controlled by adjusting the tip-sample separation [65].
It is also suitable to mention a reverse approach explored by [66] who deposited benzonitrile on Si(001) to increase local site reactivity in order to promote the growth of Pb and Al chains.
Part II

METHODS
PHYSICAL PRINCIPLES OF METHODS

Experimental data in this thesis were acquired using our non-commercial scanning tunnelling microscope (STM) and at the Materials Sciences Beamline at the Elettra Synchrotron facility in Trieste, Italy. This chapter describes their physical principles.

2.1 SCANNING TUNNELLING MICROSCOPY

2.1.1 Atomic resolution before STM

The field emission microscope (FEM), invented by Erwin Müller in 1936, was one of the first devices almost able to reach atomic resolution. It consists of a cathode in the form of a sharp metallic tip located in an evacuated chamber together with a fluorescent screen serving as anode [67]. High electric voltage is applied between both electrodes to bend the energetic barrier around the tip which otherwise prevents electrons from escaping. Electrons close to the Fermi level can tunnel through the narrow, bent barrier and are accelerated towards the screen. The work function of various crystallographic faces differs so the contrast of the displayed image is rather representative of crystallographic faces of the tip than of individual atomic steps.

True atomic resolution was achieved by Erwin Müller in 1951 with the field ion microscope (FIM), which is a small modification of the FEM. Voltage polarity in this arrangement is reversed and the chamber is filled with an inert gas, such as helium [67]. Helium atoms are polarized in the inhomogeneous electric field and drawn towards the tip. In its proximity, their electrons can tunnel into the tip and the resulting He ions are accelerated to the screen. The displayed image is representative of individual atoms and atomic steps on the tip.

2.1.2 Invention of STM

Both FEM and FIM allow to investigate surfaces and visualize changes in real time, but their application is restricted to sharp metallic tips. A significant breakthrough was achieved by Gerd Binnig et al. in 1982 who managed to sufficiently isolate vibrations with the help of superconducting magnets allowing them to measure tunnelling current across a variable vacuum gap and show its exponential dependence [68]. They have later
demonstrated its potential as a powerful microscopic technique by resolving atomic steps on CaIrSn$_4$($1\over 10$) and Au($1\over 110$) [69]. G. Binning and H. Rohrer were rapidly awarded the Nobel prize for their invention in 1986.

Since STM relies on tunnelling current flowing between the sample and the sharp tip, its application is limited only to metallic and semiconducting samples, but it has nonetheless revolutionized surface science as it allowed to observe substrates with atomic resolution directly. It is thus useful in observing local defects and it can provide local real-space information about the structure of the substrate where diffraction techniques with their integral nature such as LEED (low energy electron diffraction) or RHEED (reflection high-energy electron diffraction) fail to provide a clear answer.

The requirement for conducting samples was overcome four years later with the invention of atomic force microscope in 1986 [70] which replaced the tunnelling current for the deflection of a cantilever with a mounted tip. The technique has gone through some great improvements resulting in the development of non-contact methods with astonishing resolution capable of resolving molecular backbones. They achieve so with the help of oscillating cantilevers with functionalized tips which can sense the fine force interactions in the proximity of the molecule.

### 2.1.3 Principles of STM

STM functions similarly to a record player: The music is recorded as a height profile in the form of a dense spiral on a plate. The plate rotates and a tip follows the height corrugations. The corresponding signal is then passed to the speakers which reproduce the sound.

Schematic view of STM operation is shown in figure 2.1. Bias voltage of a few volts is applied between a sharp metallic tip and a conducting or semiconducting sample, although thin insulating layers on conducting samples can be studied as well. The tip is approached to the sample until the
Figure 2.2: Scanning modes of STM: constant mode keeps the tunnelling current constant while adjusting height $z$, the constant height mode keeps the plane of the tip constant and registers the changes of the tunnelling current. The picture also shows a potential collision of the tip with the sample on the right.

tunnelling current starts flowing within nanometres distance. The approach is stopped when a preset current value is reached. The tip remains hovering above the sample so the method is non-contact and non-destructive, although its proximity allows for direct manipulation. Operating currents are very small (typically under 1 nA) so they need to be amplified with an amplifier and are further read by the computer (distance control and scanning unit) which visualizes the data.

The tip is mounted on a piezoelectric tube\(^1\) which performs the scanning motion above the sample. Scanning is performed in a row-wise manner with voltage signals controlled by the computer. The image of the sample can be obtained in two modes (see figure 2.2):

**Constant-height mode:** The $z$ coordinate of the tip is kept constant, e.i. the tip keeps scanning in the same plane while changes of the tunnelling current are registered. The resulting image is a map of variable tunnelling current $I(x, y, z = \text{const.})$. This mode allows for very fast scanning speeds, but the tip is very vulnerable to collisions with the sample.

**Constant-current mode:** A feedback loop regulating the height of the tip above the sample is employed to keep the tunnelling current constant. The resulting image is a map of the height of the tip $z(x, y, I = \text{const.})$. This is the preferred mode of operation since the tip is protected from collisions with the substrate, but at the cost of slower scanning speeds.

STM does not resolve the type of atoms and their position on the surface. Instead, the nature of the method based on electric current means that it

\(^1\) Sometimes the sample is mounted on the piezoelectric drive instead.
senses the electronic structure of the sample, but is also intertwined with the electronic structure of the tip. The next few parts should provide a physical insight into the nature of the tunnelling current and into the interpretation of images. Let us start with the tunnelling effect.

### 2.1.4 Tunnelling effect

In classical physics, a particle can overcome a potential barrier if it possesses higher energy. In quantum physics, the wave nature of particles allows them to overcome such a barrier even if their energy is lower. This effect is called the *tunnelling effect* and has no analogy in classical physics. Its first successful application was the elucidation of the nature of alpha radioactive decay by G. Gamow in 1928 [72].

A scheme of the tunnelling effect is shown in figure 2.3. Particle with energy \( E \) in area I, where the potential is zero, is separated from area III, where the potential is zero too, by a narrow potential barrier of height \( V_0 \) and thickness \( d \) (area II). This can represent a simplified model of metal-insulator-metal interface where the insulator presents a potential barrier for the propagation of electrons.

The stationary solution of Schrödinger’s equation for particle with mass \( m \) and energy \( E \) in area I can be considered in the form [73]:

\[
\psi_I = A \exp(i k_0 x) + B \exp(-i k_0 x),
\]

where \( A \) is the amplitude of the incident wave and \( B \) of the reflected wave. The wave vector \( k_0 \) is introduced in the form \( k_0 = \sqrt{2mE/h} \).
The solution for area II can be considered in the form:

\[ \psi_{II} = \alpha \exp(i \kappa x) + \beta \exp(-i \kappa x), \quad (2.2) \]

where the wave vector is \( \kappa = \sqrt{2m(E - V_0)/\hbar} \), where \( E < V_0 \).

Finally the solution for area III:

\[ \psi_{III} = C \exp(i k_0 x). \quad (2.3) \]

The probabilities of transmission and reflection expressed as \( T \) and \( R \) coefficients are defined as the amplitude ratios of the oncoming vs. transmitted and reflected wave respectively:

\[ T = \left| \frac{C}{A} \right|^2 \quad R = \left| \frac{B}{A} \right|^2. \quad (2.4) \]

The requirement for the wave function and its first derivative to be smooth in all points then gives the following formula of the probability of transmission:

\[ T = \left[ 1 + \frac{1}{4} \left( \frac{k_0}{\kappa} + \frac{\kappa}{k_0} \right)^2 \sinh^2 \kappa d \right]^{-1}, \quad (2.5) \]

which relates to the reflection coefficient as \( R + T = 1 \). The general shape of the \( T \) coefficient is shown in figure 2.4.

2.1.5 Tunnelling current

Electrons have lower energy in a metal than in the surrounding vacuum — they would escape otherwise — so there is an energetic barrier at the metal surface characterized by the work function \( \phi \) defined as the smallest quantum of energy needed to remove an electron. To gain an insight into
this barrier, let us assume a Sommerfeld’s model of metal and a perfectly smooth surface \([74]\). Removing an electron along the \(z\) axis perpendicular to the surface will cause the metal electrons to reorganize so as to compensate for the extra field induced by the leaving electron. This problem can be solved with the method of mirror charges and the electric potential in the proximity of the surface can be approximated as:

\[
V(z) = -\frac{1}{4\pi \varepsilon_0} \frac{e}{2z}
\]  \(\text{(2.6)}\)

Superimposing a strong homogeneous electric field of intensity \(\varepsilon\) will facilitate tunnelling by bending the energetic barrier according to the formula:

\[
V(z) = -\frac{1}{4\pi \varepsilon_0} \frac{e}{2z} - \varepsilon z
\]  \(\text{(2.7)}\)

which is displayed in figure \(2.5\) (arbitrary units).

When two different metals (with work functions \(\phi_1 < \phi_2\)) are brought sufficiently close together, electrons will tunnel through the barrier from the higher lying occupied energetic states of metal 1 to the unoccupied states of metal 2 until an equilibrium is reached. Applying a voltage \(V\) between both electrodes brings the system out of equilibrium: electronics states in both metals are shifted by \(eV\) apart, the barrier is bent by the applied voltage and electrons start tunnelling from the occupied electronic states of one metal into the unoccupied electronic states of the other which results in a net current flow. The occupied and unoccupied states are often interchangeably called filled and empty states.

The tunnelling current flowing between two metal electrodes separated by two metal electrodes, i.e. the sample and the tip, depends on the shape of the electrode, their separation as well as the height of the potential barrier,
but it can be well represented in WKB approximation with the expression [75]:

\[ I = VA(V) \exp \left( -z \sqrt{\frac{2m_e \phi}{\hbar^2}} \right), \]  

(2.8)

where \( V \) represents applied voltage, \( A(V) \) describes the dependence of tunnelling current on the voltage, \( z \) represents the separation between both electrodes, \( \phi \) represents the effective height of the potential barrier and \( m_e \) the mass of electron.

This equation shows that the tunnelling current exponentially decays with distance, but it only applies to a simplified model of two planar metal electrodes which is far from the real-world situation of a sharp tip in the proximity of a planar sample with a complex electronic structure. A general formula for the tunnelling current can be expressed with the help of perturbation approach using Bardeen’s formalism[76, 77]. The perturbation approach is modified since the strong tip-sample interaction prevents a separation of the Hamiltonian. Instead of creating the wave function from the unperturbed solutions of the system, it is formed as a superposition of the wave functions of the isolated tip and sample with time dependent amplitudes. Applying the Fermi’s golden rule we obtain the expression for the transition rate

\[ w_{ts} = \frac{2\pi e}{\hbar} |M_{t,s}|^2 \delta(E_t - E_s) \]  

(2.9)

where \( \delta \) is the Dirac distribution and \( M_{t,s} \) a matrix containing perturbation elements of \( \langle \psi_t | \hat{H} | \psi_s \rangle \). The \( \psi_t \) are states of the tip and \( \psi_s \) of the sample in the absence of tunnelling and \( E_t \) and \( E_s \) are their corresponding energies. The matrix element can be written as:

\[ M_{t,s} = -\frac{\hbar^2}{2m_e} \int_S dS \cdot (\psi_s^* \nabla \psi_t - \psi_t \nabla \psi_s^*) \]  

(2.10)

where \( S \) is an arbitrary surface between the tip and the sample.

The final expression for the tunnelling current is a weighed sum of all initial and final states

\[ I = \frac{4\pi e}{h} \sum_{t,s} \left[ f(E_t) - f(E_s - eV) \right] n_t(E_t)n_s(E_s + eV) |M_{t,s}|^2 \delta(E_t - E_s), \]  

(2.11)
where \( f(E) \) is Fermi distribution function, \( V \) applied voltage and \( n_{t,s} \) represent the local density of states of the tip and sample (LDOS).

Application of this formalism to a rectangular barrier is exactly solvable and the solution including transmission probability per time interval for 1D case can be found in a work by Reittu [78].

2.1.6 **Resolution in STM and interpretation of images**

Exponential dependence of the tunnelling current on distance, cf. eq. 2.8, accounts for the great vertical resolution of STM. A small change of the sample-tip distance, all other things being equal, leads to a dramatic increase or decrease of the tunnelling current. The constant current scanning mode therefore takes advantage of this in its feedback loop. Small changes of the tip height during scanning translate into big changes of the current. The feedback loop can thus quickly respond and adjust the tip position accordingly. The vertical resolution is therefore mostly limited by the by the quality of vibration isolation and to a lesser degree by the sensitivity of used current amplifier, background noise, quality of used electronics and piezodrives.

The lateral resolution in STM depends on the quality of the scanning tip. The tip needs to be ultra sharp and ideally terminated with a single atom, otherwise the tunnelling current will flow through multiple sites (effect of double tip). Ultra sharpness of the tip is not a necessity when studying samples with large flat terraces, but becomes important when scanning corrugated surfaces where its shape needn’t be able to accurately follow smaller corrugations and narrow trenches. On flat samples with large crystallographic terraces, a blunt tip can produce well resolved images provided it is terminated with a small protruding cluster of atoms, which it usually is. The lateral resolution in such cases is given by the width of the tunnelling channel. The exponential decay of tunnelling probability with distance is advantageous in this case as most of the current entering a spherically approximated tip will flow through a narrow spot. The width of the tunnelling channel can therefore theoretically provide subatomic resolution, but there are a few things to consider: first, rougher sampling raster can also lead to a partial loss of resolution, but allows for faster scanning speeds, and second, the resolution is also limited by the lateral blurring of electron clouds — meaning that even a narrow tunnelling channel cannot provide a better resolution where the local electronic structure is homogeneous.

Interpretation of STM images is not straightforward. Features with corrugation exceeding 1 Å usually capture contours of underlying atoms (step edge, atomic clusters) while smaller features usually stem from the local corrugations of the electronic structure. To explain the nature of the obtained image (in the constant current mode), let us have a look at a model de-
veloped by Tersoff-Hamann [79]. They approximated the scanning tip with a non-directional s-like wave function. For small voltages, the conductivity of the tunnelling gap can then be expressed as:

\[ \sigma \propto \exp(2\kappa R) \sum_s |\psi_s(r_0)|^2 \delta(E_s - E_F) \]  

(2.12)

where \( \kappa \) is a constant, \( r_0 \) the position of the s-like centre of the tip and \( R \) its radius. The conductivity is then directly proportional to the total electron density at \( E_F \) in \( r_0 \). In other words, the tip follows the corrugations of the local density of states of the sample \( n_s \) at Fermi energy. This view is an obvious oversimplification, since it does not consider the real structure of the tip and other phenomena (e.g. the relaxation of tip atom positions due to sample-tip interaction etc.), but it nicely illustrates that the tunnelling is mostly dominated by electrons near the Fermi energy and that the tip senses the local electronic structure of the sample which can be greatly modified with adsorbates and therefore STM images need to be interpreted with caution and care. Moreover, STM does not provide chemical resolution so it cannot identify individual atoms on the surface and therefore this information needs to be inferred from other methods, such as density functional calculations.

The condition of the scanning tip is crucial in obtaining well resolved images. STM surprisingly proved able to resolve corrugations on close packed metal surfaces, which do not have a complex electronic structure such as the nearly free-metal Al(111) [80], when the tip was brought very close. Chen [81] provided an explanation by considering the actual electronic states terminating the tip participating in the tunnelling (i.e. the actual atomic orbitals) and found that the high contrast stems from tunnelling into \( p_z \) and \( d_{z^2} \) like orbitals which sense the lateral gradient of the surface wave function. He also concluded that only \( d \)-metals (W, Pt etc.) or Si terminated tips with \( p_z \) like dangling bonds should be able to provide such high resolution.

In recent years, carefully chosen termination of the scanning tip (so called functionalization) has proved able to provide dramatically improved resolving power when displaying molecules with STM. The work by Gross et al. [82] shows how a tip carefully functionalized with a CO molecule (picked up from the sample) shows a much improved resolution of the HOMO state of a naphthalocyanine molecule in contrast to an s-type tip terminated with Cu, see figure 2.6. The authors explain this enhanced contrast by constructive and destructive overlaps of the tip s and p-type mixed wave functions with the wave functions of the molecule in contrast to an only s-type wave function of the Cu terminated tip.
2.1 Scanning Tunnelling Microscopy

2.1.7 Scanning tunnelling spectroscopy

The tunnelling current is made of electrons occupying energetic states close to the Fermi level. When the sample is biased negatively with respect to the tip, the tunnelling current is formed by electrons tunnelling from the filled electronic states of the sample into empty states of the tip and vice versa. The tunnelling current thus depends on the electronic structure of both the tip and the sample. It can be therefore employed to obtain spectroscopic information about the sample provided the electronic structure of the tip is simple.

According to Lang et al. [83], the tunnelling current can be approximated as a convolution of the local density of states (LDOS) of the sample \( n_s(E) \) and of the tip \( n_t(E) \) weighted by decreasing tunnelling probability for energy levels lying farther away from the Fermi level \( (E_F) \) or for larger tip-sample separation \( s \) expressed as:

\[
I(V) \propto \int_{E_F}^{E_F+eV} dEn_t(E - eV)n_s(E) \exp \left[ \left(-2s\sqrt{m}/\hbar\right)\sqrt{2(\phi + E_F - E) + eV} \right]
\]

(2.13)

where \( \phi \) is the work function and \( m \) electron mass.

Expression 2.13 shows that when the applied voltage is increased by a small amount, new electronic states participate in tunnelling and the current increases. When a local peak in the electronic structure is reached, the current experiences a sharp rise. These local variations of the electronic structure can thus be characterised by measuring differential conductance \( dI/dV \). The principle of this approach is schematically illustrated in fig-
Figure 2.7: Tunnelling spectroscopy scheme: The sample is negatively biased with respect to the tip, electrons tunnel from the occupied states of the sample into the unoccupied states of the tip (and vice versa when the bias polarity is reversed). The sample has a complex electronic structure (illustrated as discrete bands), the tip has a simple electronic structure. The tunnelling current contains a fingerprint of the sample electronic structure the distinct features of which can be characterized by measuring $\frac{dI}{dV}$.

The dependence on the tip-sample separation in $\frac{dI}{dV}$ can be suppressed by measuring so called normalized conductance [84]:

$$\frac{dI/dV}{I/V} \propto \frac{n_s(eV)}{\int_{-eV}^{eV} n_t(E)dE}.$$  \hspace{1cm} (2.14)

The denominator will change slower than the numerator if the electronic structure of the tip is simple, e.i is metallic and only states of the tip deriving from s-orbitals participate in tunnelling. As a result, the normalized conductance will be dominated by the sample density of states and thus carries its ‘fingerprint’. LDOS of the sample can therefore be characterized by measuring $I(V)$ characteristics and obtaining $dI/dV$ numerically or measuring it simultaneously using a lock-in amplifier. Using lock-in amplifier is preferable since numerical differentiation of $dI/dV$ curves exacerbates noise which has to be suppressed by averaging over many data-sets. Its advantage, though, is speed at which the data can be obtained.

The requirement for metallicity of the tip poses a problem when scanning non-metallic samples. Substrate material will eventually contaminate the tip and alter its tunnelling characteristic. Spectra obtained with such tips therefore do not reflect the real electronic structure of the sample. It is therefore necessary to verify that the tip has spectroscopic abilities by measuring spectra of known structures and/or to obtain verification from other spectroscopic methods such as photoelectron spectroscopy.
2.2 PHOTOELECTRON SPECTROSCOPY

Chemical composition of a sample as well as its electronic structure can be analyzed using photoelectron spectroscopy (PES). The technique is based on the photoelectric effect. The sample is irradiated with ionizing electromagnetic radiation of a well-defined energy $h \nu$ which is absorbed by electrons in the sample and they are raised to energetically higher levels or emitted out of the sample. The kinetic energy $E_k$ of emitted electrons (called photoelectrons) can be related to their binding energy $E_B$ as

$$E_k = h \nu - E_B - \phi$$

(2.15)

where $\phi$ is the work function of the sample. The energetic levels of electrons in a solid are quantized and so the distribution of photoelectrons, $N(E)$, consists of a series of discrete bands which reflect the atomic shells. Mostly valence electron participate in bonding while there is negligible overlap between core electrons. Since the energy levels of core electrons are defined mostly by the charge of the nucleus, the technique is element specific and is employed to probe the chemical composition of the samples. It also provides information about their electronic structure including the valence band.

The shortest mean free path of photoelectrons is when their energy lies within $50–200 \text{ eV}$ [85]. The mean free path for this energy interval is a few Å effectively probing only a few atomic layers of the surface. Synchrotrons are therefore especially suitable for studying processes on surfaces because they generate X-rays of variable wavelength and the energy of the incident photons can be adjusted to satisfy this criterion to the core level of a given element found on the surface.

2.2.1 Theory of photoabsorption

In the simplest approximation, the probability of photoabsorption is considered uniform for all electrons in the sample. In such a case, the energetic spectrum $N(E)$ of emitted electrons would be a direct image of the sample electronic structure. In the real world, however, the probability of photoabsorption, expressed by photoabsorption cross-section, differs among the electronic levels.

In theoretical descriptions [86], the flux of emitted electrons is considered to be proportional to the transmission probability $w_{if}$ of an electron from initial state $\psi_i$ to final state $\psi_f$ using the Fermi’s Golden Rule$^2$:

$$w_{if} \propto | < \psi_i | H' | \psi_f > |^2 \delta(E_f - E_i - h \nu)$$

(2.16)

$^2$ The rule has actually been derived by Dirac and Bohr [87], but dubbed ‘golden’ by Fermi [88].
where $|\langle \psi_i | H' | \psi_f \rangle|^2$ is the transition matrix element, $H'$ is the perturbation Hamiltonian operator describing the electric field of the incident photon acting on the electron and $\delta(E_f - E_i - h\nu)$ is the delta-distribution ensuring energy conservation during the excitation. The Hamiltonian can be expressed as

$$H' = -\frac{e}{2m}(p \cdot A + A \cdot p)$$

(2.17)

where $p = -i\nabla$ is the electron momentum operator and $A$ is the vector potential. It is possible to ensure that the term $p \cdot A$ remains zero. For linearly polarized light, the Hamiltonian operator becomes

$$H' = A \cdot p$$

(2.18)

Solutions of this problem lead to selection rules: For an initial state described with one-electron wavefunctions with quantum numbers $n, l, m$ as $U_{n\ell m}(r)Y_{\ell m}(\theta, \phi)$ and the final continuum state $U_{n'\ell' m'}(r)Y_{\ell' m'}(\theta, \phi)$ the transitions in the dipole approximation are allowed if

$$l' = l \pm 1$$

$$m' = m$$

2.2.2 Effects on binding energy

The first theoretical estimations of electron binding energies were done by Koopmans [89]. In his simplified approximation, the perturbation is acting only on the ejected electron and relaxations of the final state after the removal of the electron are not regarded. The initial $N$-electron and final $N-1$ electron system are thus seen as frozen and the binding energy $E_B$ can be related to the energy derived from Hartree-Fock calculations as $\varepsilon_k = -E_B$.

Calculations of binding energies determined with XPS need to consider other effects involved during the process of photoemission [90]. The adiabatic approach treats photoionization as a slow process during which the $N-1$ system has sufficient time to relax into the lower energetic state and screen the created hole so the photoelectron experiences a decreased pull. The determined binding energy is thus lower than values obtained by the frozen orbital approach. The ‘sudden approximation’ is more realistic and treats the photoionization process as a rapid perturbation during which other electrons in the atom may be excited into bound (below $E_{\text{vac}}$) or unbound states (above $E_{\text{vac}}$) leading to the appearance of satellite peaks.

The effects playing part during photoionization process can be categorized as:
Figure 2.8: A simple scheme of photoabsorption and some accompanying effects:
(a) Photon of energy $h\nu$ is absorbed and emitted above the vacuum level. (b) The hole is filled with a higher lying electron and an Auger electron is emitted. (c) Shake-up effect by exciting another electron into the unoccupied valence states, photon re-emission may occur too. (d) Shake-off effect by exciting another electron above the vacuum level.

- **Initial state effects**: Induced by polarization of the ground state (atoms interacting via their valence electrons with the surrounding or intra-atomic effects) leading to so called ‘chemical shift’ and spin orbit splitting (intra-atomic).

- **Final state effects**: Effects resulting from changes in the electronic structure due to the photoemission, such as structure rearrangement (shake-up, shake-off, plasmons, auger electron emission) or excited-state polarization (see figure 2.8).

These effects also play part in the duration of the core hole lifetime, which causes lorentzian broadening of spectral peaks and is inversely proportional to its FWHM (full width at half maximum).

Chemical changes in the environment of an atom result in the redistribution of valence electrons which impacts the core electron levels. This translates in the recorded photoelectron spectrum as a shift of the binding energy (chemical shift). The effect can be illustrated on a simple model of electrostatic interaction in terms of electronegativity. When the studied atom becomes bonded to a more electronegative element, electrons in the bond are pulled farther away from the core which becomes less shielded. The electronic levels are thus shifted to lower binding energies than when the atom is bonded to a less electronegative element. For small differences in electronegativity $\Delta\chi$ the core level shift $\Delta E$ is nearly equal to $\Delta\chi$, but at larger values saturates [91]. This can be used to predict the direction of the chemical shift, but comprehensive all electron level calculations are necessary to correctly account for energetic shifts.
EXPERIMENTAL SETUP

3.1 SCANNING TUNNELLING MICROSCOPY

The experiments were conducted at our STM microscope of our design. The nature of the experiments requires to operate under UHV conditions so as to keep the contamination from ambient atmosphere at negligible levels during the duration of the experiment. The scheme of UHV system is drawn in figure 3.1. The base pressure was better than $5 \times 10^{-9}$ Pa (measured with a Bayard-Alpert type ionization gauge) but sometimes, after depositing organic compounds, would stabilize at $5 \times 10^{-8}$ Pa, but this had no noticeable impact. To reach UHV, the system is pumped from atmospheric pressure with a diaphragm (primary) and turbomolecular pumps (secondary) while being degassed at 120°C for 48 h. A sputter ion-pump is employed once high vacuum has been reached and maintains UHV conditions in the chamber after cooling down and sealing off the system. The vacuum conditions can be further improved with a Ti sublimation pump.

During the course of this research, the system was expanded to accommodate additional evaporators (solid, liquid and gas phase). The additional solid phase evaporator can be sealed off from the main chamber through a gate valve and refilled without interrupting the vacuum of the main chamber.

The apparatus is mounted on pneumatic vibration isolation system providing isolation for frequencies above 1.5 Hz.

STM head

Side-view scheme of the STM measuring head is shown in figure 3.2. The vapour beam of deposited material arrives from the left and hits a vibrating quartz crystal for thickness monitoring (1) mounted on a frontal panel (2) and further — through a closable aperture — hits the sample mounted on a rotating sample holder (3). After sample preparation, the holder is rotated by 180° to position the sample in front of the scanner (4). The scanner consists of a tungsten tip mounted on a piezoelectric tube performing the scanning motion, which itself is mounted on a piezoelectric linear drive employed to approach the sample (5). A small evaporator for deposition under the tip is mounted above (6). The sample holder and the scanner are mounted on a support (7). During sample preparation, the support is fixed with a lock (8) and the sample holder can be rotated with the rotations of a manipulator (9).
transferred through gears (9). The support is unlocked during scanning and suspended on springs (10) and damped magnetically with eddy currents. The whole system is mounted to a flange (right) containing a bushing (11) to transmit electric signals into the UHV system.

The scanner is controlled via a DSP electronic unit with an implemented PID feedback loop allowing real-time drift correction. Recorded data are stored in a custom binary format and later processed with Gwyddion image processing software, which has been developed with focus on the needs of scanning probe microscopies (data levelling, contrast adjustment, filtration, Fourier transforms, distortion corrections etc.) [92].

For our experiments, the sample holder was equipped with n-type Si(001) and (111) monocrystals (heavily Sb doped, resistivity $\leq 0.14 \, \Omega \cdot \text{m}$). The scanning tips were electrochemically etched according to procedure in [93]. To treat the scanning tip in-situ, a Pt(111) bead-shaped crystal and a tungsten stripe were installed too. Scanning on the Pt(111) crystal allows to improve the tip by transferring some of the soft platinum onto the tip. The tungsten stripe was used as a cathode for annealing of the tip with electron bombardment or alternatively, the tip apex of blunt or unstable tips was reshaped by touching the incandescent stripe.

Figure 3.1: Simplified block scheme of the of the UHV STM apparatus.
Figure 3.2: STM head

The silicon samples are resistively annealed to temperatures exceeding 1000 °C which heats other parts of the microscope and leads to thermal drift artefacts during scanning. The drift is therefore compensated electronically in all three axes with the digital signal processing electronics. The creep of the piezoelectric scanner can be minimized by moving stepwise instead of large transfers.

Deposition

Solid material was deposited from evaporation sources heated with incandescent tungsten filaments. Tin (99.999% purity) was deposited from a tantalum crucible, indium (99.98%) was deposited from a small droplet condensed on a helix-shaped tungsten filament directly. Both of these sources were located in the main chamber and their deposition rate could be established with the crystal thickness monitor. CuPc (resublimated, 99.9%) was deposited from a boron-nitride crucible located in a separable part, but the geometry of the system did not allow to measure its deposition rate with the thickness monitor so it was assessed from performed experiments.

Ethylene (99.8%) was deposited via a precision leak-valve by filling the vacuum chamber directly. The tubing before the leak-valve was cleaned with several flush-fill cycles before each deposition. The geometry of the system did not allow for any fragments produced by the sputter-ion pump to hit the sample directly without undergoing several collisions with the wall.
Sample treatment and preparation

Silicon samples are covered with a natural passivation oxide layer which needs to be removed by thermal treatment. Escaping solved gases would damage the flatness of the surface during the flash so the samples are first degassed for several hours at 500 °C. The oxide layer is then removed by resistive heating with passing DC current (‘flashing’) to 1200 °C for a few seconds.

At the beginning of each experiment, the samples were cleaned from previous adsorbate by flashing to 1200 °C and then the the Si(001)–2×1 and Si(111)–7×7 reconstructions were recreated so as to have well-defined initial conditions. The sample was let to cool down to room temperature. Afterwards, Sn or In was deposited. Typical deposition rates were in the order of $10^{-3}$ ML/s. Details of sample preparation are included in each experimental section.

Notes on shown STM images

- Indicated voltage is biased with respect to the sample. Scanning at negative voltage corresponds to imaging in the filled states, scanning at positive voltage to imaging in the empty states.

- The scale of shown images relates directly to the periodicity of the resolved substrate. The lattice constant of the unreconstructed 1×1 surface is $a = 3.84$ Å for both Si(001) and (111) surfaces. On Si(001)–2×1 this means 7.68 Å separation of two dimer rows. On Si(111)/Sn–√3×√3 the distance between two Sn atoms is 6.65 Å, and so on for other reconstructions. The values obtained via the control software can be subject to a substantial error (30%) due to thermal drifts and/or creep of the piezoelectric scanning elements.

- The images have been processed on an IPS type LCD monitor and used colour schemes were chosen to show a maximum level of detail. The STM images are therefore sometimes in greyscale and sometimes in colour (or even another colour scheme) depending on whichever would perform better in the particular context.

3.2 Photoelectron spectroscopy

The photoelectron spectroscopy experiments were conducted at the Material Science Beamline (MSB) at Elettra synchrotron in Trieste, Italy. X-radiation is fed into the beamline via a bending magnet providing a continuous spectrum of linearly polarized light. The spectrum is filtered at an SX-700
The energy range of the monochromatic light can be varied continuously between 22–1000 eV (the resolution or the light ranges from 10 to 1000 meV).

The normalized photon flux is in range $1.1 \times 10^{13}$ photons/s per 300 mA of accumulated current in the storage ring for most of the tuned energies. The incoming photocurrent is measured by a gold mesh placed before the UHV chamber.

The incoming photocurrent is measured by a gold mesh placed before the UHV chamber.

The base pressure in the experimental system is held in the $10^{-8}$ Pa range with turbomolecular and titanium sublimation pumps. The vacuum conditions during the experiments can be further improved cryogenically with liquid nitrogen. The experimental system consists of a main and a preparation chamber and a fast load lock entry. Photoelectrons are analyzed with a hemispherical Specs Phoibos 150 analyzer. The system is equipped with several electron-beam type evaporators, leak valves for precise gas deposition and Ar+ sputtering gun. The samples can additionally be studied with LEED and with a Mg/Al X-ray source. Installed manipulator allows azimuthal and polar rotations of the sample and the samples can be annealed to temperatures exceeding 1000 °C or cooled with liquid nitrogen to -100 °C.

This configuration allows Angle Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS), X-ray Photoelectron Diffraction (XPD), Resonant Photoelectron Spectroscopy (RPES), valence band mappings, or Near Edge X-ray Absorption Fine Structure (NEXAFS). Along with usual XPS, LEED, and SRPES measurement, these methods make MSB beamline highly versatile and practical.

During our experimental run, MSB was used for studying ethylene adsorption on Sn and In passivated Si(001) samples with SRPES in combination with LEED and standard XPS measurements.
Part III

RESULTS
Ethylene (C₂H₄) is a small hydrocarbon molecule with significant technological applications. It is a precursor in the production of polyethylene, a widely used plastic material, or finds use in agriculture since it is an important plant hormone controlling the ripening and flowering processes.

Both carbon atoms are bound with a σ and a π bond resulting from the overlap of their respective 2sp² hybridized and 2pz orbitals. The C—H bonds are formed similarly by the overlap between the C 2sp² and H 1s orbitals. The molecule is thus planar and it is the smallest hydrocarbon molecule containing a double bond.

The unsaturated character of ethylene (the presence of a π bond) plays a major role in its chemistry. It allows ethylene to polymerize into long chains, to produce graphene on catalyst surfaces or to participate in various other reaction types such as oxidation, alkylation or cycloaddition [94, 95]. Ethylene can moreover create complexes with transition metals due to a constructive overlap between the occupied metal d-orbitals and vacant π* antibonding ethylene state. Adsorption on transition metal surfaces has therefore been of scientific interest as the stretching of the C==C bond, weakened due to the interaction with the antibonding state, provides insights into catalytic processes [96].

Interaction of ethylene with silicon surfaces

The simplicity of ethylene, its significance and unsaturated character have attracted interest into its interaction with silicon surfaces. Understanding of the underlying physical mechanisms could provide insights for functionalization with larger organic molecules.

Adsorption of ethylene on Si(001)–2×1 has been investigated with a wide range of experimental and theoretical studies and has revealed a complex picture. Ethylene was found to adsorb on top of Si dimers of the 2×2 reconstruction via a [2+2] cycloaddition [97]. Despite the fact that a [2+2] cycloaddition reaction is symmetry forbidden according to the Woodward-Hoffmann rules, ethylene was found to adsorb readily on Si(001)–2×1 up to a coverage of ~50 % [98, 99] with a sticking coefficient of 0.5 at RT (0.7 at 100 K, dropping to 0.1 at 500 K) [100]. Once the 50 % coverage
is reached, the sticking probability drops and ethylene exposures several orders of magnitude larger are needed to fully saturate the surface which is attributed to nearest neighbour repulsion of adsorbed molecules \[101\]. The discrepancy between the symmetry ‘forbiddenness’ of the reaction and the obvious readiness of ethylene to chemisorb on Si(001) provoked DFT studies proposing various reaction pathways. DFT studies identified pathways involving transition states of ethylene $\pi$ bonding to the lower, electron deficient Si atom within the surface dimer or a via a di-radical mechanisms \[17, 102\]. The reaction type was therefore described as a ‘[2+2]-like’, but a different theoretical study suggested that a true [2+2] concerted symmetric pathway can on the surface occur too due to electronic states crossing the Fermi level although it requires a precise alignment of the reactants so this pathway should not play a major role \[103\] . A temperature dependent STM study has moreover shown that the adsorption proceeds via a long-lived precursor state \[104\].

DFT calculations also predicted a minority ‘end-bridge’ adsorption configuration of ethylene bonded across two Si dimers in the same row. This configuration was identified with STM after partially passivating the surface with atomic hydrogen which increased the adsorption yields for this particular configuration \[105\]. The reason why the end-bridge configuration was not found earlier is that it appears in STM as a C-defect (dissociated H$_2$O molecule, a typical contaminant in UHV systems).

On Si(111)–7×7, early HREELS studies \[106\] suggested that ethylene chemisorbs non-disociatively and that it rehybridizes into $sp^3$ which was later confirmed with STM and STS studies \[107\] suggesting that ethylene forms a di-Î¶ bonded adduct on the adatom-restatom pair. Further XPS studies identified a minor dissociation adsorption product and showed that the maximum coverage of ethylene on Si(111)–7×7 is larger than made possible of ethylene binding only to adatom-restatom pairs indicating a possible adsorbate-induced surface reconstruction \[99\]. DFT studies moreover identified a direct di-radical adsorption pathway without precursor states \[108\].

This overview illustrates that even the interaction of a very small and simple organic molecule on Si(001)–2×1 can be complex.

*Tin and indium terminated Si(001) surfaces*

When tin or indium are deposited onto Si(001)–2×1, they assemble into linear chains growing perpendicularly to the underlying Si dimer rows by a mechanism called *surface polymerization reaction* \[109\]. The mechanism proceeds in two steps: After an initial nucleation of a diffusing atom (e.g. on Si dimers rendered reactive by a C-defect), the atom itself becomes reactive and acts as a trapping site for diffusing atoms. A second atom binds to the
initial atom and to two Si atoms from the adjacent dimer row. The $\pi$ bonds of the involved Si dimers are cleaved which increases the radical nature of the other atom in each dimer. These Si atoms now act as a trapping site for diffusing atoms, the process repeats and chain growth ensues.

The structure of both In and Sn chains therefore resembles that of Si dimers forming the $2 \times 1$ surface reconstruction of Si(001): The chains consist of M–M dimers located in-between the dimer rows and backbonded to two Si atoms on each side [110]. The structure of the M–M dimer-bond is different between tin and indium: The trivalent indium forms only a $\sigma$ dimer bond whereas the tetravalent tin forms an additional $\pi$ bond. STM studies and DFT calculations have shown that also the geometry of the M–M dimers is different. The In–In dimer is flat, but the Sn–Sn dimer is tilted (‘buckled’) which is accompanied with a charge transfer from the lower Sn atom to the upper atom similarly to the Si dimers of Si(001)–$2 \times 1$ [111, 112]. Contrary to the Si dimers, the orientation of the Sn dimer tilt is within a chain uniform and does not oscillate.

With increasing atom deposition, the growing chains create an apparent $2 \times 2$ surface reconstruction. We use the description ‘apparent’ here to reflect the fact that the periodicity of the structures may locally be $2 \times 2$, but it does not uniformly fill the entire surface such as the Si(001)/Sn–$4 \times 4$ reconstruction which is achieved through annealing of the surface and involves large-scale rearrangement of surface atoms. In the presented case, the reconstruction has a local character and depends also on the local growth of the chains. The shortest distance between two chains can be $2a$, $a$ being the lattice parameter, but sometimes the separation is $3a$ due to the randomness of nucleation and following chain growth. Another reason for describing the periodicity as ‘apparent’ is that Sn dimers are buckled and the tilt of the dimers within the chain experiences modulation along its length which has been attributed to strain relaxation [110]. Moreover, the direction of buckling of the chains is random so it does not produce a sharp pattern in LEED. These arguments do not apply to indium chains due to the absence of a dimer tilt.

When approaching 0.5 ML coverage ($1$ ML $= 6.78 \times 10^{18}$ atoms/m$^2$) the dangling bonds of Si dimers are almost all saturated with overlying dimer chains and compact areas with (‘apparent’) $2 \times 2$ periodicity are formed. We call the 0.5 ML coverage the saturation coverage.

### 4.1 Experimental

The clean $2 \times 1$ reconstruction was obtained by flashing the samples to 1200 °C for 20 s while the pressure in the chamber remained in the $10^{-8}$ Pa range. After the sample cooled down, a saturation layer 0.5 ML of Sn or In was deposited at RT or at slightly elevated temperatures (100-150 °C) for
enhanced diffusivity. Ethylene was afterwards deposited via a leak valve and the pressure did not exceed $1 \times 10^{-6}$ Pa.

PES: Recorded PES spectra are averages of ten sweeps with 0.004 eV step size and were recorded in normal emission. High surface sensitivity was ensured by applying excitation energies approximately 100 eV higher than the binding energy of the investigated core levels, offering a good balance between secondary electron background and photoelectron escape depth. The deposition rate of the evaporators could not be measured with a thickness monitor so it was calibrated by performing a series of depositions and subsequent recordings of LEED patterns and PES measurements of the valence band. The $\pi$-state of Si dimers kept decreasing with increasing Sn/In coverage until it vanished upon the formation of the saturation layer.

4.2 INTERACTION WITH BARE SI(001) – 2×1

An example of a Si(001) – 2×1 surface exposed to 0.3 L of ethylene is shown in figure 4.1. The dimer rows forming the 2×1 reconstruction run diagonally and the oval shapes encircle typical defects of Si(001) – 2×1. The A-type (B-type) defects is a missing Si dimer (two missing dimers) [113], the C-type defect is a dissociated water molecule [114] and the split-off defect, which appears as an A and B defect separated by a dimer, has been attributed to strain relaxation, which can also be induced by nickel, oxygen or tungsten contamination [115].

In the empty-states images at −2.0 V and below (figure 4.1a) ethylene is barely recognizable and appears as subtle modulation of the Si dimer rows (arrows 1 and 2). When the bias is raised to −1.5 V (figure 4.1c), ethylene appears a depression within the Si dimer row similarly to A-type defects. In the empty state images (figure 4.1b,d), it is visible at both opposite polarities as a feature embedded within the dimer rows. The reason for this embedded position in the empty states images is that the displayed troughs correspond to the nodal plane of the Si dimer $\pi^*$ antibonding state, i.e. the troughs run above the centre of the dimer rows.

The images also show the tendency of ethylene to avoid adsorption on dimers adjacent to already occupied sites. This nearest-neighbour repulsion leads to the formation of local pseudo-ordering such as shown by the rectangular area: the row on the left is in anti-phase with the middle row which is in-phase with the row on its right. Arrow with asterisk moreover points to a peculiar area where ethylene is aligned across several rows.

Adsorption configurations of ethylene are schematically shown in figure 4.2. In addition to the on-dimer configuration, proceeding via a [2+2]-like cycloaddition, ethylene can adsorb across two Si dimers within the same row giving rise the end-bridge minority configuration [105]. Due to the radical nature of the unoccupied Si atoms after the scission of the $\pi$ Si
Figure 4.1: Si(001)–2×1 exposed to 0.3 L of ethylene. Ethylene (marked with arrows) has a tendency to form locally ordered areas (asterisk, rectangle). In the filled-states images it becomes visible at −1.5 V, notice the change of contrast after the line in image (a). Typical types of surface defects marked with oval shapes. 12×12 nm², 300 pA.
4.3 Interaction with Tin Passivated $\text{Si}(001) - 2 \times 1$

A typical STM image of Sn deposited onto $\text{Si}(001) - 2 \times 1$ is shown in figure 4.4. 0.4 ML of Sn were deposited onto a sample held at room temperature while the deposition rate was kept low ($10^{-3}$ ML/s) to facilitate the growth of well ordered structures. The image shows four consecutive atomic terraces covered with tin chains locally forming islands with $2 \times 2$ ordering. Since the compactness of observed islands was not good enough we performed depositions at slightly elevated temperatures (100–150 °C) to increase the surface diffusion of deposited tin atoms. An example of such a layer grown at 100 °C is shown in figure 4.5. The image was taken at $\pm 1.0$ V and shows large compact areas with $2 \times 2$ periodicity. The white arrows mark the onset of a forming second layer and the black arrows in the empty-states image mark bright chain ends. The chain ends may appear brighter at this voltage when being terminated by C-defects.

---

1 Gerson Mette has privately told me that C-defect and the end-bridge configuration can be distinguished with STM, but that the resolution in STM needs to be exceptionally good, which I never succeeded in obtaining myself.
Figure 4.3: C 1s spectrum of a Si(001)–2×1 sample exposed to 1 and 10 L of ethylene. The peak maximum is at 283.9 eV for small exposures (< 1 L) and shifts to 284.0 eV for higher exposures (10 L). $E_{\text{hv}} = 410$ eV.

Figure 4.4: Filled-states STM image of 0.4 ML Sn on Si(001)–2×1 deposited at RT. $-2.0 \text{ V}, 50 \times 35 \text{ nm}^2$, 300 pA.
When we exposed the Si(001)/Sn–2×2 sample to a 2.5 L dose of ethylene, we observed changes affecting individual Sn dimers. A set of images taken at ±1.0 and ±1.5 V is shown in figure 4.6. The image contrast has been adjusted so as to enhance the details of Sn dimers. The affected dimers (marked with arrows) are visible in the empty-states images at 1.0 V (a). Their intensity is decreased so they resemble a depression within the dimer chain, albeit an equivalent change is not visible at −1.0 V in the filled-states image. At +1.5 V (b), the depression becomes very subtle and in the filled states at −1.5 V appears only as a very faint modulation of the dimer intensity visible in the high-contrast image. Standard contrast picture of image (a) is shown for reference in image (e). The inset chart furthermore shows a profile along the AB line extracted from the ±1.0 V images.

Equivalent depressions in Sn chains at +1.0 V and other voltages were not observed in the unexposed samples (cf. figure 4.4 or 4.5).

The STM images show that ethylene exposure induces changes in individual Sn dimers which indicates that ethylene interacts with individual Sn dimers. The geometric and electronic structure between the Sn and Si dimer allows to draw analogies. Both dimers are tilted and the tilt is accompanied with a charge transfer from the lower to the higher atom. Both dimer bonds consist of a σ and a weak π bond. We therefore propose that the [2+2] cycloaddition also holds true for ethylene when adsorbing on Sn dimers by forming a di-σ bonded adduct after breaking the respective π bonds of ethylene and the Sn dimer, see scheme in image (f). The scheme also shows geometric changes expected in analogy with adsorption on Si dimers: the bond angles of carbon atoms assume an sp³ geometry configuration and the Sn dimer evolves a flat geometry.
Figure 4.6: 0.35 ML of Sn on Si(001)–$2 \times 1$ exposed to 2.5 L of ethylene. The image contrast has been adjusted to highlight the details of Sn dimers. Ethylene adsorption sites are visible in the empty-state images at +1.0 V (a), but not in the filled-state images at -1.0 V (b). At +1.5 V (c) ethylene adsorption sites show a very subtle decrease of intensity of Sn dimers and at -1.5 V only a faint modulation (d). The +1.0 V image with a standard contrast for reference (e). The inset contains a line profile along the AB line from the ±1.0 V images, the arrows denote the location of adsorbed ethylene. Proposed model of ethylene adsorption on a Sn dimer (top and side view) and a structural scheme of the system. The encircled dot marks the same site in the images. 100 pA.
Figure 4.7: C 1s spectrum of 30 and 105 L of ethylene deposited onto Si(001)/Sn – 2×2 and 1 and 10 L on Si(001) – 2×1 for comparison. $E_{hv} = 410$ eV

Since the theoretically calculated reaction pathways for the attachment of ethylene on Si reveal that it is a nonconcerted process proceeding from a precursor state formed between ethylene and the Si down atom, we expect a similar scenario to apply to the attachment of ethylene on Sn dimers: e.i. to proceed via a nonconcerted pathway from a precursor state formed with the Sn down atom. We did not observe indications of a precursor state in our experiments, but theoretical calculations or experiments performed at different temperatures might reveal its existence.

In contrast to adsorption on Si(001) – 2×1, we did not identify any features suggestive of an end-bridge or any other configuration. The closest distance between two Sn chains ($2a$) 7.68 Å seems too large for ethylene to form stable bonds. This would be equivalent to ethylene bonding across two Si dimer rows on Si(001) – 2×1 which had not been reported.

The results of photoelectron spectroscopy experiments are shown in figure 4.7. The graph shows C 1s spectra Si(001)/Sn – 2×2 exposed to 30 and 105 L of ethylene and the background signal before the exposure. The deposition of 30 L yielded a small broad peak with a maximum located at 284.3 eV. After adding further 75 L (105 L totally), the peak maximum has shifted to 284.4 eV. The 1 and 10 L spectra from deposition on Si(001) – 2×1, shown for comparison, developed much more intense peaks at lower exposures.

The peak analysis of the 30 and 105 L peaks are shown in figure 4.8. After the subtraction of the background signal, the spectrum was fitted with four voigt-type peaks:
We associate the major component at 284.5 eV, the intensity of which rose after adding 75 L, with ethylene adsorbing on top of Sn dimers. The binding energy of this peak is shifted by 0.6 eV towards higher binding energy with respect to the 1 L reference peak on Si(001)\(\text{-}2\times1\). This shift is indicative of a different bonding state and the shift towards higher binding energies is in agreement with the simple model of carbon nuclei experiencing lower electron screening when bonded to the more electronegative Sn atoms (1.96 for Sn in comparison to 1.90 for Si) [91].

The component at 283.8 eV can be associated with adsorption on the remaining Si dimers. These areas were saturated by the first deposition.

A small component appears at 283.1 eV is negligible in comparison to other components and we suspect it to be caused by adsorbing fragments of dissociated ethylene at the ion gauge. The component at 286.3 eV contains a large shift towards higher binding energies and we suspect it to arise from interaction with contaminant oxygen species (most likely water) since we saw a small O 1s peak develop over time on the unexposed Si(001)\(\text{-}2\times1\) surface and since oxygen is known to shift binding energies to higher values. The component at 283.1 eV and 283.8 slightly decreased after raising the the exposure from 30 to 105 L correlating with increased oxygen contamination between both doses.

The peak intensities also reveal different reactivities of both surfaces. The peak arising from the 105 L dose onto Si(001)/Sn\(\text{-}2\times2\) is less intense than the 1 L reference peak from Si(001)\(\text{-}2\times1\) and thus shows a lower reactivity of the Sn terminated surface compared to the clean Si(001).

The relative reactivity of the Si(001)/Sn\(\text{-}2\times2\) surface can be assessed with equation 4.1 by taking the ratio of the peak areas \(A\) normalized to the respective ethylene dose \(L\),

\[
R = \left( \frac{1}{\Theta} \frac{A_{Sn}}{L_{Sn}} \right) / \left( \frac{A_{Si}}{L_{Si}} \right),
\]

where \(A_{Sn}\) represents the area of the fitted component for dose \(L_{Sn}\) corresponding to ethylene adsorbing on Sn dimers, \(\Theta\) represents normalization to estimated Sn coverage. Since the sticking probability of ethylene on Si(001) drops abruptly after reaching quasisaturation around 1 L, we use the 1 L reference peak for this evaluation \((A_{Si} \text{ and } L_{Si})\). The relative reactivity of the Si(001)/Sn\(\text{-}2\times2\) evaluated for the 30 L dose is 0.007 and 0.004 for the 105 L dose. We estimate the values to be burdened with 50 % uncertainty. The lower value for the higher dose appears to be related to the decreasing availability of the free adsorption sites.

The lower reactivity of the Sn dimers is also visually noticeable when comparing the area density of reacted sites in STM, see figure 4.9. The tin terminated surface contains notably fewer reacted dimers despite having
Figure 4.8: Peak analysis of 30 and 105 L ethylene deposited on Si(001)/Sn -2×2 (spectra from figure 4.7, background signal subtracted). Identified were four components: 284.5 eV corresponding to ethylene adsorbing on Sn dimers with a visible increase from 30 to 105 L, a saturated component at 283.8 eV corresponding to ethylene adsorbing on residual Si dimers, 286.3 eV is attributed to interaction with contaminant oxygen species, and 283.1 eV was not specified.

<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
<th>Si</th>
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<tr>
<td>ethylene exposure [L]</td>
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<td>1.5</td>
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<tr>
<td>counted adsorbed ethylene molecules</td>
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<td>171</td>
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<tr>
<td>area (nm²)</td>
<td>48×48</td>
<td>12×12</td>
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<tr>
<td>calculated relative reactivity of Sn dimers</td>
<td>0.02</td>
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Table 4.1: Statistics of adsorption of ethylene molecules on Si(001) -2×1 and Si(001)/Sn -2×2
been exposed to double the exposure of the clean Si(001)–2×1 surface. We counted ~120 molecules after 3 L dose per 50×50 nm² on Si(001)–2×1 in contrast to ~120 molecules per 10×10 nm² area after a 1.5 L dose on Si(001)–2×1 (for parameters and exact values see table 4.1). The relative reactivity of Sn dimers can be estimated using

\[ R = \frac{n_{Sn}}{L_{Sn}} / \frac{n_{Si}}{L_{Si}}, \]  

(4.2)

where \( n \) is the area density of adsorbed ethylene molecules on the Si(001)/Sn–2×2 and Si(001)–2×1 areas and \( L \) applied ethylene dose. The established value 0.02 ± 0.01 is qualitatively in good agreement with the values established by PES. Considering the experimental and systematic uncertainties, we estimate the reactivity of Si(001)/Sn–2×2 to be two orders of magnitude lower than that of the clean Si(001)–2×1.

A distinct feature of ethylene adsorption on Si(001)–2×1 is the formation of locally ordered structures attributed to short range interactions of adsorbed ethylene molecules. Coverage in our STM experiments was not high enough to observe an eventual formation of locally ordered structures on Si(001)/Sn–2×2, but we noticed that there appears to be a tendency of ethylene to adsorb on outer chains of compact 2×2 areas leaving larger areas void of ethylene, and to adsorb in the proximity of other molecules (see figure 4.9), although an analysis from higher coverage would be needed.
to confirm this notion. A potential factor playing role might be the degree of dimer tilt. Glueckstein et al. [110] observed that two adjacent, 2a spaced Sn chains experience a modulation of dimer tilt along the part of their length where they are adjacent. Moreover, the dimer tilt varies along the length of the chain which the authors attribute to stress relaxation. The modulations of the dimer tilt might therefore play part in the adsorption process by rendering some dimers more susceptible to ethylene adsorption. Reaction of a Sn dimer with ethylene might also influence the stress relaxation along the chain and therefore also influence the reactivity of some dimers too, but theoretical calculations and better resolved experiments with higher coverage are needed.

Another factor in the adsorption might be the size of the bandgap. As shown by Fan et al. [103], concerted [2+2] cycloaddition of ethylene on C–C dimers of diamond C(001) (the dimers are flat), does not occur whereas it can occur on Si(001). The authors attribute this difference to a small surface bandgap present in Si dimers (~0.5 eV) as opposed to a big surface bandgap in C(001). The electronic structure of Sn dimers as measured by STS (akin to other group III and IV ad-dimers on Si(001) – 2×1) exhibits a larger surface bandgap ~1.0 eV. It is thus possible that the lower reactivity of Si(001)/Sn–2×2 for ethylene in comparison with Si(001)–2×1 might be caused by a combination of factors, including a larger surface bandgap, modulations of dimer tilt and possibly also the absence of dynamic flipping in Sn dimers, but further theoretical and experimental research is needed to provide a more conclusive answer to their particular role/influence.

Moving beyond the first layer

So far we have investigated the interaction of ethylene with a single layer of Sn. Epitaxial growth of Sn on Si(001)–2×1 at RT has a complex nature and falls within the Stranski-Krastanov mode. Additional deposition of Sn leads to the formation of further 2D layers until ~2 ML when 3D clusters start to form [110]. The structure of 2D layers differs from the saturation layer, however their atomic structure is not known. They show a local 3×3 order in STM, but our LEED measurements (in agreement with earlier studies) showed a 1×1 pattern of the underlying Si substrate with increased diffuse background implying the absence of a long-range order and/or that there is a considerable disorder within the layer.

We have extended our PES studies to include such a layer. A representative C 1s spectrum of ethylene deposited onto a 2 ML layer of Sn is shown in figure 4.10. The figure also contains reference spectra from two other coverages of Sn: a subsaturation coverage marked as <0.5 ML and a complete saturation layer Si(001)/Sn–2×2 (as described earlier). It provides
4.3 Interaction with Tin Passivated Si(001) – $2 \times 1$

Figure 4.10: C 1s spectra of ethylene on Si(001)/Sn with variable Sn coverage: Subsaturation coverage (<0.5 ML), saturation coverage $2 \times 2$ (0.5 ML) and Sn multilayer 2ML. The difference of signal before and after ethylene deposition onto Sn multilayer is negligible.

an overview of ethylene interaction with the Si(001)/Sn system for various Sn coverages.

The most intense peak arose from a 10 L dose on Si(001)/Sn with subsaturation coverage. The maximum of the peak located at 283.9 eV indicates that the biggest contribution of the signal arises from ethylene adsorbing on the available Si dimers uncovered with Sn dimer chains. This is in agreement with the conclusion that the sticking probability of ethylene on Sn dimers is considerably lower than on the Si dimers of the clean Si(001) surface. This fact is further supported by the second most intense peak in this comparison: The earlier discussed peak of 30 L on Si(001)/Sn – $2 \times 2$ is notably less intense despite a higher ethylene dose. The least intense peak in the comparison stems from the interaction of 50 L of ethylene with 2 ML on Si(001). The peak intensity does not differ from the C 1s peak of the unexposed sample — apart from a subtle broadening around 283.8 eV and a rise of the component at 286.3 eV attributed to interaction with oxygen. This shows that multilayers of Sn on Si(001) are inert to ethylene adsorption or that their reactivity is further decreased. It is possible that the lack of adsorption is caused by an absence of π bonds in the layer, however understanding of the atomic structure of the layer is necessary to confirm or reject this speculation. The broadening around 283.8 eV is likely caused by ethylene adsorbing at defect sites in the Sn multilayer since the Sn layers are not smooth and perfectly ordered and the broad flat background spectrum of the unexposed
4.4 Interaction with Indium Passivated Si(001) – 2×1

Indium deposited at RT onto Si(001) – 2×1 also assembles into linear chains with the parallel ad-dimer structure growing perpendicular to the underlying dimer rows of the silicon substrate. The mobility of indium atoms at RT is much higher than of Sn atoms and they can easily detach and attach to chain ends. Because of this, the chains often change length during scanning. Odd chain ends (i.e. single atom instead of a dimer) appear very bright since they have a much higher DOS. Indium atoms also attach and detach underneath the tip during scanning which causes imaging artefacts in the direction of the fast scanning axis and which makes observation at high indium coverages difficult.

An example of 0.3 ML In/Si(001) surface is shown in figure 4.11. At this coverage, the indium rows are 3a spaced, but convert to 2a at higher coverages (cf. figure 4.13). The filled states image (left) contains bright spots due to odd chain ends.

After exceeding 0.5 ML, the 2×2 layer is compact and local 3×3 order within the In layer occurs, see figure 4.13, which has been attributed to rebonding of In atoms within the In layer [116].

The geometric and electronic structure makes indium dimers a suitable system for studying the role of the π bond in the adsorption of ethylene. Indium dimers are flat and lack a π dimer bond. If the proposed nonconcerted [2+2] cycloaddition mechanism of ethylene adsorption on Sn dimers

Figure 4.11: STM images of 0.3ML In on Si(001) in filled (left) and empty-states (right). Odd chain ends appear as bright terminations, the white arrow denotes a defect between the 3a spaced In chains and the black arrow points to C-defects within the In chain. ±1.5 V, area 20×15 nm², 50 pA

multilayer stems from carbon contamination thermally desorbed from Sn evaporators during Sn deposition and a partially growing permanent carbon contamination of the sample after many cycles of flashing and ethylene depositions.
Figure 4.12: C 1s spectrum of Si(001)/In substrate with variable indium coverage exposed to ethylene: clean Si (blue), subsaturation (green), and saturation (red and black).

Figure 4.13: 0.6 ML of In: After the completion of the 2×2 saturation layer, local reordering with 3×3 periodicity occurs. −1.5 V (filled states), 50×50 nm², 50 pA.
is valid, the absence of the π dimer bond in In dimers can be expected to render the Si(001)/In−2×2 inert for ethylene, unless other mechanisms get involved such as a scission of the dimer bond.

During our STM experiments we did not observe any changes in the In dimers after ethylene deposition. This is in agreement with the assumption that the In are inert for ethylene. To confirm this, we performed additional PES experiments summarized in figure 4.12. The figure compares the C 1s spectra from a clean Si(001)−2×1 substrate with 10 L (for reference), Si(001)/In with less than saturation coverage of In exposed to 50 L, Si(001)/In−2×2 with saturation coverage before and after being exposed to 50 L of ethylene.

The most intense peak is the reference peak of 10 L dosed on Si(001)−2×1 surface. The second most intense peak stems from 50 L deposited on In/Si(001) with the incomplete saturation layer. The maximum of the peak located at 284.0 eV indicates that ethylene adsorbed on Si dimers in residual areas not saturated with In dimers. The strength of interaction of ethylene with In dimers can be inferred by comparing spectra recorded before and after dosing 50 L onto Si(001)/In−2×2 with the complete saturation layer. Nearly no increase of peak intensity is visible after ethylene deposition apart from a subtle increase around 284.7 eV which probably stems from ethylene adsorbing at various defect sites in the indium layer. This observation is in agreement with the STM experiments and confirms that indium dimers of Si(001)/In−2×2 are inert to ethylene adsorption.

4.5 CONCLUSIONS AND FINAL REMARKS

Our experiments have shown how an ultra-thin layer of group III and IV metal can modify the chemical reactivity of the Si(001) surface for a small unsaturated molecule. The building blocks of the Sn (In) layer are linear chains consisting of tilted (flat) dimers with unsaturated (saturated) character.

This saturated (unsaturated) character facilitates (inhibits) the adsorption of ethylene at RT proceeding via [2+2]-like cycloaddition. The geometric constraints of the Sn layer furthermore allow some selectivity since only one adsorption configuration of ethylene has been identified (on-dimer) whereas ethylene can additionally bond across two adjacent Si dimers of the clean Si(001)−2×1 surface.

On the other hand, the reactivity of the Sn layer is reduced by several orders of magnitude with respect to the Si(001)−2×1 surface. While it might

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2 The indium coverage slightly exceeded 0.5 ML and corresponding to the situation shown in figure 4.13
be desirable for some applications, it means that attachment (functionalization) to an isolated Sn dimer chain ought to be difficult since the molecules will preferentially adsorb on the surrounding Si substrate.

The indium layer has proved inert for the adsorption of ethylene and might be considered as a method of surface passivation. Unlike the hydrogen or chlorine passivated Si(001) surfaces, the indium atoms still possess an empty $p_z$-like orbital which suggests that they might still datively bind Lewis bases such as ammonia or water. On the other hand, we noticed during our SRPES experiments that the signal from oxygen contamination (attributed to water) did not rise after indium deposition so such bonding possibly does not play a major role, but rigorous research would be needed to provide a more conclusive answer.

The use of indium as a decoupling layer for deposition of larger molecules has a disadvantage: the indium chains change at RT as indium atoms detach from chain ends and re-attach elsewhere. This effect can be suppressed with cooling. Alternatively, other group III metals forming dimer chains on Si(001)–$2 \times 1$ could be employed since the same chemical considerations regarding their saturated character should hold. In our first hand experience, aluminium — despite its strong chain stability — is not very suitable as it is difficult to achieve a well ordered layer since the dimer chains grown at room temperature are not perfectly linear. This effect can be minimized by deposition at elevated temperatures, but requires good control over temperature and deposition rate.

It might be useful to finish this part with some closing remarks regarding the drawbacks and problems which we encountered and realized during the course of the experiments. In contrast to the clean Si(001) surface, the Sn/In terminated surfaces proved very difficult to study. The surface gap of the Sn and In terminated surface is broader than of the clean Si(001). This makes observation in STM at small voltages (< 1 V), which were determining in our observations, very difficult: the tip is brought very close to the surface and easily collides with it resulting in loss of resolution. The Sn and In layers are furthermore far from perfectly ordered which not only makes the characterization of observed features more complicated, but also further increases the risks of tip collisions.

Another difficulty turned out to the observation of the Si(001)/Sn–$2 \times 2$ in the empty states. While observation in the filled states is relatively easy to accomplish, reversing the bias would often immediately crash the tip and the hard won resolution was lost. This seemed to happen when the surface was covered with a significant amount of Sn. The $I - V$ curve would often exhibit a diodic character preventing a successful observation in the empty states. I hazard a speculation that some Si atoms would be transferred to the tip resulting in the development of a Schottky barrier. In combination with small DOS in the empty states of the substrate (let alone at a small bias) this
would have detrimental impact on the resolution in the empty states. This was not the case of the indium terminated layers since those contain a high density of unoccupied states related to the empty $p_z$-like orbitals. This experience has taught us a lesson that while interesting processes might proceed in a system, they can be very difficult to observe with STM if the substrate is not sufficiently well ordered and/or conducting. So when we expanded the apparatus to allow the deposition of larger molecules (copper phthalocyanine), we chose a conducting surface which made observations in STM easier. The results of these experiments are summarized in the next chapter.
The results of this chapter were published in *J. Phys. Chem. C* 2019, 123, 16232–16238.

Phthalocyanines (Pc’s) are a group of macrocyclic heteroaromatic molecules synthesized for the first time nearly a century ago. The molecule consists of four aza-bridged (= –N—) isoindole units forming a ligand with −2 oxidation state able to chelate a very wide range of elements, predominantly metal atoms.

The metal-free phthalocyanine contains two hydrogen atoms in the central cavity (H₂Pc). Depending on the size of the central +2 cation, metallated Pc’s can be planar, e.g. CuPc shown in figure 5.1, or non-planar if the central atom is too large to fit into the cavity (eg. SnPc [118]) which sometimes offers the possibility of sandwiching a large central atom between two Pc ligands akin to ferrocene, e.g. when choosing lutetium as the central atom (LuPc₂) [119].

Spectroscopic studies have shown that instead of the isoindole or its pyrrole subunits, the properties of Pc’s can be characterized in terms of the benzene moieties and an 18 π-electron di-anion model of a 16 atom main conjugated pathway [120–122]. The properties of phthalocyanines can be modified either by substituting the central atom for another element or by substituting the hydrogen atoms at its periphery [123]. The insoluble
Interaction of Cupc with tin and indium passivated Si(111)

Phthalocyanine can, for example, be made soluble in water by substituting hydrogen for carboxylate or sulphonate groups or in organic solvents with aliphatic chains [124, 125].

The industrial interest into phthalocyanines stems from its intense bluish colouration which predisposes them for applications as dyes or pigments [126], aided by the fact that the molecule is very stable. The application range is not limited to pigments only, but the molecules are being used for energy conversion in dye-sensitized solar cells [127].

Pc’s are also referred to as synthetic analogues of porphyrins, colourful molecules consisting of four methine (= =CH—) bridged pyrrole units which are central parts of important proteins (haemoglobin or chlorophyll) performing fundamental biological processes such as oxygen transport or photosynthesis. The industrial preference for using Pcs’s over porphyrins stems from their higher stability, cheaper production costs and more vibrant colouration [126].

Owing to their excellent photo-absorption properties and diverse coordination and structural properties, phthalocyanines are being used in light emitting diodes (LED’s) [128], organic thin film transistors [129] or in organic photovoltaics as both n- and p- type semiconductors [130]. They also exhibit rich catalytic properties [131] and were proposed for gas sensing [132, 133], as optical limiting elements in non-linear optics [134] or even proved to be able to function as potential q-bits for quantum computing [135].

A particularly intriguing aspect of phthalocyanine application is the possibility of using them as sensitizers in photodynamic therapy of skin cancer in medicine [136]. For me, this particular application highlights human ingenuity: Phthalocyanines absorb strongly in the far-red spectrum between 600 and 850 nm which are the wavelengths that can pass through skin tissue. Skin can therefore be irradiated with red light, which is absorbed by phthalocyanine which could be delivered in virus-like particles [137]. The excitation is passed on to another complex which converts dissolved triplet state O₂ molecules into the cytotoxic singlet state damaging the tumour cells [138]. This approach is therefore very local and specific.

Interaction of CuPc with semiconductor surfaces

The presence of dangling bonds on silicon surfaces leads to strong chemisorption of CuPc. The molecules adsorb in multiple, flat-lying configurations, their mobility is severely limited or absent and no molecular ordering is observed [139]. On Si(001) – 2×1 the molecules have several adsorption configurations, some of which are symmetric, on Si(111) – 7×7 the adsorption configurations are asymmetric and the molecules are bound stronger [140, 141]. In contrast, on various III–V semiconductors (III terminated) the inter-
action is weaker and phthalocyanines form ordered structures where the central metal atom plays a strong role [139].

On the hydrogen passivated Si surfaces, STM observations revealed that CuPc and CoPc are very mobile, but that they can be anchored on individual (dehydrogenated) dangling bonds. Based on the size of observed features, the interaction was attributed to interaction via the benzene moiety or the central Cu atom. Interaction via the central atom was not observed for CoPc [142, 143].

On the silver passivated Si(111)/Ag - $\sqrt{3} \times \sqrt{3}$ substrate, the interaction is weak too. The molecules freely diffuse and ordering observed when a full layer completes [38]. On the thallium passivated Si(111)/Tl - $1 \times 1$ substrate, CuPc forms ordered domains in the presence of an aligned electric field and they can be switched with voltage pulses [53].

This brief overview shows how strongly the nature of CuPc interaction with silicon substrates depends on the termination of the surface: from strong chemisorption on the bare surfaces to weak interaction and high mobility on the Ag, H and Tl passivated surfaces.

Our experiments with the tin terminated Si(111) surface present an intermediate case. The main focus is on the Si(111)/Sn - $\sqrt{3} \times \sqrt{3}$ and less attention is paid to the Sn - $2\sqrt{3} \times 2\sqrt{3}$ reconstructed substrate. In contrast to the large complex unit cell of the bare Si(111) - $7 \times 7$ surface where the Si are not equivalent, the Sn - $\sqrt{3} \times \sqrt{3}$ reconstruction is very simple. It is an adlayer where all Sn atoms are equivalent and each of them contains an unpaired electron in its dangling bond. Moreover, substitutional defects within the layer offer isolated sites with different dangling bond state occupancies. The Si(111)/Sn - $\sqrt{3} \times \sqrt{3}$ substrate thus presents a way of introducing a less complex system of dangling bonds to Si(111) - $7 \times 7$ surface which can serve to study various factors playing a role in the adsorption of phthalocyanine.

5.1 EXPERIMENTAL

The Si(111)/Sn - $\sqrt{3} \times \sqrt{3}$ substrates were prepared in-situ by depositing $1/3$ ML (1 ML = $7.83 \times 10^{18}$ atoms/m$^2$) of Sn atoms (purity 99.999%) onto Si(111) samples held at RT. The amount of deposited material was measured with a vibrating quartz crystal monitor. The Sn - $\sqrt{3} \times \sqrt{3}$ reconstruction was created by resistively annealing the sample to 600 °C for two minutes. Afterwards, the sample was let to cool down to RT. The temperature range when the reconstruction forms is broad (~390–860 °C [144]), but according to published information this procedure yields substrates with the lowest defect density of about 3 % [145].

To maintain well defined initial conditions for the formation of the Sn - $\sqrt{3} \times \sqrt{3}$ reconstruction, the Si(111) - $7 \times 7$ reconstruction was always recre-
ated before the tin deposition. This was done by flashing the samples to 1200 °C followed by controlled slow decrease of heating power over 10 minutes and then let to reach RT over 20 minutes. Employed monocrystalline Si(111) samples were heavily doped with antimony (n-type) yielding resistivity better than 0.014 Ωcm. According to the manufacturer Virginia Semiconductor the crystals were grown with the Czochralski method and dopants were added directly to the melt. The manufacturer refers to a publication [146] stating that this corresponds to dopant density $10^{18} - 10^{19}$ per cm$^3$ while the Si atom density is $\sim 5 \times 10^{22}$ cm$^{-3}$.

CuPc (99.9 % purity) was deposited onto samples held at room temperature from a resistively heated boron-nitride crucible. The experimental STM system was expanded in order to accommodate the new CuPc evaporator, but the geometry of the system did not allow for the molecules to hit the vibrating quartz crystal. The deposition rate of CuPc evaporators was therefore assessed from already performed experiments. Due to the very brittle nature of bulk CuPc material (it forms brittle needle-like structures due to planar stacking of the molecules), the deposition rate tends to decrease over time once the weaker bound phases have been deposited so increased heating power is needed.

The CuPc evaporator was degassed at ~200 °C for several hours in UHV and several dummy depositions prior to deposition were made in order to remove atmospheric contamination. The pressure in the system during the deposition remained in the $10^{-8}$ Pa range.

**STS parameters:** The presented STS spectra were obtained with the lock-in technique under the following settings: duration: ~10 s per spectrum, modulation amplitude 50 mV, modulation frequency 938 Hz. The spectra were recalibrated so as to fulfil $\int (dI/dV)dV = I$ and therefore the $(dI/dV)/(I/V)$ is dimensionless. The spectra were processed with a technique by Prietsch et al. [147] which removes noise near the Fermi level: the division by $I/V$ is modified as $[(I/V)^2 + c^2]^{1/2}$ where $c$ is a small parameter 0.01. To improve the dynamic range near the Fermi level, the tip-sample distance was continuously varied as $s = s_0 - a(\|V_0\| - |V|)$ where the tip was fixed at $s_0$ defined by the feedback parameters $V_0 = -2.5$ V and $I_0 = 100$ pA and $a = 0.1$ nm/V [148]. Applying this procedure did not shift any peaks. The known spectra of the substrate were regularly measured so as to ensure the credibility of molecular spectra. The drift was electronically compensated in all three dimensions.

**5.2 Si(111)/Sn−√3×√3 R30° surface**

Figure 5.2 shows the Si(111)/Sn−√3×√3 R30° serving as a substrate for the deposition of CuPc (R30° hereafter omitted). A typical filled-states STM image is shown in (a) and the structural model of the surface in (b). Sn
(a) Typical filled-states STM image of Si(111)/Sn-$\sqrt{3}\times\sqrt{3}$ surface containing Sb substitutional defects (Sb), vacancies (V), the single (1) and double (2) Si substitutional defects and the proposed sublayer Sn substitutional defects in the first (Sn$_1$) and second (Sn$_2$) Si layer. 300 pA.

(b) The model of the surface. Sn-$\sqrt{3}\times\sqrt{3}$ and the base $1\times1$ cell marked. The side view shows the dangling occupancy of the dangling bonds.

(c) STS spectra of the Sn atom, Si and Sb defect and above the vacancy defect (V).

Figure 5.2: Overview of the Si(111)/Sn-$\sqrt{3}\times\sqrt{3}$ substrate.
atoms reside above the 2nd layer Si atoms in the \( T_4 \) positions. They are \( \sigma \)-bonded to the three underlying 1st layer Si atoms with bonding geometry corresponding to \( sp^3 \)-hybridization. The surface unit cell is rotated by \( 30^\circ \) with respect to the underlying \( 1 \times 1 \) unit cell of the 1st layer Si atoms. The spherical appearance of Sn atoms in STM stems from their \( p_z \)-like orbital containing an unpaired electron sticking out of the plane of the surface.

The STM image (figure 5.2a) reveals various point defects found within the surface. The image contains approximately 70 point defects for 2000 positions corresponding to a defect density \( \sim 3.5 \% \). The defects within the surface were studied in detail by Jemander et al. [149]. They identified five types of defects and attributed them to substitutional Si atoms, substitutional Sb atoms, vacancies and two minor defects were attributed to Sn substitutional atoms within the 1st and 2nd Si layer respectively (Sn\(_{1,2}\)).

- The vacancy defect (V in 5.2) is undecorated and appears as a missing Sn atom within the layer.

- The well established Si substitutional defect appears in the filled-states images as a decorated petal-like vacancy: the vacancy is in the position of the Si atom which is surrounded by brighter Sn atoms [150, 151]. The electronic structure of the defect has been studied via DFT by Kaminski et al. [152] who found that the Si atom redistributes its unpaired electron from the \( p_z \)-like orbital among the neighbouring Sn atoms. The increase of charge density by \( 1/6 \ e \) is accompanied with upward vertical displacement resulting in brighter appearance in STM. This effect can be seen in the subfigure (c) summarizing the results of our tunnelling spectroscopy measurements above the surface and the significant defects. The spectrum of a Sn atom in the unperturbed Sn \(- \sqrt{3} \times \sqrt{3} \) areas contains a nonzero DOS at the Fermi level and a peak at \(-0.4 \) eV and \(0.6 \) eV. The spectrum measured above the Si atom has a similar, albeit less intense peak at \(-0.4 \) eV, but contains high DOS above the Fermi level with peaks at \(0.5 \) and \(1.0 \) eV in agreement with the calculated depletion of its \( p_z \)-like valence orbital.

The DFT calculations furthermore studied the impact of multiple Si substitutional atoms on the electronic structure of the surrounding Sn atoms and found out that there is an even greater vertical upward displacement of those Sn atoms adjacent to multiple Si atoms. The manifestation of this effect can be seen in the STM image on the double Si defect where the Sn atoms neighbouring to both Si atoms are more intense than the other adjacent decorated Sn atoms.

- The Sb substitutional defect appears as bright atom surrounded by darker atoms. Jemander et al. [149] and Uhrberg et al. [153] attributed this defect to Sb substitutional atom in the layer based on STM and AES measurements. The nature of this defect has not been yet conclusively
confirmed with DFT, but Sb substitution atoms in the bare Si(111)−2×1 surface — which is obtained without annealing by in-situ cleaving in UHV conditions — have later been identified and studied with STM and DFT [154].

A substitutional, tri-σ-bonded pentavalent atom should posses a lone electron pair in its $p_z$-like valence orbital (filled dangling bond) which is supported by our STS spectrum exhibiting a pronounced peak below the Fermi level at $−0.8$ eV and zero DOS at the Fermi level. Jemander et al. moreover stated that they observed an increase of Sb defects after repeated annealing. The Sb dopant density in their study was comparable to the dopant density in our samples. Annealing of heavily Sb-doped Si monocrystalline samples — as performed in our experiments too — leads to out-diffusion of Sb atoms towards the surface and eventually to a dopant loss [155] in agreement with the observation by Jemander et al. The authors of the study note that the effect of out-diffusion was even more pronounced for the Si(111) surface than for Si(001). We consider this to be sufficient evidence to accept the interpretation of the type B defect as Sb substitutional atom.

• The proposed Sn substitutional defects in the underlying Si layers (Sn$_{1,2}$) are inconspicuous and appear as a slightly more intense single Sn atom or a triplet of Sn atoms (marked in the image) and require truly great resolution of the tip to be imaged.

**Electronic structure of the substrate**

The Si(111)/Sn−$\sqrt{3} \times \sqrt{3}$ surface has been subject of scientific interest since the related Sn/Ge(111) system undergoes a transition from Sn−$\sqrt{3} \times \sqrt{3}$ to Sn−3×3 reconstruction at low temperatures [156] which has been later explained by stabilization with Ge substitutional defects [157]. For the Si(111)/Sn system, the PES spectra revealed two Sn 4d components at odds with the model of Sn atoms equally occupying the T$_4$ sites of Sn−$\sqrt{3} \times \sqrt{3}$ [153], but no such transition to Sn−3×3 has been observed in STM even at very low temperatures as low as 6 K [158]. Jemander et al. [149] suggested that the Si defects may play a role in such an eventual transition to Sn−3×3 on Si(111), but the aforementioned DFT study by Kaminski et al. [152] ruled such stabilization out.

The electronic structure of Si(111)/Sn−$\sqrt{3} \times \sqrt{3}$ surface studied with STS and PES at RT and low temperatures [159] was found to undergo a conducting-semiconducting transition below 70 K. At 5 K, the STS spectra have zero DOS at the Fermi level and a rise of intensity at ±1.5 eV whereas at RT the spectra have a metallic character with nonzero DOS at the Fermi level and two peaks at $−0.4$ and 0.4 eV. Our STS spectra of the Sn surface show
a slight shift of the empty state peak to 0.6 eV, but otherwise they exhibit all the features of the spectra (such as the minima at ±1.0 eV) [160]. The semiconducting-conducting transition of the system at low temperatures is in agreement with predicted Mott-Hubbard ground state calculated for the system [161] and the authors suggest that doping of the Sn layer with alkali metals might facilitate superconductivity.

The metallic character of the surface at RT can be explained by simple electron-counting arguments where the dangling bond of Sn is half-filled and thus can participate in tunnelling schematically shown in the side view of figure 5.2b. The scheme furthermore shows the DB occupancy of the defects and visualizes the origin of the observed defect decoration in STM:

For the Si defect — the unpaired electron in the dangling bond of Si is redistributed among the adjacent Sn atoms. The charge density on those atoms is increased (formally increased by 1/6e each) according to [152] and the atoms are vertically displaced upwards.

For the Sb defect — Sn atoms adjacent to the Sb substitutional atom appear darker in filled-states STM images while the central Sb atom is very bright. We propose that a similar effect occurs on the Sn atoms. In our understanding, the filled dangling bond of Sb presents a local surplus of electric charge in the grid or half-filled dangling bonds on the surface. It exerts a stronger electric field to which the adjacent Sn atoms respond by partially redistributing their charge towards the underlying Si atoms. This allows the field of the Sn cores to be screened less and thus to compensate the extra field of Sb lone pair. In this simple view, we expect the decrease of electron density of the Sn atom to be accompanied with vertical lowering to assume a more sp² character which may explain the observed decoration of the Sb defect, as is also schematically shown in figure 5.2b.

The vacancy defect shows no decoration and its STS spectrum largely resembles the spectrum of the Sn atom except that there is a flat DOS above the Fermi level and a sharp rise at ~1.1 V.

5.3 Interaction of Cupc with Si(111)/Sn – √3 × √3

CuPc molecules deposited onto Si(111)/Sn – √3 × √3 are displayed in STM as bright objects that are often found clustered in disordered surface areas. The structure of such areas is complex and CuPc molecules adsorbed in such areas exhibit large variability preventing their classification according to shape observed in STM. Any symmetry element of the free CuPc molecule — belonging to the D₄h point group — is lost after adsorption in such areas which hints at a complex interaction. In the following, we shall therefore focus on the isolated molecules where some level of classification is possible.
5.3 Interaction of CuPc with Si(111)/Sn−√3 × √3

5.3.1 The role of surface defects

During the course of our experiments we developed a notion that the molecules are adsorbed on surface defects. Some of the reasons was the preference of CuPc to adsorb in disordered areas which means that they are stronger bound there than on the unperturbed Sn−√3 × √3 substrate but also the visual decrease of defects after CuPc deposition, see figure 5.3.

We have also directly observed, although on rare occasions, a defect underneath the adsorbed molecule. One such observation is shown in figure 5.4a, displaying a sequence of three successive STM images. The first image (left to right) shows two CuPc molecules, one of which is adsorbed next to a Si substitutional defect. In the second image we observe the appearance of a part of a molecular lobe after the Si defect has been scanned. This indicates that adsorption of CuPc has occurred which is shown in the last image. The arrow points to the centre of the Si defect and the configuration of the newly adsorbed CuPc molecule is different from the other two molecules.

Hopping of CuPc between two (3a spaced) Si defects is displayed in a set of sequential STM images in figure 5.4b. The images show an area containing several Si defects and two CuPc molecules. The molecule on top-right is bright (red) and remains stationary throughout the observation. The molecule on its left is a lot less intense and hops to the Si defect above whilst uncovering an Si defect underneath.

The molecule hops back onto the initial Si defect, but is not in the initial configuration — its lobes are poised towards the stationary molecule. The
5.3 Interaction of CuPc with Si(111)/Sn-$\sqrt{3}$×$\sqrt{3}$

(a) Direct observation of adsorption of CuPc on a Si defect during scanning. −1.5 V (filled states), 80 pA.

(b) Hopping of CuPc between two adjoining Si defects. −1.3 V (filled states), 80 pA.

Figure 5.4: Direct observation of Si defects underneath an adsorbed CuPc molecule.

switch to the original state occurs before the last image when the molecule has assumed the original state.

Both described events were rare. The hopping between two Si defects was moreover observed with a tip that was unstable during the backward motion when the empty-states picture was obtained. It is thus likely that the molecule was destabilized by the presence of other defects and made hop by the interaction with the unstable tip.

Other hopping of molecules between defects was not observed. Adsorbed molecules are very stable and survived all our attempts of directed tip manipulation which would ultimately always lead to surface degradation.

The geometry of our apparatus did not allow to deposit CuPc under the tip during scanning. So in order to correlate the defect density with adsorbed molecules, we performed an experiment when we established the density of point defects before the deposition of CuPc and deposited an estimated 1:1 amount of CuPc molecules. The deposition rate of the CuPc evaporator was assessed from previous measurements.

The results are summarized in figure 5.5: The as-prepared Si(111)/Sn-$\sqrt{3}$×$\sqrt{3}$ substrate is shown in figure 5.5a. The surface contains predominantly Si defects. Less frequent are Sb defects, which do not show the central Sb atom as a protrusion but as a depression (This was due to altered tip imaging conditions — the Sb defect is displayed without the central protrusion usually at −0.5 V [149]). The least frequent defects are vacancies (encircled) shown typically as undecorated missing Sn atoms.
5.3 Interaction of CuPc with Si(111)/Sn - $\sqrt{3} \times \sqrt{3}$

(a) The substrate before CuPc deposition with Si > Sb > vacancy defects. $-1.0 \text{ V (filled states), } 60 \times 60 \text{ nm, } 400 \text{ pA}$

(b) The same substrate after depositing an amount of CuPc (approximately) matching the defect density. $-1.0\text{ V, } 40 \times 40 \text{ nm}^2, 400 \text{ pA}$

(c) The tip conditions have changed so the clustered molecule areas are imaged with altered contrast (darker). Large defect-free areas are visible. The noisiness is more visible in the upper part of the image. $-1.0 \text{ V (filled states), } 30 \times 30 \text{ nm}^2, 400 \text{ pA}$

(d) Some defects remain as shown in the encircled area (containing a Si and vacancy defects). Rectangle frames a Sb defect. $-1.0 \text{ V (filled states), } 30 \times 30 \text{ nm}^2, 400 \text{ pA}$

Figure 5.5: Higher coverage of CuPc molecules sealing point defects (filled-states images).
The image after CuPc deposition (figure 5.5b) shows disordered bright clusters of CuPc. There is also a considerable noise present when scanning over these clusters and some of the bright objects slightly change position within these clusters between images. The black area in the bottom left corner is very noisy (suppressed by image processing) and consist of a lower lying terrace with Sn$_{-2\sqrt{3} \times 2\sqrt{3}}$ reconstruction. The noise in the images has been suppressed with various image-processing techniques leading to occasional smearing artefacts.

The molecular clusters are separated by areas void of molecules containing very few defects. This is better visible in the figures 5.5c,d which show a different contrast of the molecular islands due to a change of the scanning tip conditions. The image (c) contains large CuPc-free areas containing almost no defects while there are some remaining defects visible in the image (d). The image (d) has been included in addition to (c) to show that despite the change of imaging contrast, the resolution of the tip remained sufficient to resolve point defects within the surface. The encircled area contains one Si substitutional defect and three vacancies. The rectangle frames a feature typical of a Sb defect (bright spot) which were also occasionally observed in the CuPc-free areas.

The images show two things:

- CuPc molecules do not form locally ordered structures,
- The density of Sb and Si defects has significantly decreased.

One would expect a different topography if the the molecules adsorbed on the unperturbed Sn$_{-\sqrt{3} \times \sqrt{3}}$ areas — the molecules ought to be more evenly distributed on the surface and not leave significant defect-free areas void of isolated molecules. The dominant defects remaining in the CuPc-free areas were vacancies. We therefore conclude that CuPc adsorbs on Sb and Si substitutional defects and does not adsorb on the unperturbed Sn$_{-\sqrt{3} \times \sqrt{3}}$ areas or vacancy defects.

The CuPc clusters did not change shape apart from some switches at their perimeter. The scanning noise observed above the clusters and small rearrangements within them were not accompanied with new molecules adsorbing in the CuPc-free areas on remaining defects. In our understanding, adsorbed CuPc molecules first nucleate on defects and thanks to covalent interaction with the substrate (as discussed in the next section) probably become attractive for diffusing molecules after deposition. Once a critical cluster forms, the molecules are bound in the cluster and cannot leave.

The disordered nature of the clusters and an increase of observed dark areas within them shows that the interaction with the surface is complex. This is hardly surprising since the surface contains Sn atoms with radical nature after all.
As far as adsorption of low CuPc concentration (~5% of a full layer) is concerned though, the CuPc molecules adsorb on Si and Sb substitutional defects.

5.4 ISOLATED CUPC MOLECULES

Adsorption configurations of single CuPc (figure 5.6) can be classified according to their symmetry as:

- asymmetric — very bright (mostly) configurations lacking any symmetry element.
- symmetric — semi-bright objects containing one or two symmetry planes.

Most of the asymmetric configurations are two-lobed objects containing a central trough (depression optically dividing the molecule into two lobes). They are usually very bright, but some lesser bright configurations exist too, such as the three-lobed object marked with asterisk (*) corresponding to the three-lobed configuration of the hopping molecule in figure 5.4b. It is less frequent and thus is a minority adsorption configuration. Another atypical configuration is shown in the top left circle. The top left square shows a peculiar dark triangular area which we observed only on the substrate after CuPc deposition.

5.4.1 Symmetric configurations

We identified two symmetric configurations and based on their appearance in STM images named them as:

- fuzzy (shown in more detail in figure 5.7)
- static (shown in more detail in figure 5.9).

We use the word fuzzy to describe that the molecule appears noisy in STM, i.e. it is displayed with fuzzy streaks always in the direction of the fast scanning axis, which are especially well visible at +0.8 V. The tunnelling current measured above the molecule exhibits two state fluctuations \((I - t)\) and a visual split of the \(I - V\) characteristic may be observed, see figure 5.8. The time constant of these fluctuations is in the order of milliseconds.

The shape of the fuzzy configuration consists of two mirror symmetric lobes separated by a central trough, which is parallel to one of the surface symmetry axes (dashed line). Its symmetry places the adsorption configuration into the \(C_{2v}\) point group, i.e. it contains two perpendicular mirror symmetry planes (marked with \(\sigma\)): one plane contains the molecular trough,
Figure 5.6: Symmetric and asymmetric configurations of CuPc in empty (top) and filled states (bottom). $25 \times 25 \text{ nm}^2$, 100 pA.
Figure 5.7: Fuzzy symmetric configuration resolved at various voltages in the empty (top) and filled-states (bottom). \((\sigma)\) denotes its mirror symmetry planes. Black cross marks position of \(I-V\) and \(I-t\) measurement (figure 5.8). Proposed orientation of CuPc superimposed as an outline over the observed configuration. Asterisk (*) shows the image obtained right after the \(\pm 0.8\) V image of the static configuration in figure 5.9. 100 pA.

Figure 5.8: Current fluctuations in the \(I-t\) and \(I-V\) characteristics measured above the centre of the lobe of the fuzzy molecule (location marked by black cross in figure 5.7).
the other bisects the lobes in two (arrow). All shown symmetric molecules in figure 5.6 are fuzzy.

Figure 5.9: Static symmetric configuration of CuPc resolved at various voltages in the empty (top) and filled-states (bottom). ($\sigma$) denotes its symmetry plane. CuPc outline is superimposed over the ±0.8 V images. The Sb-defect-like appearance of the site at the tip of the arrow can be attributed to interaction with a molecular lobe. (*) After the images where acquired at ±0.8, the voltage was increased to ±2.5 V and the molecule switched into the fuzzy configuration as shown in figure 5.7. 100 pA.

We named the other symmetric configuration ‘static’ as a way of expressing ‘not-fuzzy’, i.e. it does not exhibit any fuzzy streaks nor current fluctuations (figure 5.9). It contains one mirror symmetry plane (marked with an arrow), which is perpendicular to one of the surface symmetry axes (dashed). This symmetry places the static configuration into the $C_\infty$ point group. The appearance of the configuration is rather inconspicuous and consists of two smaller lobes next to a pronounced depression (in filled-states images) separated by the symmetry plane. Also, two Sn atoms adjacent to the lobes are imaged slightly more intense. The tip of the arrow points to a site visually reminiscent of a Sb defect, but this is only a seeming resemblance as we shall show next.

We avoided the word stable when naming the static symmetric configuration because this configuration can switch. Both sets of the static and fuzzy configurations (figures 5.7 5.9) were obtained above the same area. After increasing the voltage from ±0.8 V to ±2.5 V, the molecule switched into the fuzzy state (both images are marked with an asterisk).

Switching among the symmetric configurations is shown in figure 5.10 displaying an image sequence of two symmetric CuPc molecules. The top molecule remained fuzzy throughout. The bottom molecule started off in the

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1 In English, the word ‘static’ is often associated with static noise on TV, which is — ironically — how the fuzzy configuration appears in STM. Unfortunately, none of the synonyms (still, stationary, fixed, constant, steady...) seemed more suitable and ‘stable’ could not be used as explained further on.
Figure 5.10: Transitions between adsorption states of the symmetric adsorption configurations in filled (top) and empty (bottom) states. The top molecule remains fuzzy. The bottom molecule starts in the static state and switches to the chiral counterpart. After raising the voltage to ±3.0 V, the static molecule converts to fuzzy and remains fuzzy. At ±0.5 V the fuzziness is suppressed and the four lobed shape emerges. Asterisk (*) marks an observation of an object transparent in filled states which disappeared in the next image leaving unperturbed Sn − √3×√3 surface underneath. 100 pA.
Figure 5.11: Left: Removal of the fuzzy molecule from figure 5.7. Black-head arrow: start of scanning over the same line above the centre of the molecule while the tip was forced closer to the surface during the backward motion and the feedback was turned off. The white arrow shows the removal event. Right: Unveiled double Si defect after CuPc removal. 100 pA.

static state (left). In the next image, it switched (see arrow) to its equivalent chiral counterpart (mirrored about its depression). The voltage was next increased to ±3.0 V. In the following image, the static molecule switched (see arrow) to the fuzzy configuration and remained fuzzy further on. The last image shows both fuzzy molecules at low bias ±0.5 V: the fuzziness is suppressed and a slight four-lobed shape emerges.

The asterisk (*) marks an object that became very intense at ±3.0 V, but was transparent in the filled-states images as the typical surface pattern was shown at its position. The object disappeared in the next image revealing an unperturbed Sn-√3×√3 surface underneath. However, this event had no effect on the switch from the static to fuzzy state of the bottom molecule since such static-fuzzy transitions were observed without such events in their vicinity.

We have succeeded in removing the fuzzy CuPc molecule shown in figure 5.7 from its adsorption position, see figure 5.11. The tip was brought closer to the sample during the backward motion and the feedback was turned off. During the forward motion the feedback was turned on again. The tip was repeatedly scanning the same line above the centre of the molecule (black-head arrow marks the onset of the single line scanning) until a removal event was observed (white head arrow) revealing an unperturbed double Si effect (both right images). The arrow points to the same site as in figure 5.9 resembling an Sb-defect which means that the Sb-defect-like appearance is an electronic effect of the CuPc molecule interacting with the underlying Sn atom.

When we deposited CuPc onto a sample containing a high density of double Si defects, we observed that nearly all CuPc molecules were adsorbed in the fuzzy symmetric configuration, see figure 5.12. Despite the fact that plentiful single Si defects were available, the molecules occupied preferentially the double Si defects. Moreover, none of the observed molecules were found adsorbed in the static symmetric configuration despite
Figure 5.12: Empty states image of CuPc on a Sn-$\sqrt{3} \times \sqrt{3}$ with a high density of double Si defects. Almost all molecules are adsorbed in the fuzzy symmetric configuration. $+3.0 \ V$ (empty states), $30 \times 30 \ \text{nm}^2$, $100 \ \text{pA}$. 
its being an alternative configuration at this adsorption site. We can draw several conclusions from this observation:

- The double Si defect is the most favourable adsorption site of CuPc on Si(111)/Sn-√3×√3
- The fuzzy symmetric configuration is the most favourable adsorption state of CuPc overall.

We noticed, in line with this observation, that there was a higher probability of the static configuration switching to fuzzy than the other way around. We also tried many times to induce a switch by manipulation with the scanning tip, trying out various approaches such as touching the molecule with the scanning tip, voltage pulses, raising the current, tip approach with various voltage pulses, but none of these attempts was successful.

We never observed a switch directly when scanning over the molecule. The switches always occurred once the molecule had been scanned. We thus conclude that the tunnelling current does not play a role in switch mechanism. We have noticed though that raising the scanning voltage increased the chances of the static configuration switching to fuzzy, but that decreasing the voltage did not initiate a reverse transition. Such fuzzy → static transitions were sometimes observed, but were less frequent.

**Proposed bonding model of the symmetric configurations**

We understand the preference of CuPc to adsorb on the double Si defects to stem from favourable electronic conditions: Each nitrogen atom linking
the isoindole subunits of the CuPc molecule contains a lone electron pair residing in a $sp^2$-like orbital not participating in the aromatic system \([121, 162, 163]\). This allows the nitrogen atom to interact with the depleted $sp^3$-like orbital on the Si atom. While the molecule is diffusing on the surface, the N and Si atoms can electrostatically attract, their orbitals overlap and form a dative bond. A second dative bond can be formed between the second Si atom and the opposite equivalent N atom of CuPc, see figure 5.13. Since the N–N distance of free CuPc (\(~6.7\) Å \([117]\)) matches the separation between the Si atoms (6.65 Å, figure 5.2b), this bonding imparts a geometric strain on the molecule as the resulting out-of-plane bond angle conflicts with the preferred planarity of bonds for aromatic systems, but such bonding does not decompose the molecule.

The central Cu atom is not involved in the bonding as we observed equivalent fuzzy configurations with H$_2$Pc molecules lacking a central metal atom (not shown). A similar bonding model involving Si–N bonds has been proposed for the H$_2$Pc adsorbed on the chlorine passivated Si(111) surface, although applied DFT calculations could not satisfactorily elucidate it \([164]\).

The fuzzy imaging of the configuration appears to be caused by flip-flop motion\(^2\) (similar to the flip-flop motion of Si dimers on Si(001)) of the strained molecule about an axis parallel to the underlying double Si defect. The possibility of hopping between two adsorption sites, as proposed for a reported fuzzy configuration CuPc on Au nanowires on Au-Ge(001) \([62]\), is contradicted by observed square-like lateral dimensions of the symmetric fuzzy configuration. The fuzziness might arise electronically as well, e.g. charge capture or inelastic tunnelling, but charge capture is unlikely due to the high conductivity of the heavily Sb doped sample and the absence of a larger surface gap facilitating the necessary transient charging of the molecule.

For the static configuration we suggest a bonding model obtained by rotating the molecule from the proposed fuzzy state by 45°. This allows both Si atoms to bond to the two linking nitrogen atoms at opposite ends of the same isoindole subunit. The symmetry of the system is now lowered and corresponds to the symmetry of the observed configuration: the $C_{2v}$ symmetry is reduced to $C_s$ with symmetry plane perpendicular to the axis of the Si double defect.

The enhanced Sn atoms next to the small molecular lobes are within the geometric reach of the molecule (cf. superimposed CuPc outline in figure 5.9). A flip-flop motion in this configuration is now suppressed in line with the static appearance in STM. Rotating the molecule by $-45^\circ$ from the proposed fuzzy configuration gives rise to the enantiomeric static

\(^2\) A better expression would be ‘seesaw’ motion, but this is not well established.
configuration in agreement with switch between both static configurations in 5.10.

This proposed model also suggests why there could be a higher probability for the static molecules to switch to the fuzzy state than the other way around. The static configuration may be energetically less favourable than the fuzzy configuration, e.g. due to geometric strain or unfavourable interaction with farther lying Sn atoms, but separated from the lower energetic state by an activation barrier as schematically shown in figure 5.13. Scanning at higher voltages could therefore provide the energy or activate the necessary states required to reach the more favourable fuzzy configuration.

We also considered other bonding models for both symmetric configurations, but the mismatch between the three-fold symmetry of the substrate and the four-fold symmetry of the molecule and the geometric dimensions between the Sn atoms (6.65 Å) impose significant constraints. Some of the considerations are outlined below:

For the fuzzy configuration: The symmetry of the configuration suggests that bonding might proceed with the Sn atoms adjacent to both Si atoms experiencing the biggest increase of charge density [152]. However, the configuration exhibits the most pronounced fuzziness in the centre of its lobes (see image at +0.8 V in figure 5.7), which is above these Sn atoms. The bonding thus has to occur elsewhere. If we disregard the proposed Si–N bonds, the isoindole subunits each would have to bond with one Sn atom symmetrically. In solution, aromatic molecules prefer to undergo substitution reactions rather than addition reactions as addition disturbs the delocalized \( \pi \) electron system providing the molecule with increased stability. The Sn atoms could substitute a hydrogen atom on the isoindole subunits, but we have shown that the molecule is fuzzy and that it can switch to the static configuration and vice versa. Moreover we have removed the molecule showing no sign of surface modification. The proposed Si–N bonded model, on the other hand, is consistent with the mechanism of dative bond formation between Lewis bases and acids, preserves the symmetry of the observed configuration in a simple way and possesses a degree of freedom for a flip-flop motion.

For the static configuration: The static configuration looks strange in STM — it is inconspicuous with a pronounced depression in the filled-states images. Moreover, with CuPc oriented as proposed, the trough displayed along the mirror plane of the configuration bisects two opposite isoindole subunits of CuPc along their own mirror plane in figure 5.9. However, if the molecule is not rotated by 45° with respect to the fuzzy molecule, the same requirements from above for symmetric bonding on two isoindole subunits apply. Such bonding is difficult to propose. Not only would it have to be rather complex, but geometrically it would not account well for both associated features: the Sb-defect-like site and the enhanced neighbouring Sn atoms. On the other
Figure 5.14: High resolution images of the asymmetric configurations of CuPc in the filled (left) and empty states (right). 100 pA.

hand, if the molecule is rotated by 45° with respect to the proposed fuzzy configuration, the Si–N bonding mechanism can be applied too. It satisfies the symmetry requirements and allows for a chiral transition to the other enantiomeric static configuration. Moreover, such bonding does not allow a flip-flop motion of CuPc in agreement with observed static appearance. The $C_s$ symmetry of the proposed bonding ought to disrupt the planarity of the molecule and induce a nodal plane in some of the electronic states which could explain the observed trough along the mirror plane.

In our opinion, the proposed mechanism of Si–N bonds addresses all observed features of the static and fuzzy symmetric configurations in a consistent manner.

5.4.2 Asymmetric configurations

Among the asymmetric isolated molecules we were able to identify two major adsorption configurations. We have labelled them as type A and type B and they are show in figure 5.14. Both are very bright two lobed objects and are very stable: the molecules did not change shape configuration scanning and were never observed to leave their adsorption site or hop aside. They also resisted all our manipulation attempts with the scanning tip in order to make them hop, change adsorption configuration or be removed. Such attempts always resulted in otherwise unobserved structures suggestive of molecular dissociation or surface degradation.

Based on the observation that CuPc adsorbs on Si and Sb substitutional defects, we attribute the type A configuration to CuPc adsorbed on a single Sb defect and type B on Si defect respectively. We derive this assignment
Figure 5.15: Type A configuration imaged at different voltages, STS spectra obtained at various sites of the configuration and a proposed adsorption scheme. CuPc is adjacent to another Sb defect in the bottom voltage-set (marked in the ±1.0 V image with an asterisk), but not in the ±0.8 V image which was a different molecule. 100 pA.

from the observation of CuPc at various voltages and STS spectra measured at significant positions of the configurations.

Type A configuration

Both lobes of the type A configuration are separated with a slightly curved trough aligned (approximately) with one of the surface symmetry axes. A semi-bright feature visually resembling an Sb defect is displayed at the end of one of the elongated lobes. In the empty-state images, this site is resolved as a depression partially covered by the molecular lobe. Based on the tunnelling spectra and the visual resemblance with an actual Sb defect, we attribute this site to a Sb defect as discussed below.
STM images resolved at additional voltages, tunnelling spectra and a proposed model of adsorption are shown in figure 5.15. The spectra from the Sb terminated lobe are shown in reddish colours, spectra from the other lobe are in blue-greenish hues.

Let us first turn our attention to the bottom part of the graph showing the spectra from the vicinity of the Sb defect. The spectrum obtained above the depression displayed in the empty-states image (black) resembles the spectrum of a free-standing Sb defect (orange-dashed): Its peaks below the Fermi level are shifted towards higher energies by 0.3 eV, but above the Fermi level both spectra are nearly identical. The spectrum measured at the edge of the lobe (red) follows the contours of the spectrum from the depression, but we observe an onset of a molecular peak in the (+0.6, +2.0) eV range. This peak is fully developed above the centre of the lobe as shown in the upper part (red spectra). The visual similarity of the Sb-defect-like site of the molecule, its spectral features shared with an Sb type defect led us to propose that it is genuine Sb type defect.

Tunnelling spectra obtained throughout the rest of the molecule showed little variation within each lobe. Below the Fermi level, the spectra of both lobes have a similar shape with two maxima at −0.5 eV and −1.5 eV. The intensity of all spectra — except the topmost positions of both lobes — drop to zero at −0.1 eV opening a gap region which is 0.5 eV wide at the Sb-terminated lobe and 0.7 eV wide at the opposite lobe. The spectral similarity of both lobes is lifted above the Fermi level: The Sb-terminated lobe has two maxima at +0.9 eV and +1.5 eV in contrast to a single maximum at +1.7 eV at the opposite lobe. This spectral character is also reflected in the appearance of the type A configuration — the configuration looks rather homogeneously bright in the filled-states images, but displays a pronounced difference between both lobes (dominated by the Sb-terminated lobe) in the empty-states images.

Since the spectrum of the Sb-defect-site of the configuration is not significantly altered in comparison with a free Sb defect, we propose that the molecule does not covalently interact with the Sb atom itself. Instead, we attribute the reactivity of the site to the altered electronic structure of adjacent Sn atoms. The proposed decrease of charge density (schematically shown in the scheme) renders Sn atoms susceptible to a nucleophilic attack from the diffusing CuPc molecules. This promotes covalent interaction and renders the site attractive for CuPc adsorption.

Type B configuration

The type B configuration, shown in figure 5.16, is imaged as two bean-shaped molecular lobes separated by a slightly curved trough approximately 30° rotated with respect to the one of the surface symmetry axes. In the filled-
Figure 5.16: Type B configuration imaged at different voltages, STS spectra obtained at various sites of the configuration and a proposed adsorption scheme. The arrow marks the position of the Si defect. 100 pA.

states images, a defect-like depression appears at one end of the trough. In the empty-states images, the molecule shows a pronounced asymmetry at +0.8 V when it consists of three lobes: a small lobe neighbours the depression site, two larger lobes separated by the molecular trough are on its opposite end and an eventual fourth lobe next to the depression — expected from the four-fold symmetry of the molecule — is missing at this voltage (‘missing lobe’).

The upper part of the graph contains spectra from the frontal part of CuPc (edge) adjacent to the depression site. The spectrum from the depression-end of the trough (black) and from the ‘missing lobe’ differ the most from the remaining spectra of the molecule. Those are shown in the bottom part of the graph and all share broad maxima around −0.9 and 1.9 eV and furthermore contain a broad peak of variable intensity in the (0.0, +1.2) eV range. In contrast, the spectra from the depression end of the trough (black) and from the ‘missing lobe’ (purple) contain a gap not found anywhere else in the type B configuration. The gap in the spectrum at the depression-end of the trough spans from −0.2 to +0.4 eV. moreover, the spectrum contains two intense maxima at +0.8 and +1.4 eV not found elsewhere. The intensity of these two states is reduced to a subtle corrugation in the spectrum above the ‘missing lobe’, which has an even broader gap spanning from −0.4 to +0.4 eV.
We associate the depression with the Si defect — Not only does the spectrum from the depression-end of the trough differ from the rest of the molecule, but also the appearance of the depression is similar to the way the Si atoms are imaged in the symmetric static configuration of CuPc, i.e. a depression in the filled states and a diffuse feature in the empty states (cf. figure 5.9). We assume, in analogy with the adsorption on the double Si defect, that CuPc interacts with a single Si defect by forming a dative bond between the aza-bridging N atom and the empty orbital on the substitutional Si atom. Such interaction would populate the empty state of the Si defect found above the Fermi level and move the newly formed bonding (antibonding) state below the Fermi level (farther from the Fermi level) and open a gap, as we can observe at this site.

A single bond alone, though, does not account well for the observed high stability of the type B configuration as it would potentially allow for a rotation of the molecule during our various tip-manipulation attempts. Additional bonds with the substrate stabilizing the molecule therefore ought to be present, possibly in the vicinity of the ‘missing lobe’. Polycyclic aromatic molecules are typically $\sigma$-bonded to silicon substrates with their $\pi$-electrons [4], which has also been shown for LuPc$_2$ on Si(001) – 2 × 1 [165], but the asymmetry and high stability of the type B configuration also hint at the possibility of hydrogen substitution.

The loss of molecular symmetry observed in both asymmetric configurations and the measured electronic spectra show that the frontier orbitals of the isolated CuPc molecule are not preserved after adsorption. Their loss and the very stability of both configurations imply a covalent interaction with the surface. This interaction, however, has a different impact on the electronic structure of both asymmetric configurations:

- The gap in the spectra of the type A configuration is found across the entire molecule (except for a marginal area) indicating a non-metallic electronic structure.

- The type B spectra have a non-zero DOS at the Fermi level throughout the larger part of the configuration (except in the vicinity of the assumed Si defect) suggesting that the configuration has metallic character in this case.

According to our STM observation, the double Si defect is the preferred adsorption site cf. figure 5.12) despite the higher stability of CuPc adsorbed on single Si and Sb type defects. This effect can be explained kinetically: diffusing molecules first enter a precursor state by temporarily adsorbing on the defects, and then either detach or further chemically interact with surface atoms. Adsorption on a single defect arguably involves larger structural changes, e.g. hydrogen substitution or bond cleavage, than adsorption on a
double Si defect by the proposed dative bonding of CuPc via nitrogen lone pairs. Adsorption on a single defect is thus less probable and so the double Si defects get occupied preferentially.

5.5 ANNEALING TREATMENT

To gain further insight into the interaction of CuPc with the Sn$-\sqrt{3}\times\sqrt{3}$ layer, we subjected the system to annealing. We deposited a slightly higher amount of CuPc (approximately 10-15% of full layer) and then annealed the sample at ~250 °C for two minutes. According to Ichikawa [144], the coexisting Sn$-2\sqrt{3}\times2\sqrt{3}$ layer is molten at this temperature, but the Sn$-\sqrt{3}\times\sqrt{3}$ layer is still well within its temperature stability range (up to 500 °C). The motivation behind this experiment was to see whether such treatment could facilitate any kind of local ordering of CuPc molecules.

Images of the sample after the temperature treatment are shown in figure 5.17. They reveal a significant mass transport within the layer.

- The top image shows small domains of Sn$-2\sqrt{3}\times2\sqrt{3}$ bordering to disordered areas (top left, bottom right). The lower lying terraces also contain Sn$-2\sqrt{3}\times2\sqrt{3}$ areas.

- The bottom image shows a significantly distorted Sn$-\sqrt{3}\times\sqrt{3}$ layer. CuPc molecules are incorporated within the layer (highlighted by frame). There are also distorted areas around.

Both images represent two limiting types of areas observed on the surface which mostly contained a mix of both and mainly disordered structures. Furthermore, the size of Sn$-2\sqrt{3}\times2\sqrt{3}$ areas increased after annealing. These results are analogous to those reported by Gruznev et al. [166] who observed that deposition of fullerenes on Si(111)/In$-2\times2$ and In$-\text{hex}$$-\sqrt{7}\times\sqrt{3}$ induced an increase of areas containing the more dense In$-\text{rec}$$-\sqrt{7}\times\sqrt{3}$ reconstruction. The authors attributed this effect to fullerenes displacing indium atoms from within the layer while forming bonds with Si atoms of the underlying Si(111) substrate.

The incorporation of CuPc within the Sn$-\sqrt{3}\times\sqrt{3}$ layer and the observed increase of the more dense Sn$-2\sqrt{3}\times2\sqrt{3}$ areas show that annealing provided energy for (some) CuPc to displace Sn atoms and bond to the Si atoms directly.
Figure 5.17: Filled-state images of a sample with adsorbed CuPc molecules annealed at 250 °C for 2 minutes: the layer exhibits a significant reordering. The rectangle highlights a distorted area within the Sn $\sqrt{3} \times \sqrt{3}$ layer with possibly incorporated CuPc molecules. $-2.0 \, V, 50 \times 50 \, nm^2, 50 \, pA$. 


5.6 CuPc interaction with Si(111)/Sn$-2\sqrt{3}\times 2\sqrt{3}$

In our experiments on Si(111)/Sn$-2\sqrt{3}\times 2\sqrt{3}$, we would often encounter coexisting areas of the Si(111)/Sn$-2\sqrt{3}\times 2\sqrt{3}$ reconstruction. The surface is semiconducting with a bandgap of $0.8 \pm 0.2$ eV [169]. It consists of two Sn layers, but the structural model is still subject of debate [167, 170, 171]. Recent extensive DFT calculations [168] favour the original model by Tornevik et al. [167], see figure 5.18, but the authors admit that there is room for further optimization as the DFT calculations cannot satisfactorily account for all features, let alone identify the transition to a Sn$-4\sqrt{3}\times 2\sqrt{3}$ phase on the hole doped Si(111) substrates.

With CuPc deposited, the presence of the Sn$-2\sqrt{3}\times 2\sqrt{3}$ areas would be instantly recognized — even in the absence of sufficient resolution — by noise. This effect is illustrated in figure 5.19 where it is rather moderately expressed. The upper part shows the substrate without CuPc — the boundaries between the phases are well marked and no scanning noise is observed. On the other hand, the filled and empty states image in the bottom part show a typical imaging situation of Sn$-2\sqrt{3}\times 2\sqrt{3}$ when CuPc molecules are present. Streak artefacts are observed along the fast scanning axis when scanning over the Sn$-2\sqrt{3}\times 2\sqrt{3}$ areas. Those can be seen in the image above and below the central Sn$-\sqrt{3}\times \sqrt{3}$ island where no such noise is observed.

Images of a Sn$-2\sqrt{3}\times 2\sqrt{3}$ area with CuPc is shown in figure 5.20. The layer contains defects (marked with a frame) which are very inconspicuous at high zoom level (the defect in the frame is resolved at higher zoom and additional voltages above) and are better visible at smaller zoom levels. The layer also contains several disordered ‘pits’ containing CuPc.
Figure 5.19: **Top:** The Si(111) substrate with coexisting Sn $-2\sqrt{3} \times 2\sqrt{3}$ and $\sqrt{3} \times \sqrt{3}$ areas. 300 pA. **Bottom:** The presence of CuPc causes fuzzy streaks when scanning over the Sn $-2\sqrt{3} \times 2\sqrt{3}$ areas. 25 pA.
and 2 are zoomed in below. Such pits are never observed in the absence of CuPc and can therefore be attributed to CuPc eroding the Sn–2√3×2√3 reconstruction.

There was also the possibility that the pits are created by the unstable tip above the regions, but in this particular case, the displayed Sn–2√3×2√3 area slowly drifted into the filed of view from top left to bottom right when the tip had already been well stabilized. So the tip effect can be ruled out.

The zoomed in pit-areas do not reveal any √3×√3 structure, only a slightly corrugated smooth surface. The zoomed area of pit 2 shows two molecules with a four-lobed shape typical for CuPc.

There is a difference between molecule A and B. Molecule A has a trough along its symmetry plane that seems to bisect CuPc along the isoindole subunit. But the lobe is split into two and the ratio between the horizontal and vertical dimensions is quite large ~1.4. Also, there are some scanning streaks to the right of the horizontal lobe. It therefore seems most probable that the molecule is quickly hopping between two positions as shown in the scheme in the inset. On contrary, the dimensions of molecule B are almost perfectly square-like so the molecule is fixed, possibly by the objects at its perimeter. It shows a twofold instead of a fourfold symmetry which might be due to interaction with the adjacent objects, but most likely results from an unequal interaction of the lobes with the (presumably) threefold underlying substrate.

The noise observed above the Sn–2√3×2√3 areas increased with increased CuPc coverage. It is therefore linked to the presence of CuPc molecules. As can be seen in figure 5.21, the molecule hopped away from a defect site (marked by arrow). The defect is very inconspicuous and is best seen zoomed out (I suggest zooming out or looking at the picture from the distance). Better resolved images of the defect are shown in the top set of images (framed defect from figure 5.20). There is a slight fuzziness observed above the defect at ±0.3 V which possibly stems from temporary interaction between diffusing CuPc molecules with the defect. This appears to be the same defect observed by Sugimoto et al. [171]. Based on nc-AFM measurements they rejected the possibility of a Sn atom vacancy, but rather attributed the defect to an Si substitutional atom in the first or second Sn layer.

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3 The image contained a small level of the mentioned noise too, but it could be suppressed with image processing techniques.
4 I decided not to include any arrows in the image set since they draw our visual attention and make this subtle comparison more difficult.
Figure 5.20: CuPc eroding Sn\(\text{–}2\sqrt{3}\times2\sqrt{3}\). The frame marks a defect in the layer. Pits 1 and 2 are zoomed in. The unit cell is marked in the zoomed-in image of pit 1. Zoomed-in image of pit 2 shows two CuPc molecules and their proposed orientation. The white circle denotes the same site within the images. Filled-states images left, empty-states right. \(\pm 1.5\) V, \(200\) pA.
5.7 CONCLUSIONS

Our experiments reveal a pivotal role of Si and Sb substitutional defects on the Si(111)/Sn−√3×√3 surface on the adsorption of CuPc. The molecules adsorb in symmetric and asymmetric configurations: The symmetric configurations are switchable and are located on double Si defects. In contrast, the asymmetric configurations are very stable and located on Sb and single Si defects. The overall preferred adsorption site is the Si double defect, where CuPc can adsorb in two configurations: fuzzy and static, of which the bistable fuzzy configuration is the preferred adsorption state.

The hallmark of these adsorption sites is that their electronic structure is altered compared to the Sn atoms. The Si substitutional atom has an empty $p_z$-like dangling bond and we propose that the interaction proceeds via a nucleophilic attack by the aza-N atoms containing lone electron pairs. On the other hand, the Sb substitutional atom has a filled dangling bond, but based on STS spectra we suggest that the covalent interaction proceeds at the neighbouring Sn atoms. We attribute the reactivity of this site to the presence of the Sb filled dangling bond which activates the neighbouring Sn atoms for adsorption of CuPc by causing a decrease of density of states.

CuPc does not adsorb on the unperturbed Sn−√3×√3 areas which is somewhat surprising given the presence of unpaired electrons in the dangling bonds of Sn atoms. Neither was it found to form ordered domains at higher coverages. Annealing of the system to ~250 °C lead to an increase of the more dense Sn−2√3×2√3 areas and CuPc incorporated itself in the
Sn-$\sqrt{3}\times\sqrt{3}$ layer showing that CuPc displace Sn atoms and bond directly to the underlying Si substrate. In this context, it is useful to mention general trends of the periodic table, namely that bond strength decreases down a periodic group. Table 5.1 shows bond enthalpies obtained of comparable silicon and tin compounds [172]. Tin forms generally weaker bonds than silicon due to a smaller overlap achievable with its larger valence orbitals. This might also hint why CuPc does not adsorb on the unperturbed Sn-$\sqrt{3}\times\sqrt{3}$ despite the radical character of the Sn atoms.

On the Si(111)/Sn-$2\sqrt{3}\times2\sqrt{3}$ surface, CuPc is mobile and was also found to temporarily adsorb on defects attributed to Si substitutions, which furthermore highlights the significance of substitutional defects in Sn layers on Si(111). CuPc was also found to erode the Sn-$2\sqrt{3}\times2\sqrt{3}$ areas.

Our experiments show that the nature of CuPc interaction with Sn-terminated Si(111) is rather complex and that substitutional defects with filled and empty dangling bond states locally significantly increase reactivity and act as important adsorption sites.

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<tr>
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<td>60–65</td>
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<tr>
<td>tin</td>
<td>76</td>
<td>54</td>
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Table 5.1: Bond enthalpies of selected tin and silicon compounds from [172].
5.8 Interaction of CuPc with Indium Reconstructed Si(111) Surfaces

We also included indium reconstructed Si(111) surfaces in our experiments, but the results are far from exhausting due to repeated issues with the evaporator and should be regarded as starting point for future experiments. Indium has a rich phase diagram on Si(111) for coverages up to 1 ML and forms a $\sqrt{3}\times\sqrt{3}$, $\sqrt{31}\times\sqrt{31}$, 4×1, a ‘striped structure’ and $\sqrt{7}\times\sqrt{3}$, 1×1 and 4×4 reconstructions close to 1 ML [173].

Indium reconstructed surfaces have served as substrate for fullerenes [48, 166] or PTCDA where the molecules were immobile on the In-$\sqrt{31}\times\sqrt{31}$ areas and assembled into ordered 1D structures along the indium wires of the In-4×1 reconstruction [174].

We observed CuPc on the In-$\sqrt{3}\times\sqrt{3}$, $\sqrt{31}\times\sqrt{31}$ and 4×1 reconstructed substrates. The structure of the In-$\sqrt{3}\times\sqrt{3}$ reconstruction is analogous to the Sn-$\sqrt{3}\times\sqrt{3}$ with the difference that the dangling dangling bond of indium atoms is empty, see figure 5.22a, which results in the presence of a surface bandgap and a stark imaging contrast between the filled and empty-states images.

The exact structure of the semiconducting In-$\sqrt{31}\times\sqrt{31}$ reconstruction is not known, and several models have been proposed [175, 176], the latter one shown in figure 5.22b.

On the other hand, the structure of the In-4×1 reconstruction is well understood, see figure 5.22c [177]. It is formed by indium wires composed of two unequal 5 zig-zag chains separated by a Si chain. The indium wires represent a 1D conducting system and undergo a transition to an In-8×2 semiconducting state at low temperatures ~130 K [178] which has provoked intense scientific debate about its driving mechanism [179].

5.8.1 Sample preparation

The samples were prepared analogously to procedure outlined in section 5.1. Indium was deposited onto Si(111)–7×7 held at RT and then the sample was annealed at 450–500 °C for two minutes. To produce the desired reconstruction, the amount of deposited indium varied between 0.3–0.6 ML according to the phase diagram in [173].

5.8.2 Interaction with Si(111)/In–$\sqrt{3}\times\sqrt{3}$

CuPc deposited on Si(111)/In–$\sqrt{3}\times\sqrt{3}$ also forms two lobed objects which adsorb on defect sites, but the molecules are bound weakly and often detach

5 They are registered differently with respect to the underlying bulk Si lattice.
Figure 5.22: Structural models of employed In-reconstructed Si(111) surfaces
during scanning. An-empty states image of the sample is shown figure 5.23. The encircled area shows two C$_{2h}$ symmetric molecules reminiscent of the fuzzy molecules on Si(111)/Sn-$\sqrt{3}\times\sqrt{3}$. They disappeared in the in the next image and revealed a double and a triple (linear) Si defect underneath.

We propose that this adsorption configuration is also formed by CuPc binding via its aza-N atoms to Si, but since the Si substitutional atom has an unpaired electron in this surface, the bonding might proceed as in the case of pyrazine on Si(001)-2×1: Pyrazine adsorbs in a bridge position between two Si dimer rows and forms two covalent Si–N bonds while keeping the lone pair of its N atoms [19].

In the case of CuPc, such bonding would remove two delocalized $\pi$ electrons from the Pc$^{-2}$ ligand aromatic system. Standard organic chemistry textbooks teach that when two electrons are removed from an aromatic system formed by a cloud of delocalized $4n + 2$ $\pi$ electrons, the extra energy gained through the electron delocalization is lost and the total energy of a molecule is raised. This accounts for the high stability of aromatic compounds and why (in solution) they readily undergo substitution reactions and resist addition reactions.

The removal of two delocalized $\pi$ electrons in CuPc might therefore partially offset the energy gained through the formation of Si–N bonds. Of course, this is only a crude comparison since the Hückel rules for aromaticity are valid only for planar monocyclic hydrocarbons and it neglects all other effects that play a role and need to be considered, but it might provide an insight why adsorption on a double Si defect in Si(111)/In-$\sqrt{3}\times\sqrt{3}$ is weaker than on Si(111)/Sn-$\sqrt{3}\times\sqrt{3}$.
5.8.3 Interaction with Si(111)/In−√31×√31

CuPc deposited on Si(111)/In−√31×√31 transiently adsorbs on defects which is shown in figure 5.24 containing a set of images numbered 1–7. Shown are images recorded in the filled states because the In−√31×√31 surface looks smeared in the empty-states images when CuPc molecules are present: see inset in image 1 where the √3×√3 is resolved clearly at +2 V in contrast to √31×√31 (The asterisk marks the same Si substitutional defect). Image 4 has therefore not been included since it was imaged at +2 V in both the forward (fw.) and backward (bw.) scanning direction. The values of fw. and bw. scanning voltage for each image are given in table 5.2. The left and right column display consecutive images (i.e. the situation before and after). The image on the right is repeated in the next row on the left.

The circles mark sites where a change of CuPc position was registered. The square in image 1 marks a CuPc molecule that remained stable throughout the whole observation.

- Image 1 was obtained while scanning at the opposite bias in the bw. direction. The majority of CuPc molecules appear as though they are being sliced and transiently detaching. When the scanning was performed at the negative bias in both directions as shown in img. 2, the ‘slicing’ disappeared.

- Image 3 was also obtained at negative bias in both scanning directions and the number of registered CuPc changes between images decreased. On contrary, image 4 (not shown) was scanned at positive bias in both scanning directions and the number of registered CuPc changes increased in image 5 (recorded at negative bias in fw. and bw. direction).

- Image 6 was scanned at negative bias only and the number of registered changes between images decreased, but it increased again when scanning at a positive bias was turned on during the backward motion in image 7. The ‘slicing’ of CuPc as in image 1 appeared again.

The voltage in image 7 was raised to ±2.5 V which changed the imaging contrast of surface defects. They appear as a bright protrusion at this voltage (marked with white arrow).

The role of these defects, which have not been discussed in the literature, for anchoring of CuPc can be seen in figure 5.25 where hopping between these defects is clearly visible.

These images show that CuPc is mobile on Si(111)/In−√31×√31 and that it transiently anchors on defects. Scanning in the empty states increases the detachment rate of CuPc from the defects significantly.
Figure 5.24: Hopping of CuPc on In - $\sqrt{31} \times \sqrt{31}$. The unit cell shown in image 1. The asterisk in the inset points to the same Si defect in image 1. For detailed description see text. $30 \times 30 \text{ nm}^2$, 120 pA.
Table 5.2: Scanning voltages of images in figure 5.24 during forward (fw.) and backward (bw.) motion of the tip.

<table>
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<tr>
<th>image no.</th>
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<td>scanning voltage (fw./bw.)</td>
<td>±2.0</td>
<td>+2.0</td>
<td>+2.0</td>
<td>−2.0</td>
<td>+2.0</td>
<td>+2.0</td>
<td>±2.5</td>
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Figure 5.25: Hopping of CuPc between defects which are well recognizable in the filled states at −2.5 V. (The rate of hopping was increased by scanning at +2.5 V during the backward direction). 120 pA.
5.8.4 Interaction with Si(111)/In\(-4\times1\)

STM images of CuPc deposited on Si(111)/In\(-4\times1\) are shown in figure 5.26: the bright indium wires are separated by troughs consisting of Si chains, cf. model in figure 5.22c.

Figures 5.26a and 5.26b illustrate the role of the tip imaging conditions on the observation of CuPc. They both show the same same area and were obtained with the same scanning parameters. A change at the tip occurred during scanning which made CuPc molecules visible as bright object with their centres positioned above the Si chains.

The majority of adsorbed molecules exhibit fuzzy streaks. The rectangle outlines an area where CuPc hopped to a different adsorption site in figure 5.26c revealing a defect under both adsorption sites. Some molecules did not exhibit fuzzy streaks. They are marked with circles and they adopted a \((\times)\) orientation with respect to the indium wires. Small scanning streaks are observed above defects, but not above the unperturbed \(4\times1\) areas. This is well visible in figure 5.26d, where the streaks reveal how CuPc transiently attaches and detaches from defect sites. It also reveals CuPc molecules twice their size (one of them marked with 4) implying they are quickly hopping between two rows during scanning.

The defects observed in the images are similar to vacancy defects reported by Lee et al. [181], but despite the considerable experimental and theoretical attention that has been paid to various aspects of this surface, there appears to be no study classifying its intrinsic defects.

The numbered arrows point to sites where \(I-t\) characteristics were measured. Site 1 is an unperturbed indium row and the tunnelling current shows no fluctuations. Site 2 exhibits some scanning streaks and is adjacent to a CuPc molecule. The current drops to zero implying that a CuPc molecule was present in the tunnelling junction, but hopped away during the measurement. Site 3 shows spikes of tunnelling current of \(\sim4\) nA implying CuPc hopping into the tunnelling junction. Site 4 exhibits three-level fluctuations which suggests that CuPc may also switch between different adsorption states.

Recent DFT calculations of MPcs (Mn, Co, Fe) on In\(-4\times1\) identified several adsorption positions: on the indium zig-zag chains, the molecules preferred a \((\times)\) rotated orientation, above the Si chains they aligned (+) with respect to the chain direction. [182]. The authors furthermore conclude that the magnetic moment of all three molecules ought to be reduced due to interaction with the substrate which proceeds via the aza-N atoms and the central metal atom.

These images show that CuPc molecules are mobile at RT and their interaction with Si(111)/In\(-4\times1\) is weak. CuPc also transiently anchors on defects, however the strength of this interaction is weak.
My colleagues have followed up on these experiments and found out that CuPc can form 2D tiled ordered domains on this surface at high coverages. The weak interaction of CuPc with the indium reconstructed surfaces contrasts to PTCDA which was found to be immobile on Si(111)/In-\(\sqrt{3} \times \sqrt{3}\) and assembled into 1D chains along the indium wires of the In-4\(\times\)1 reconstruction [174].

5.9 CONCLUSIONS

Our STM observations of CuPc deposited onto various In reconstructed Si(111) surfaces revealed a weak molecule-substrate interaction: the molecules are mobile and anchor on surface defects. On In-\(\sqrt{3} \times \sqrt{3}\) CuPc adsorbs on double Si defects similarly to Si(111)/Sn-\(\sqrt{3} \times \sqrt{3}\), but detaches readily in contrast. On Si(111)/In-\(\sqrt{31} \times \sqrt{31}\), CuPc also temporarily adsorbs on surface defects and the experiments revealed that the detachment rate can be increased when scanning at positive sample bias. On Si(111)/In-4\(\times\)1, the CuPc molecules are very mobile and also temporarily attach to defects. Follow-up experiments revealed that this weakly-interacting substrate facilitates 2D molecular ordering of CuPc.
Figure 5.26: CuPc on Si(111)/In–4×1. Top: Images (a) and (b) show the role of the tip as the molecules become visible after a change on the tip occurred. The rectangle shows a hop of CuPc between defects, cf image (c). Stationary CuPc’s are encircled. (d) Detail of CuPc interaction with defects. Bottom: $I - t$ characteristics ($V = -2$ V) recorded above sites 1–4 in image (d). 50 pA
Part IV

SUMMARY
SUMMARY

Our experiments aimed to investigate how a modification of the Si(001) and Si(111) substrates with ultra-thin metal layers of tin and indium would affect their interaction with organic molecules and also to test whether it would facilitate molecular ordering.

First we investigated the interaction of ethylene, a small unsaturated molecule, with Sn and In chains grown on Si(001) – 2×1. For both elements, the chains consist of dimers with structure similar to Si dimers forming the underlying Si(001) – 2×1 reconstruction. Ethylene was found to adsorb on Sn dimers whereas it was not found to adsorb on indium dimers. We attribute this difference to the presence/absence of a π bond in the Sn/In dimer which allows ethylene to adsorb on Sn dimers via [2+2]-like cycloaddition. The reactivity of Sn dimers was significantly decreased in contrast to the bare Si(001) – 2×1 surface, and only one adsorption configuration was identified.

Next we turned our attention to an aromatic polycyclic molecule, copper phthalocyanine, and investigated its interaction with Sn reconstructed Si(111) surfaces. The interaction with Si(111)/Sn – √3 × √3 revealed that CuPc molecules are anchored on substitutional defects in the Sn layer. The preferred adsorption site were Si double defects where CuPc can switch between a fuzzy and a static configuration. The fuzzy configuration turned out to be the most favourable adsorption state. CuPc was also found to adsorb on single Si and Sb defects which, unlike the Sn atoms, possess a filled and empty dangling bond. We proposed a that the interaction with the Si defect proceeds via the lone pairs on the aza-N bridging atoms and its empty dangling bond. In contrast, we proposed that the Sb atom does not interact with CuPc directly, but its activates the adjacent Sn atoms for adsorption of CuPc. CuPc molecules adsorbed on these defects are very stable.

CuPc also adsorbs on defects in Si(111)/Sn – 2√3 × 2√3, but is weakly bound and readily detaches. Curiously, CuPc was also found to erode the substrate.

We also studied the interaction of CuPc with the indium √3 × √3, √31 × √31 and 4×1 reconstructed Si(111) surfaces. In all cases, CuPc was found to adsorb on surface defects, but is only weakly bound and detaches readily. Follow-up experiments by my colleagues found that the In – 4×1 surface facilitates 2D ordering.

These results show that the interaction of CuPc with the tin and indium modified surfaces is significantly decreased in comparison with the bare
Si(111)-7x7 substrate and reveal a major role of surface defects in the metal modified surfaces as anchoring sites.


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ACRONYMS

AES Auger electron spectroscopy
AFM (non-contact) atomic force microscopy
CuPc copper phthalocyanine
DB dangling bond
DFT density functional theory
DOS density of states
DSP digital signal processor/processing
HOMO highest occupied molecular orbital
HREELS high resolution electron energy loss spectroscopy
L Langmuir, unit of gas exposure $1 \text{ L} = 1.33 \times 10^{-2} \text{ Pa s}$
LDOS local density of states
LEED low-energy electron diffraction
LUMO lowest unoccupied molecular orbital
ML monolayer
(M)Pc (metal)phthalocyanine
nc-AFM (non-contact) atomic force microscopy
PES photoelectron spectroscopy
PTCDA perylene tetracarboxylic acid
RT room temperature
SRPES photoelectron spectroscopy with synchrotron radiation
STM scanning tunnelling microscopy
STS scanning tunnelling spectroscopy
UHV ultra-high vacuum
XPS X-ray photoelectron spectroscopy
LIST OF PUBLICATIONS

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