An atomistic approach to graphene and carbon clusters grown on a transition metal surface

A thesis submitted for the degree of Ph. D.

by

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Supervised by Dr. Renald Schaub

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September, 2010
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Graphene

Carbon clusters

Growth at $T > 873K$

Scanning tunnelling microscopy & spectroscopy

$dZ/dV$

$dI/dV$
Abstract

In this thesis, graphene (i.e. monolayer carbon film) and carbon clusters supported on a transition metal surface are systematically studied by local probe techniques, with respect to their structures, electronic properties and formation mechanisms.

The main tools used are low-temperature scanning tunnelling microscopy and spectroscopy (STM and STS), which are introduced in Chapter 2. The mechanism of the resonance tunnelling at electron energies higher than the work function of the surface is discussed in detail, and a qualitative explanation of the Gundlach oscillations in the corresponding spectroscopy is presented.

Epitaxial graphene synthesised on the Rh(111) surface by ethylene dehydrogenation is investigated by STM in Chapter 4. Such carbon film exhibits a hexagonal Moiré pattern due to a lattice mismatch between graphene and the rhodium substrate. The periodicity and local registries of the graphene/Rh(111) superstructure are carefully analysed. Based on a thorough discussion about the “commensurate vs. incommensurate” nature of the Moiré pattern in surface science field, the graphene/Rh(111) system is identified to have a non-simple-commensurate superstructure.

The surface electronic properties and geometric buckling of graphene/Rh(111) are investigated by resonance tunnelling spectroscopy (RTS) and density functional theory (DFT) calculations in Chapter 5. Spectroscopy measurements reveal a modulation of the electronic surface potential (or work function $\Phi$) across the supercell of epitaxial graphene. Based on the microscopy/spectroscopy data and the extended DFT calculations, we examined the electronic coupling of the various local C-Rh registries, and identified both experimentally and theoretically the local atomic configurations of maximum and minimum chemical bonding between graphene and the rhodium substrate.

We studied in Chapter 6 the growth mechanism of graphene on Rh(111) at elevated temperatures. This part starts by investigating the dehydrogenation of ethylene into ethylidyne. When the dehydrogenation process is complete, monodispersed carbon
species, identified as 7C₆, are found to dominate the cluster population on the rhodium terraces. A significant coalescence of the 7C₆ clusters into graphene islands occurs at temperatures higher than 873 K. The structural and electronic properties of the 7C₆ carbon clusters are examined by high-resolution STM and STS, and compared with coronene molecules, i.e. the hydrogenated analogues of 7C₆. DFT calculations are further used to explain the stability of 7C₆ supported on the Rh(111) surface, and also the structural characteristics of such magic-sized carbon clusters.

**Keywords:** STM, STS, resonance tunnelling spectroscopy, work function, graphene, Rh(111), Moiré, geometric buckling, carbon clusters, DFT calculations, coke formation.
Acknowledgment

I would like to thank my supervisor Dr. Renald Schaub, for introducing me to a magic world of atoms/molecules and surfaces. His valuable support, encouragement and enthusiasm helped me throughout my PHD study, especially in the early days when we had to start our activities from scratch. I thank him for teaching me how to debug and solve problems independently when managing the UHV and STM facilities.

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Thanks to EaStCHEM for funding my PHD scholarship at the University of St Andrews.
<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunnelling Spectroscopy</td>
</tr>
<tr>
<td>SFEM</td>
<td>Scanning Field Emission Microscopy</td>
</tr>
<tr>
<td>FER</td>
<td>Field Emission Resonance</td>
</tr>
<tr>
<td>RTS</td>
<td>Resonance Tunnelling Spectroscopy</td>
</tr>
<tr>
<td>DOS</td>
<td>Density Of States</td>
</tr>
<tr>
<td>Φ</td>
<td>work function</td>
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<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
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<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>fcc</td>
<td>face centred cubic</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close packed</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>ML</td>
<td>Mono Layer(s)</td>
</tr>
<tr>
<td>TM</td>
<td>Transition Metal</td>
</tr>
<tr>
<td>TPG</td>
<td>Temperature Programmed Growth</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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Chapter 1 – Introduction

1.1 Heterogeneous catalysis

Catalysis plays an important role in the chemical industry as a basis to sustain modern civilization. In the last century, catalysts have been ubiquitously used in manufacturing fuels, commodities, fine chemicals and pharmaceuticals. Today, the solutions to various new challenges (e.g., alternative fuels, cleaning environmental pollution and global warming) are still closely associated with chemical catalysis. The vast majority of catalytic processes are heterogeneous in nature, typically involving a solid catalyst (often an active phase finely dispersed on a high-surface-area support) and gas- or liquid-phase reactants. The heterogeneous catalysis process can roughly be divided into three steps, including the adsorption of the reactants to the catalyst surface, the reaction at the active sites and followed by the desorption of the products from the solid surface into the fluid phase. The main advantage of heterogeneous catalysis is the easy separation of the catalyst and the products, which allows the use of continuous-flow reactions in industry. Moreover, the solid phase in heterogeneous catalysis affords enough flexibility to build up complex atomic ensembles, which can be tuned for specific reactions.

1.1.1 Coke formation

We know that the catalyst is not consumed or changed despite its participation into the catalysed reactions. Nevertheless, the real catalyst used in the chemical industry has a limited life-time. This loss of catalytic reactivity over time is called deactivation. Several common deactivation mechanisms are coking, poisoning, sintering and phase transformation. The first two mechanisms (shown in Figure 1.1) are more related to the specific chemical process, whereas the last two are physical in nature.

Coke formation usually occurs when hydrocarbon molecules or carbon monoxide are involved as reagents under high reaction temperatures. The carbon residues left as by-products tend to physically cover the catalyst surface, and block the active sites. Hence the minimisation of coke formation on catalysts is of prime interest, especially in
Figure 1.1: Schematics of two important deactivation mechanisms caused by chemical reactions, *i.e.* coke formation and poisoning. From reference 1.

the petrochemical industry. However, in this thesis the coking reaction is employed as a chemical approach to fabricate the single-layer carbon film (*i.e.* graphene) on a transition metal surface. The motivation of our work is two-fold: (1) the epitaxial graphene layer prepared by this approach has a high structural quality, hence making it possible to systematically study the structures and electronic properties of such novel material (see section 1.2); (2) The growth of graphene on the metal single crystal, representing a surface science model of coke formation on catalysts, can be investigated by our local probe microscopy and spectroscopy techniques.

1.1.2 Rhodium catalysts

Rhodium (Greek *rhodon* meaning "rose") was firstly discovered from platinum ore by William Hyde Wollaston in 1803.\(^5\) Rhodium metal has a silvery white colour with a high reflectance. As one of the most precious noble metals, rhodium is relatively inert and corrosion resistant at ambient conditions. Nevertheless, rhodium is well known in chemistry for its high catalytic activity in the three-way conversion:

\[
2 \text{NO}_x \rightarrow x \text{O}_2 + \text{N}_2. \tag{1.1}
\]

This is regarded to be a very successful technology in environmental catalysis, which greatly reduced the NO component in the vehicle exhaust gas.\(^6\) A report from the USGS (U.S. Geological Survey) showed that the world production of rhodium at present is
mainly consumed by the manufacturing of three-way catalytic converters.\textsuperscript{7}

Besides this, rhodium is also an important catalytic metal in another famous chemical reaction, namely, the Fischer-Tropsch (F-T) synthesis.\textsuperscript{6} The F-T reaction involves catalytic CO hydrogenation to hydrocarbon products that range from methane (C\textsubscript{1}) to high molecular weight waxes (> C\textsubscript{100}). This reaction provides a leading gas-to-liquid option to yield hydrocarbon-based fuels and chemicals from natural gas.\textsuperscript{8} This reaction is gaining more and more interest by large chemical companies, as the oil resources will be depleted in the near future.

Rhodium is usually compared with other transition metals in the VIIIIB group, because these are usually active for the same type of reactions. Take the F-T reaction as an example.\textsuperscript{9} The metals at the upper-left side of VIIIIB group (\textit{i.e.}, Fe, Co and Ru), strongly dissociate CO and catalyse the preferential formation of methane and higher hydrocarbons in CO hydrogenation. However, the metals at the opposite side of the periodic table (\textit{i.e.}, Pt, Ir and Pd) chemisorb CO non-dissociatively and lead preferentially to methanol. Accordingly, rhodium, located in the middle of the VIIIIB group, is described as the intermediate catalyst metal among the F-T metals, and therefore it exhibits a catalytic activity for the syngas (CO + H\textsubscript{2}) reaction to produce carbon-two (C\textsubscript{2}) oxygenates such as C\textsubscript{2}H\textsubscript{5}OH, CH\textsubscript{3}CHO and CH\textsubscript{3}OOH.

The main work of this thesis is closely related to the catalytic reactivity of rhodium for the dehydrogenation/carbonisation reactions. Specifically, the transformation from hydrocarbon species to carbon clusters or film (\textit{i.e.} graphene) at elevated temperatures is catalysed by the Rh(111) surface. Our results in this aspect may lead to substantial new insight into the coke formation on transition metals.

1.2 Graphene

1.2.1 Basics of graphene

Graphene is made up of carbon atoms sp\textsuperscript{2}-bonded in a planar honeycomb network. It is a 2D allotrope of carbon with only one atom thickness, which makes it the thinnest known material in the universe. The term graphene was first used in 1987 to describe a single sheet of graphite as a basic component of graphite intercalation compounds.\textsuperscript{10} Figure
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1.2A presents a ball-and-stick model of graphene. The C-C bond in graphene has a length of 1.42 Å. The rhombus unit cell, defined by the lattice vectors $a_1$ and $a_2$, encloses two carbon atoms (A and B). Hence the graphene lattice can also be regarded as a combination of two interpenetrating triangular carbon sublattices. The simplicity of the honeycomb structure makes graphene the building block of other graphitic materials with different dimensionalities (*i.e.*, fullerenes, carbon nanotubes and graphite). As demonstrated in Figure 1.2B, (1) fullerenes can be obtained by wrapping up graphene with the help of pentagon rings; (2) carbon 1D nanotubes can be formed when graphene is rolled up along a given direction into cylinders; (3) when multiple layers of graphene are stacked together by van der Waals forces, 3D graphite is formed. Based on these structural relationships, graphene was often used as a starting point for theoretical calculations on graphitic materials even before the experimental isolation of graphene.

![Figure 1.2: (A) Ball-and-stick model of graphene. From reference 12. (B) Schematics of the relationship between graphene and other graphitic materials, showing that graphene is the elementary building block for the other graphitic materials, *i.e.*, fullerenes, carbon nanotubes and graphite. From reference 13.](image)

A brief overview of the history of graphitic materials will help us understand how scientists explored the magic world of carbon. Graphite materials have been around us for about 500 years, ever since the invention of the pencil, as its main component is graphite. Fullerenes were discovered by Kroto *et al.* in 1980, and carbon nanotubes...
were discovered by Iijima in 1990\textsuperscript{16-17}. Nevertheless, the first experimental isolation of single layer graphene was realised by Geim \textit{et al.} from Manchester University in 2004.\textsuperscript{18} One can ask why graphene, being the fundamental element of the other graphitic materials, was only discovered and widely studied recently. This can be explained by two main reasons.

The first reason is theoretical. In fact, a strictly 2D crystal was believed to be thermodynamically unstable and hence could not exist. Peierls and Landau pointed out that thermal fluctuations would destroy long-range order of a 2D lattice and lead to its melting at any finite temperature.\textsuperscript{19-20} Therefore, the first experimental observation of graphene at ambient conditions by Geim and Novoselov\textsuperscript{18} is intriguing by itself. The stability of exfoliated graphene, as explained by the discoverers, is due to the fact that the 2D crystallites are quenched in a metastable state since they are extracted from 3D graphite. The small size (<< 1 mm) and strong interatomic bond (as compared to the interlayer bond) prevent the generation of dislocations or other crystal defects by thermal fluctuation even at elevated temperature.\textsuperscript{13,21-22} Besides that, extracted graphene becomes intrinsically stable by gentle crumpling in the direction perpendicular to the 2D surface.\textsuperscript{23-24} Such 3D warping leads to a gain in elastic energy but suppresses thermal vibrations, and hence minimises the total free energy above a certain temperature.

\textbf{Figure 1.3:} Graphite flakes with different thicknesses show different contrasts under the optical microscope. From reference\textsuperscript{12}. 

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The second reason is related to the fabrication technique of graphene. It has been known that multilayer graphene films can be extracted from graphite by micromechanical cleavage.\textsuperscript{25} This approach, in simple words, is repeated peeling of a graphite sample by Scotch tape. Geim \textit{et al.} carefully examined the fragments after a cleavage of the graphite flakes, and found that some fragments are only one atom thick. As the discoverers put it: “Graphene is relatively straightforward to make, but not so easy to find.”\textsuperscript{26} The fact that single- and double-layer graphene have a slightly different contrast under the optical microscope, when they are supported on a smooth SiO\textsubscript{2}/Si(111) surface, played a critical role in the isolation of graphene. Usually it takes several hours to spot a high-quality graphene flake. Despite of its inefficiency, this seemingly simple method utilising only Scotch tape and an optical microscope provided the first opportunity to investigate graphene experimentally.

\textbf{Figure 1.4:} The number of publications about graphitic materials since the 1970s. Modified from reference\textsuperscript{27}. 

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An explosion of interest in graphene occurred soon after the extraction of single-layer graphene from graphite was reported to be technically possible in 2004. Figure 1.4 shows the number of articles related to graphitic materials published ever since the 1970s. It can be clearly seen that the number of publications skyrockets after 2004. Besides Geim and Novoselov’s pioneering work in exfoliated graphene, there are also other important factors that contributed to this graphene “fever”, e.g. the chemical approach to the synthesis of graphene. This will be introduced in section 1.2.3.

1.2.2 Electronic properties of graphene

The carbon atoms in the unit cell of graphene are sp²-hybridised to constitute a hexagonal network. The 2s orbital and two 2p orbitals (i.e. 2pₓ and 2pᵧ, assuming the z axis is perpendicular to the graphene plane) participate on the formation of the covalent bond between the two neighbouring carbon atoms. The remaining 2pzte orbitals overlap in a shoulder-by-shoulder manner to form π (valence) and π* (conduction) bands, which are less bonded to the carbon atoms and hence relatively delocalised. The electronic structure of graphene calculated by a tight-binding method is shown in Figure 1.5. Interestingly, the π and π* bands of neutral graphene meet at the so-called Dirac points (K and K’ in the

![Figure 1.5: Band structure of graphene calculated using a tight-binding approximation. A zoom-in at the boundary of the Brillouin zone shows that the conduction band touches the valence band at the K (or K’) point. From reference 24.](image)

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Brillouin zone) at the Fermi energy. Near these Dirac points, the electron energy is linearly dependent on the wave vector. Such a linear dispersion is quite different from the energy spectrum in conventional metals and semiconductors, which has approximately a parabolic (free-electron-like) dispersion relation.

The linear dispersion relationship \( E = \hbar k v_F \) in graphene mimics the physics of quantum electrodynamics \( E = c k \) for massless fermions. Hence, the electrons in graphene behave like relativistic particles (i.e. Dirac fermions). However, the speed of electrons \( (v_F = \text{the Fermi velocity}) \) is a constant of about \( 10^6 \text{ m/s} \), 300 times slower than the speed of photons \( (c) \). As a consequence, many of the unusual properties of quantum electrodynamics can show up in graphene but at much smaller speeds.\(^{28-30}\) Moreover, new physical phenomena such as the anomalous integer quantum Hall effect were experimentally observed when graphene is subjected to magnetic fields.\(^{18}\) Another important feature of graphene associated to the relativistic effects is the ballistic charge conductivity. Transport measurements show that graphene has a remarkably high electron mobility \( (> 15,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}) \) at room temperature.\(^{13}\) And the resistivity of a graphene sheet is less than that of silver \( (1.6 \times 10^{-6} \Omega \text{cm}) \). Such a high conductivity makes graphene a promising material for applications in electronic devices.

### 1.2.3 Epitaxial graphene by chemical approaches

The micromechanical cleavage method used by Geim and Novoselov is a physical approach to prepare free-standing graphene.\(^{13}\) This approach is based on the fact that the Van der Waals interaction between the neighbouring layers in graphite is much smaller than the in-plane C-C covalent bond. Nevertheless, a large-scale production of graphene by micromechanical cleavage is unlikely to be feasible, due to its inefficiency with respect to the time-scale and yielding. Recently, various chemical reactions have been employed to fabricate epitaxial graphene in a well-controlled manner. For instance, graphene/SiC(0001) can be prepared by the decomposition of the SiC crystal at high temperatures.\(^{31-32}\) The silicon content of the surface is evaporated into the vacuum upon annealing and the remaining carbon stays in the form of graphene on the SiC surface. A well-defined number of graphene layers is, however, difficult to achieve on SiC, since the decomposition reaction usually leads to a mixture of mono-, bi- and multiple layers of
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Graphene with distinct electronic properties.

Another widely used chemical reaction for the synthesis of graphene is the catalytic decomposition of hydrocarbon molecules (or carbon oxide) on transition metal (TM) surfaces.\textsuperscript{31-33} Such a “bottom-up” chemical approach is closely related to coke formation,\textsuperscript{33} as mentioned in section 1.1. Interestingly, the metals used to support graphene growth are located in the VIIIB group of the periodic table (see Table 1.1), because of their high catalytic reactivity in dehydrogenation reactions.

Table 1.1: Comparison of the close-packed surfaces of the VIIIB metals used to grow epitaxial graphene.

<table>
<thead>
<tr>
<th>Hexagonal surface</th>
<th>Metal type</th>
<th>Surface lattice constant (Å)</th>
<th>Mismatch ((d_m-d_g)/d_g) (*)</th>
</tr>
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<tbody>
<tr>
<td>Free-standing graphene</td>
<td></td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>Co(0001)</td>
<td>3d</td>
<td>2.50</td>
<td>1.6%</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>3d</td>
<td>2.49</td>
<td>1.2%</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>4d</td>
<td>2.69</td>
<td>9.3%</td>
</tr>
<tr>
<td>Ru(0001)</td>
<td>4d</td>
<td>2.71</td>
<td>10.2%</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>4d</td>
<td>2.75</td>
<td>11.8%</td>
</tr>
<tr>
<td>Ir(111)</td>
<td>5d</td>
<td>2.72</td>
<td>10.6%</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>5d</td>
<td>2.77</td>
<td>12.6%</td>
</tr>
</tbody>
</table>

(*) \(d_m\) and \(d_g\) denote the lattice constants of the metal and free-standing graphene, respectively.

Compared to free-standing graphene, graphene supported on transition metals (graphene/TM) exhibits two types of superstructures, depending on the mismatch between the 2D carbon and the metal lattices (see Table 1.1). A simple \((1 \times 1)\) superstructure is formed when graphene is supported on the 3d transition metals with relatively small atomic diameters.\textsuperscript{34-36} For instance, a \((1 \times 1)\) graphene/Ni(111) and a \((1 \times 1)\) graphene/Co(0001) epitaxy was observed by STM, as shown in Figure 1.6. The high-resolution image in Figure 1.6B shows that the \((1 \times 1)\) graphene/Ni(111) system has a honeycomb pattern, in which every carbon atom is imaged as a bright protrusion. This
Figure 1.6: STM images of (A) and (B) graphene/Ni(111) (from reference\textsuperscript{35}) and (C) graphene/Co(0001) (36 Å × 36 Å) (from reference\textsuperscript{36}). The inset in (A) is the LEED pattern of graphene/Ni(111).

is in contrast to graphite, for which only half the number of carbon atoms appears as protrusions in STM images.\textsuperscript{37–38} For these (1 × 1) structures, it can be expected that the C-C bond in graphene is slightly expanded (< 2 %) with respect to that of free-standing graphene, in order to eliminate the small lattice mismatch between graphene and the 3d metal substrate.

However, when graphene is supported on metals with relatively larger atomic diameters, such as 4d or 5d transition metals, a Moiré superstructure is usually generated by the

Figure 1.7: STM images of graphene/Ir(111). The supercell of the Moiré pattern is marked by a white rhombus in (B). From reference\textsuperscript{39}.
significant mismatch between the carbon and metal lattices. The Moiré pattern of epitaxial graphene is characterised by a hexagonal pattern with a large periodicity (~ 3 nm), as shown in Figure 1.7. More details about the graphene Moiré on metal surfaces will be presented in Chapter 4.

It is worth noting that graphene/TM shows many distinct features when compared to graphene/SiC. For instance, only monolayer graphene is produced on metals by the catalytic decomposition approach, since the carbon film blocks the catalytically active surface and prevents the further growth of multiple carbon layers. A strong C-TM interaction usually exists in graphene grown on the metal substrates (especially for 3d and 4d TM), which plays an important role in determining the electronic properties of graphene.

**Figure 1.8:** Band structure of graphene/Ni(111) from ARUPS measurements. Open and filled dots were measured with HeI and HeII excitations, respectively. The broken lines are the $\pi$ and $\sigma$ bands of bulk graphite, and the shaded areas are the Ni 3d band. From reference 40.

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graphene/TM. Take the (1 × 1) graphene/Ni(111) system as an example. Its band structure in Figure 1.8 shows that the $\pi$ band is 3 eV below the Fermi level, and the cone-shaped $\pi^*$ band of free-standing graphene can hardly be recognised here, as a result of a strong hybridisation between the C 2p$_z$ and Ni 3d states. Importantly, the electronic structure of graphene supported on 4d and 5d transition metals is characterised by an inhomogeneous C-TM interaction over the 2D surface, which is caused by the lattice mismatch between graphene and the metal substrate. This will be systematically studied in Chapter 5.

The work presented in this thesis is organised as follows. Chapter 2 will introduce the physics of the main techniques (scanning tunnelling microscopy and spectroscopy) we used. Chapter 3 will describe the experimental set-up, methodologies and theoretical calculations. Chapter 4 will present the structural characteristics of graphene/Rh(111), while the electronic properties and chemical bonding will be studied in Chapter 5. The growth mechanism of epitaxial graphene on Rh(111), including the formation of magic-sized carbon clusters as intermediate species, will be revealed in Chapter 6. Finally, Chapter 7 will present concluding remarks and a perspective for future work.

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Chapter 2 – Scanning tunnelling microscopy and spectroscopy

This chapter will present an overview of scanning tunnelling microscopy and spectroscopy. Two types of electron tunnelling behaviours, occurring at energies below and above the work function of the surface, are compared and discussed in detail. Particularly, we analyse the resonance tunnelling spectroscopy in the constant-current mode, whereby a qualitative explanation of the series of oscillations occurring in the tip-sample junction will be presented.

2.1 Scanning tunnelling microscopy

STM was invented by Gerd Binnig and Heinrich Rohrer at the IBM laboratory in Switzerland in 1981.1-3 The basic idea of STM is to bring an atomically sharp probe tip near to a sample surface, while a voltage lower than the work function of the surface is applied between the tip and the sample (Figure 2.1). When the tip-surface distance is close to few Ångstroms, a tunnelling current flows through the vacuum between the tip and the sample. By monitoring the tunnelling current as a function of tip location on the surface, more precisely by raster scanning the tip across the surface, an electronic image of the surface can be acquired with a spatial resolution down to the atomic level. The successful real-space imaging of surface atoms has been an important breakthrough in

Figure 2.1: Schematic view of the Createc STM, originally developed by Sven Zöphel et al.4 Modified from reference5.
surface science, which was recognised by the awarding of the Nobel Prize in Physics to Binnig and Rohrer in 1986.

2.1.1. Basics of electron tunnelling

Electron tunnelling through a potential barrier, which forms the basis of the STM signal, was known to physicists for a long time, and has been studied intensively in theory due to its importance in many different fields (e.g. field emission and semiconductor technology). Figure 2.2 shows a simple model in which an electron tunnels through a rectangular potential barrier. In a normal tunnelling process, the energy of the electron is lower than the height of the barrier ($E < V_0$). The transmission probability calculated by quantum mechanics is:

$$T = \frac{1}{1 + \frac{V_0^2 \sinh^2(k_1Z)}{4E(V_0 - E)}}$$  \hspace{1cm} (2.1)

where $Z$ is the width of the barrier and $k_1 = \sqrt{2m(E - V_0)/\hbar^2}$. If the wavelength of the electron is smaller than the width of the barrier ($1/k_1 << Z$), equation (2.1) reduces to:

$$T \approx c \cdot e^{-2k_1Z}$$  \hspace{1cm} (2.2)

where $c$ is a constant.

Figure 2.2: Electron scattering at a 1D rectangular potential barrier with a height $V_0$ and a width $Z$.

Equation (2.2) expresses an exponential dependence for the electron transmission probability on the width of the energy barrier. Despite the simplicity of this model, the
result (2.2) holds true for vacuum tunnelling in STM as it was observed experimentally by Binnig et al. in 1982 (see Figure 2.3). The high sensitivity of the tunnelling current with respect to the tip-sample distance is one of the critical reasons that led to the success of STM. The electron energy used in STM is usually around 0.01–1 eV, which corresponds to an electronic wavelength larger than 10 Å. If an electron with such large wavelength is employed in a traditional optical approach, as in FEM (Field Emission Microscopy) or HRTEM (High Resolution Transmission Electron Microscopy), it would be impossible to resolve single atoms. However, the quantum tunnelling featured by equation (2.2) renders STM remarkably sensitive in the direction perpendicular to the surface.

![Figure 2.3: Tunnelling resistance (left y axis) and current (right y axis) vs. displacement of the STM tip collected at different tip and sample conditions by Binnig et al. in 1982. From reference 3.](image)

There are three parameters to adjust in an STM measurement, namely, the tip-sample distance ($Z$), the bias ($V$) and the current ($I$). Two of them are independent variables for a specific tip-sample junction. For imaging purpose, a constant DC voltage is directly applied to the sample (or tip), and the tip (or sample) is electrically grounded. Depending on whether the current or the tip-sample distance is kept constant, STM can be operated...
in two different scanning modes. The so-called constant-current mode is more often used than the constant-height mode as the former provides better spatial resolution and stability. A feedback circuit is essential to realise the scanning function in the constant-current mode. It controls the tip-sample distance in the $z$ direction by comparing the current signal with a pre-defined current setpoint when the tip is moving along the $x$ and $y$ directions. Notably, the 3D positioning of the tip, with an accuracy of down to 1 pm, is realised by adjusting the voltages on different directions of the piezo crystals. This is a key technical factor for the success of STM.

For a measurement on conductive surfaces (e.g. on a metal single-crystal), the tunnelling parameters are usually set to be in the range of $V = 0.01–1$ V and $I = 0.01–10$ nA. These voltage and current magnitudes correlate with the physical properties of the junction between the metal tip and the metal substrate. In fact, the tip-sample distance is usually about 5 Å. This distance is chosen to be larger by 2–3 Å than a typical chemical bond length in order to avoid a strong tip-sample interaction. Therefore, the tip-sample gap has a resistivity larger by a factor of $10^2–10^3$ than a direct tip-sample contact, according to the exponential decay of the current as a function of tip-sample distance (equation (2.2)). Since the electrical resistivities of metals are usually around $10^{-7}–10^{-8}$ Ω·m (e.g. $\rho(W) = 5.48 \times 10^{-8}$ Ω·m and $\rho(Pt) = 2.22 \times 10^{-7}$ Ω·m), the resistivity of the tip-sample gap is approximately $10^{-5}$ Ω·m. Furthermore, the electron tunnels into (or out of) the sample surface mainly through the atom located at the apex of the STM tip. Hence the cross sectional area for tunnelling in the vacuum region is about $3 \times 3$ Å (e.g. the diameter of W and Pt atoms are roughly 2.8 Å). It follows that the resistance of a tip-sample gap can easily be estimated:

$$R = \rho \cdot L / S \approx 10^{-5} \times 5 \times 10^{-10} / (3 \times 3 \times 10^{-20}) \approx 5 \times 10^6 \Omega$$

where $S$ is the cross sectional area, and $L$ is the tip-sample distance (~ 5 Å). Indeed, the gap resistance observed in experiments is usually on the order of mega-ohms when measuring on metal surfaces. Finally, a low current is preferred for STM acquisition, as a high one focusing on the small tunnelling area can lead to the local melting of the tip-sample junction. However, there is a technical limitation one must bear in mind: the lowest current that can be resolved by electronics is usually larger than 1 pA. Hence to
guarantee a decent signal-to-noise ratio, tunnelling currents from 10 pA to 1 nA are usually used in STM measurements. This requires a voltage input ranging from 0.01 to 1 V for a gap resistance of the order of mega-ohms.

2.1.2 Theory of STM

The rectangular potential barrier model in Figure 2.2 is very crude for the simulation of the vacuum tunnelling in a real STM measurement, because the potential barrier between the tip and the sample is severely distorted by the electric field and other factors (discussed further below). Moreover, we need to consider the electronic properties of both sample and tip, such as the Fermi level, work function and so on. The vacuum tunnelling actually exhibits quite different behaviours at different bias voltages (Figure 2.4), as will be discussed in the following.

(1) Low voltage regime (|V| < 10 mV)

The Tersoff-Hamann model, which is based on perturbation theory, is widely used to simulate the vacuum tunnelling in STM owing to its simplicity. The tip and sample are treated as two separate entities. Moreover, the tunnelling is assumed to occur only at small bias voltage (< 10 mV) and low temperature. The tip has a uniform density of states (DOS), and geometrically ends up with an s-orbital that is spherically symmetric. The tunnelling current, generated by the overlap of tip and sample wavefunctions in the gap region, is then given by:

$$ I = \frac{32\pi^3 \hbar^3 e^3 V \phi^2 R^2 \kappa^{-4} e^{2\pi \kappa} D_r(E_F)\rho(r_0, E_F)}{\kappa} $$

(2.3)

where \( V \) is the bias voltage, \( D_r \) is the DOS of the tip, \( \phi \) is the work function of the tip and the sample (assumed to be equal here), \( R \) is the radius of the spherical tip, \( \rho(r_0, E) \) is the DOS of the sample at the Fermi level, \( r_0 \) is the distance between the sample and the centre of the tip curvature. For the constant-current mode of STM operation, equation (2.3) reveals that the curvature centre of the tip follows a contour of constant DOS of the sample at the Fermi level.
Figure 2.4: Scheme of vacuum tunnelling in STM at different bias voltages. (a) Voltage smaller than 10 meV. The transmission probability ($T$) adopts a constant value by approximation in the thin energy zone. (B) Moderate voltage between 10 meV and $\Phi/e$ ($\Phi$ denotes the work function of the sample surface). $T$ increases monotonically with the electron energy. (C) Voltage larger than $\Phi/e$. Standing waves are formed by interference between incident and reflected electrons in this vacuum region with a triangular potential well. $T$ is enhanced when the electron energy matches the eigenvalue of a localised resonance state.
(2) Moderate voltage region (10 mV < |V| < \Phi/e)

As mentioned in 2.1.1, STM measurements are usually conducted with a bias voltage larger than 10 mV. When applying a bias voltage \( V \) such as 10 mV < |V| < \Phi/e, the tunnelling current arises from a range of states lying within \( eV \) of the Fermi level,\(^{12}\) which is given by:

\[
I = \int_0^\infty \rho_s(r,E) \rho_t(r,E-eV) T(E,eV,r) dE
\]  

(2.4)

where \( \rho_s(r,E) \) and \( \rho_t(r,E) \) are the DOS of the sample and tip at location \( r \) and an energy \( E \) with respect to their Fermi levels. The tunnelling transmission probability \( T(E,eV,r) \) for electrons with energy \( E \) and applied voltage \( V \) is then given by:

\[
T(E,eV) = \exp \left( -\frac{2Z\sqrt{2m}}{\hbar} \sqrt{\frac{\Phi_t + \Phi_s}{2} + \frac{eV}{2} - E} \right)
\]  

(2.5)

where \( Z \) is the tip-sample distance, and \( \Phi_t \) and \( \Phi_s \) are the work functions of the tip and sample, respectively. In the constant-current tunnelling mode of STM, the contour followed by the tip is a complex function of the DOS of the sample and the tunnelling transmission probability. Equation (2.5) shows that the transmission probability decreases with the tip-sample distance, but increases monotonically with the electron energy. It reaches a maximum for the electron at the Fermi level of the negatively biased electrode tunnelling into the positively biased electrode (see Figure 2.4B).

(3) Field emission regime (\( V > \Phi/e \))

The bias can further be increased to a value higher than the work function (\( \Phi \)) of the surface, which yields a quite different tunnelling behaviour. To differentiate it from the normal tunnelling at \( V < \Phi/e \), this process will be referred to as “scanning field-emission microscopy” (SFEM) throughout this thesis. Interestingly, this technique had been known before the birth of STM as the device called “topografiner”, was invented by Young in the 1970s.\(^{13}\) Under a high bias voltage, the probe tip is retracted by the feedback circuit to maintain a moderate tunnelling current. Hence, the tip-sample distance is usually larger than 10 Å in SFEM. This is certainly not favourable for achieving a high resolution of the
surface structure, since the electronic wavefunctions of the surface vanish quickly above the interface.\textsuperscript{14} This is why the SFEM technique has been used much less by surface scientists in comparison to the normal STM at lower biases. However, the strength of the SFEM, as will be shown later, resides in its ability to measure the local work function of the surface with a lateral resolution of about 1 nm.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.5.png}
\caption{(A) Electron scattering at a rectangular potential barrier when the electron energy is higher than the barrier height ($E > V_0$). (B) Electron transmission probability ($T$) of a rectangular barrier vs. the electron energy ($E$). The height and width of the barrier are set to 5 eV and 10 Å, respectively, roughly describing the vacuum tunnelling in SFEM.}
\end{figure}

SFEM is by nature also a quantum tunnelling process, since the electrons still need to transmit through part of the potential barrier between the tip and sample, as shown in figure 2.4C. Different from a normal STM tunnelling ($0 < |V| < \Phi/e$), the electron energy
is larger than part of the potential barrier in SFEM, which leads to new electron transmission behaviour. For a simple rectangular potential barrier, the transmission probability of the electron with an energy higher than the barrier \( E > V_0 \) is given by:

\[
T = \frac{1}{1 + \frac{V_0^2 \sin^2(kZ)}{4E(E-V_0)}}
\]

(2.6)

where \( Z \) is the width of the barrier and \( k_1 = \sqrt{2m(E-V_0)/\hbar^2} \) is the electron’s momentum in the barrier region. In contrast to classical mechanics, the transmission probability in this case is not always unity. Moreover, the transmission probability oscillates with electron energy, as shown in Figure 2.5B. The transmission probability is enhanced when the energy of the particle matches an eigenenergy of a local resonance state within the rectangular potential region. This is why such behaviour is also called “resonance tunnelling” in the literature. When the electron energy is much higher than the barrier \( E >> V_0 \), the oscillation of the transmission probability is damped since we expect its value to gradually approach unity, i.e. the classical result.

![Figure 2.6: Tunnelling spectra (dI/dV vs. V) at (A) clean Ni(100); (B) oxygen covered c(2 × 2) Ni(100) with (B1) at low electric field and (B2) at high electric field; (C) disordered low oxygen coverage on Ni(100); (D) (\( \sqrt{3} \times \sqrt{3} \)) Au on Si(111) and (E) Si(111) surface. From reference 16.](image)
The oscillation of the transmission tunnelling as a function of electron energy was theoretically predicted by Gundlach in the 1960s to exist in junction structures. This so-called Gundlach oscillation was observed in tunnelling spectroscopy by Binnig and Rohrer in the 1980s. Figure 2.6 shows scanning tunnelling spectra of different metal and semiconductor surfaces. Every peak in the $dI/dV$ spectra corresponds to the occurrence of resonance tunnelling between the tip and the sample. The amplitude of the oscillation in the $dI/dV$ spectra diminishes when the voltage is increased, in line with the result derived from the simple rectangular potential barrier model.

Notably, the Gundlach oscillation only occurs when the electron energy is above the work function ($\Phi$) of the surface. Hence the resonance state is related to $\Phi$. The occurrence of resonances leads to an enhancement of the tunnelling current in SFEM imaging. Based on this, the SFEM technique can be used to identify surfaces with different $\Phi$, which is quite useful in a complex system involving more than one chemical substance. A good example of this is the Cu/Mo(110) system as reported by Jung et al. in 1995. Resolving different metal atoms by normal STM imaging is known to be difficult, because metallic systems are usually characterised by a smooth distribution of large DOS.

**Figure 2.7:** SFEM images of (A) Cu stripes attached to step edges of a Mo(110) surface (200 nm × 200 nm) with a bias of 5.3 V (from reference\textsuperscript{18}) and (B) diamond C(100) – (2 × 1) surface (10 nm × 10 nm) recorded in the near-field emission regime ($V = 5.9$ V, $I = 1.1$ nA) (from reference\textsuperscript{19}).
around the Fermi level and the valence electrons are highly delocalised at the interface of
two different metals. When the bias voltage is above the $\Phi$ of Cu and Mo, the Cu and Mo
surfaces exhibit quite a different contrast in the topography image (Figure 2.7A),
rendering the identification of these two metals rather straightforward. Besides this, the
unique capability to distinguish $\Phi$ variations allows SFEM to resolve semiconductor
surfaces, $^{20}$ or even insulator surfaces. $^{19}$ For instance, an atomic-scale imaging of an
insulating diamond surface was achieved via SFEM by Bobrov et al. in 2001. $^{19}$ A large
corrugation within the unit cell was observed in the topography image when the bias
reaches the eigenenergy of the first resonance state (Figure 2.7B). All the above
applications of SFEM make it an important complementary tool to the normal STM
imaging. However, to work out the full power of this technique, it is essential to
understand how field emission resonances are influenced by the work function of the
surface in SFEM. This information has to be extracted from resonance tunnelling
spectroscopy and will be discussed in section 2.2.2.

2.2 Scanning tunnelling spectroscopy

Scanning tunnelling spectroscopy (STS) is a continuous measurement of a given signal,
e.g. the current ($I$), as a function of bias ($V$) or tip-sample distance ($Z$) at a specific
position on the sample. Hence, this yields a local spectroscopic measurement. Different
types of STS rely on which parameter is fixed and which one is monotonically varied,
and what signal is measured. For instance, $Z$ is fixed and $V$ is ramped, while the first
derivative of $I$ with respect to $V$ is recorded in a normal $dI/dV$ spectroscopy. Considering

Table 2.1: Different techniques of scanning tunnelling spectroscopy used in STM.

<table>
<thead>
<tr>
<th>Constant parameter</th>
<th>Ramping parameter</th>
<th>Signal measured</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$</td>
<td>$V$</td>
<td>$I$</td>
<td>21</td>
</tr>
<tr>
<td>$Z$</td>
<td>$V$</td>
<td>$dI/dV$</td>
<td>22</td>
</tr>
<tr>
<td>$Z$</td>
<td>$V$</td>
<td>$d^2I/dV^2$</td>
<td>23-25</td>
</tr>
<tr>
<td>$I$</td>
<td>$V$</td>
<td>$Z$</td>
<td>16,26</td>
</tr>
<tr>
<td>$I$</td>
<td>$V$</td>
<td>$dZ/dV$</td>
<td>19,27-28</td>
</tr>
<tr>
<td>$dZ/dV$</td>
<td>$V$</td>
<td>$dI/dV$</td>
<td>29</td>
</tr>
<tr>
<td>$V$</td>
<td>$Z$</td>
<td>$I$ (or $Ln I$)</td>
<td>3</td>
</tr>
</tbody>
</table>
the three basic STM parameters \((Z, V, I)\) plus their derivatives \(\frac{dI}{dV}, \frac{d^2I}{dV^2}, \frac{dZ}{dV}, \frac{d\text{Ln}(I)}{dZ}\), there are more than 30 different combinations that could be used for STS, which offers great flexibility in choosing the proper STS technique to suit a specific purpose. The commonly used STS techniques reported in the literature are listed in Table 2.1. We need to keep in mind that the \(Z, V, I\) parameters are not independent variables for a specific tip-sample junction \((I = I(Z,V))\), hence some of the STS techniques are correlated (for example, see the comparison of \(\frac{dI}{dV}\) and \(\frac{dZ}{dV}\) in section 2.2.2).

Technically speaking, \(\frac{dI}{dV}\) and \(\frac{d^2I}{dV^2}\) are more accessible than other differential signals in most STM instruments, because the modulation and lock-in amplifier unit are usually installed on the \(V\) and \(I\) channels.

Two different methods are usually employed to collect the spectroscopic data of a differential parameter. The first method is numerical differentiation of the raw data. For instance, the \(\frac{dI}{dV}\) spectrum with a constant \(Z\) can be obtained by numerical differentiation of the \(I-V\) curve. The other method is based on a modulation technique, which was first adopted by Binnig and Rohrer. This technique introduces a small high-frequency sinusoidal voltage modulation that is superimposed on the DC components of the \(V\) or \(Z\) channel. The AC component (e.g. \(\frac{dI}{dV}\) or \(\frac{dI}{dZ}\)) in the current channel is then analysed with a lock-in amplifier. The advantage of this technique is obvious, as it provides a better signal-to-noise ratio especially in the presence of a noisy environment.

Additionally, the feedback of the acquisition system can be switched on or off when acquiring the spectroscopic data. For a \(\frac{dI}{dV}\) measurement on a single point of the surface, the feedback is usually turned off to maintain a constant tip-sample distance. In this case the modulation frequency used is set to be about several hundred Hz or higher. A higher frequency requires less measuring time, whereby minimising the effect of a possible drift in the direction perpendicular to the surface. However, when performing \(\frac{dI}{dV}\) imaging (i.e. collecting the \(\frac{dI}{dV}\) signal at every pixel of the topographic image) along with the topographic signal, it is better to keep the feedback on to maintain a constant current throughout the surface. In this case, the feedback will react to the voltage modulation by moving accordingly the tip when collecting the \(\frac{dI}{dV}\) signal. To avoid this, it is important to use a modulation frequency higher than the bandwidth of the feedback.
system (~ 2 kHz). A high frequency is of course preferred for this purpose, but there is a negative effect when the frequency is too high, because the tip-sample capacitance will react to the bias modulation.  

Two important STS techniques, namely, \( \frac{dI}{dV} \) and \( \frac{dZ}{dV} \) (resonance tunnelling spectroscopy), will be frequently used in the experimental work of this thesis. These are introduced in the following part.

2.2.1 \( \frac{dI}{dV} \) spectroscopy \((V < \Phi/e)\)

With a bias voltage lower than the work function of the sample, \( \frac{dI}{dV} \) spectroscopy is widely used to characterise the DOS of the sample. The interpretation of such \( \frac{dI}{dV} \) spectrum is generally based on the Wentzel-Kramers Brilloiuin (WKB) approximation for the tunnelling current,\(^{12}\) given by equation (2.4). Differentiating equation (2.4) yields:

\[
\frac{dI}{dV} = \rho_s(r,eV)\rho_t(r,0)T(eV,eV,r) + \int_0^\infty \rho_s(r,E)\rho_t(r,E-eV)\frac{dT(E,eV,r)}{dV}dE. \tag{2.7}
\]

The first term contains the DOS of the sample, which is the information we want to extract from the spectroscopic measurement. However, both the first and the second terms depend on the transmission probability \( T \), in a complicated manner. We know from equation (2.5) that \( T \) is a smooth and monotonic function of the voltage; hence the second term in equation (2.7) is expected to contribute by a smooth background on which the first term in superimposed. Therefore, the fine features in the \( \frac{dI}{dV} \) spectroscopy can be essentially attributed to the variation of \( \rho_s(r,eV) \) as a function of energy. This is the theoretical basis for our interpretation of the \( \frac{dI}{dV} \) data.

Useful information on the electronic structure of the surface under investigation, or an adsorbed molecule or cluster of atoms, can be directly extracted from a single-point \( \frac{dI}{dV} \) measurement. As an illustration of this, a \( \frac{dI}{dV} \) spectrum of a pentacene molecule adsorbed on Au(111) is shown in Figure 2.8A, taken from the work of the group of Gerhard Meyer.\(^{29}\) The four main peaks observed are ascribed to the frontier and two higher orbitals of pentacene. For such \( \frac{dI}{dV} \) measurement on a molecule/cluster, it is important to make sure that the peaks are induced by the electronic structure of the
molecule ($\rho_s$) rather than the tip ($\rho_t$) or the substrate itself. This can usually be checked during the measurement by collecting an additional $dI/dV$ spectrum on a clean part of the substrate for comparison. The small peak located at about -0.4 eV in the spectrum of Figure 2.8A is due to the surface state of the Au(111) substrate, as it also appears in the spectrum of bare Au(111).

$dI/dV$ imaging is another important STS technique, often used with low-temperature STM. At a given bias voltage, the $dI/dV$ signal is collected for every pixel of the topographic image, from which we can extract spatially resolved information on the electronic structure. Figure 2.8B shows several $dI/dV$ images of a pentacene molecule on Au(111) with four different bias voltages. One immediately realises that these are similar to the topologies of molecular orbitals expected for pentacene. The capability of resolving the electronic structures in real space and at the atomic/molecular level has been widely applied to the study of molecules$^{31-32}$ and clusters$^{33-34}$, which is undoubtedly the biggest success of the $dI/dV$ imaging method.

Despite this, it is important to understand the limitations of this technique and use it with caution. In fact, a $dI/dV$ signal acquired at a given energy is not only determined by the DOS of the sample, but also by the transmission probability ($T$). This is true even when

Figure 2.8: (A) $dI/dV$ spectrum of a pentacene molecule on Au(111). (B) Topographic and $dI/dV$ images of pentacene recorded at different voltages. From reference$^{29}$. 
considering the contribution from the first term only in equation (2.7). As a consequence, the $dI/dV$ image will faithfully depict the real-space electronic structure if $T$ can be regarded as constant at different positions of the surface. Unfortunately, this is not straightforward in real measurements. Like topographic imaging, $dI/dV$ imaging can also be operated in both constant-current and constant-height modes. In the constant-height mode, $T$ cannot be treated as constant when the molecule/cluster does not have a strict planar geometry. In the constant-current mode (more frequently used in the literature), the situation becomes complicated and the data may easily be misinterpreted. In order to illustrate this point, let us consider the following experiment: A $dI/dV$ image is acquired on a surface that has two points (A and B) with different electronic structures, as shown in Figure 2.9. (1) When a bias voltage $V = E_a/e$ is used, the $dI/dV$ signal at point B is, of course, higher than that at A. This leads to a higher contrast at B than at A in the $dI/dV$ image. (2) When $V = E_b/e$, the DOS at A and B are similar in Figure 2.9. In this instance, the $dI/dV$ image will not show a similar contrast for both locations A and B. As we know from equation (2.4), the current is an integration over the electronic states from the Fermi level to $eV$. The tunnelling current at point B has a high contribution from the electronic states of the resonance at $E_a$; hence the tip at location B will have a larger tip-sample

**Figure 2.9:** Schematics of $dI/dV$ measurements on points A and B, possessing different local electronic structures.
distance as compared to point A. Consequently, the transmission probability at $E_b$ at location B is smaller than that at A. This generates a lower contrast at location B than at A in the $dI/dV$ image. (3) When $V=V_c/e$, the same problem as discussed above is expected to arise. However, its effect is less significant. Because $T$ decreases exponentially with the electron energy (see equation (2.5)), we can write: $T(E_c) >> T(E_a)$. Both A and B have a large DOS at the energy $E_c$, and additionally, the contribution of the electronic states of location B at energy $E_a$ to the tunnelling current is much smaller. We therefore can expect that the $dI/dV$ image will show the correct contrast difference between the two locations A and B.

Based on these arguments, we can conclude that $dI/dV$ imaging is best recorded with an energy that equals an eigenenergy of the molecule/cluster, in order to minimise the influence of the transmission probability. It follows that a good procedure consists in collecting a $dI/dV$ spectrum at a single location on top of the adsorbed molecule/cluster to first identify the eigenenergies by their corresponding peak positions within the spectrum. The appropriate bias voltage is then applied to run the spatially resolved $dI/dV$ imaging over the whole molecule/cluster.

2.2.2 Resonance tunnelling spectroscopy ($V \geq \Phi/e$)

Resonance tunnelling spectroscopy (RTS) is collected at electron energies higher than the work function of the surface. As mentioned in 2.1.2, both SFEM and RTS have a close relationship with the work function of the sample. The work function ($\Phi$) is a fundamental electronic property of any solid surface. It is defined as the minimum energy required to remove an electron from the Fermi level of the solid to the vacuum at 0 K. The work function is the key property of materials used in electron emission when absorbing energy from different sources, i.e., photon, electric field or thermal heating. Traditionally, the work function can be probed by non-local techniques, such as photoelectron emission spectroscopy. RTS, combined with SFEM, opens the possibility to probe for local work function variations with a spatial resolution down to a few Ångströms. We will now explore the mechanisms behind this technique.
Chapter 2 – Scanning tunnelling microscopy and spectroscopy

Figure 2.10: \( \frac{dI}{dV} \) (in red) and \( \frac{dZ}{dV} \) (in blue) spectra collected on a clean Rh(111) surface. Current setpoint: 0.1 nA.

Generally, there are two different methods reported in the literature describing the acquisition of an RTS spectrum. One method consists in measuring the \( \frac{dI}{dV} \) signal while ramping the voltage. The other one relies on collecting a \( Z-V \) curve, from which a \( \frac{dZ}{dV} \) spectrum is obtained by numerical differentiation. The common aspect in both methods is that the current \( I \) is kept constant by the feedback loop of the control electronics. In fact, these two methods can be used simultaneously. Figure 2.10 shows both the \( \frac{dI}{dV} \) and \( \frac{dZ}{dV} \) spectra (the latter obtained by numerically differentiating the associated \( Z-V \) spectrum) collected simultaneously on a clean Rh(111) surface. These spectra are extracted from our own research and will be discussed in details in Chapter 5. The AC component introduced to the \( V \) channel has a negligible effect on the \( Z \) channel since it has a relatively small amplitude (\textit{i.e.} 50 meV). The series of Gundlach oscillations (or resonance peaks) in both \( \frac{dI}{dV} \) and \( \frac{dZ}{dV} \) spectra are located at the same energies, but their intensities are slightly different. This means the \( \frac{dZ}{dV} \) and \( \frac{dI}{dV} \) signals are not completely equivalent, but must originate from identical electronic excitations. Indeed, this can be understood considering the quantum mechanics of vacuum tunnelling in STM, described by:

\[
I = c \cdot e^{kZ}
\] (2.8)
where \( c \) and \( k \) are constants. It follows that:

\[
\frac{dI}{dZ} = kc \cdot e^{kZ} = kl
\]

\[
\frac{dI}{dV} = \frac{dI}{dZ} \frac{dZ}{dV} = kl \frac{dZ}{dV}
\]

Equation (2.9) shows that \( dI/dV \) and \( dZ/dV \) are different by a constant factor \( kl \) (\( I \) is kept constant in the RTS measurement), which explains why \( dI/dV \) and \( dZ/dV \) spectra are correlated to each other. Since equation (2.8) is a theoretical approximation of the vacuum tunnelling at low-voltages, \( k \) may not be a perfect constant in the high-voltage regime. The slight variation of \( k \) results in a slight difference in the peak intensities between \( dI/dV \) and \( dZ/dV \) spectra. However, this variation of \( k \) does not affect the peak positions in the two different RTS spectra.

Unlike \( dI/dV \) spectroscopy in the low bias range (\( V < \Phi/e \)) that has been a well-understood technique for the last two decades, a robust theory of RTS still does not exist. Under that perspective, several STM research groups have recently devoted considerable efforts into elucidating the fundamental mechanisms of RTS, which will be reviewed below.

The Gundlach oscillations were observed in the tunnelling spectrum soon after the invention of STM in the early 1980s. However, these oscillations were ascribed to the image states of the surface that are shifted by the electric field.\(^{16}\) It is important to mention that the effect of the STM tip, which constitutes a boundary condition at the tip-side of the vacuum gap, was ignored in this model. A more precise explanation of the oscillations in RTS was given by Becker et al. from AT&T Bell laboratories.\(^{26}\) These authors proposed that the \( dI/dV \) peaks observed on a Au(110) surface indicate the occurrence of standing waves within the tip-sample gap. A first attempt was made to numerically fit the \( dI/dV \) spectra with the model illustrated in Figure 2.11, from which they found that the eigenenergies of the Gundlach oscillation are sensitive to the tip-sample distance and the work function of the sample. In 2001, RTS was applied by Schintke et al. to an insulating MgO film epitaxially grown on a Ag(001) surface.\(^{28}\) The
Figure 2.11: Potential energy diagram used by Becker et al. to interpret and simulate the Gundlach oscillations in the RTS spectrum of Au(110) surface. From reference\textsuperscript{26}.

authors proposed for the first time that the energy shift of the lowest-order Gundlach oscillation when the tip is scanned from an MgO(001) island to the Ag(100) surface is due to the difference in local work functions. This energy shift was found to be consistent with the result from UPS (Ultraviolet Photoelectron Spectroscopy) measurements on a similar MgO(001)/Ag(001) system. In 2005, Pivetta et al. used RTS to characterise a periodical, two dimensional Moiré pattern formed by depositing NaCl on a Ag(100) surface.\textsuperscript{35} The lowest order Gundlach oscillation was seen to shift in energy when measured at different locations within the supercell. The authors, however, reported that the energy shifts did not correlate perfectly with the work function variation obtained from DFT (Density Functional Theory) calculations. This problem was solved by Lin et al. in 2007, who proposed that the work function variation can be measured from the energy shift of the higher order Gundlach oscillations, rather than the lowest order one.\textsuperscript{27} The lowest order Gundlach oscillation, as they explained, occurs at a small tip-sample distance and has an eigenenergy that is complicated by a nonlinear contribution of the image potential of the surface to the triangular electric field between the tip and sample. This nonlinear factor becomes negligible when the tip-sample distance gets larger.\textsuperscript{27}
Unfortunately, the oversimplified triangular model without a finite boundary on the tip side used in the paper of Lin et al. is not strict enough to fully justify their experimental observations. The boundary effect of the tip should present a strong influence on the resonance states as well. Nevertheless, the empirical observations made by Lin et al. are consistent and reproducible on a series of different surfaces.

**Figure 2.12:** Schematics of the triangular potential barriers for two different sets of \((Z, V)\) parameters. The shape of the potential barrier remains unchanged because the electric field \((V/Z)\) between the tip and the sample remains constant. The sample is positively biased while the tip is grounded.

RTS is essentially different from the low-voltage \(dl/dV\) spectra \((V < \Phi/e)\). The measured peaks in the later spectra arise from the eigenstates of the target molecule/cluster as discussed in section 2.2.1. The oscillations in the RTS spectra are, however, due to the resonance states between the tip and sample. Moreover, these resonance states do not belong to the same system with a fixed boundary condition, since \(V\) and \(Z\) are varying while acquiring the RTS data. Therefore it is not even straightforward to identify the
orders of the oscillations in RTS. In the following we will present a qualitative explanation on the Gundlach oscillations in RTS.

A close inspection on the $Z-V$ and $dZ/dV$ spectra originally reported by Binnig and Rohrer (see Figure 2.6) reveals that the intensity of the $dZ/dV$ oscillation is quickly damped with increasing voltage, and a linear relationship between $Z$ and $V$ becomes dominant at high voltages. In other words, the system manages to keep a constant current by maintaining a roughly linear $Z-V$ relationship. This can be explained by Figure 2.12, in which vacuum tunnelling for two different sets of parameters, i.e. $(Z_1, V_1)$ and $(Z_2, V_2)$, are compared. If $Z-V$ maintains a perfect linear relationship, the shape of the potential barrier for the $(Z_2, V_2)$ condition is a linear extension of that for the $(Z_1, V_1)$ condition. The increase of tunnelling current ($\Delta I$) from the $(Z_1, V_1)$ to the $(Z_2, V_2)$ condition is approximately an integration of the electron transmission within the energy interval $[V_1, V_2]$. However, the electron transmission within this zone has a rather small probability as a result of the high tunnelling barrier ($> V_1 + \Phi_t$) and increased tunnelling distance ($> Z_1$). Therefore $\Delta I$ is

![Figure 2.13: Schematic view of the resonance tunnelling in RTS. $V$ denotes the bias voltage. $E_n$ denotes the eigenenergies of the resonance states in between tip and sample.](image-url)
negligible when compared to the overall tunnelling current. The main contribution to the current comes from the electron transmission around the Fermi level of the tip, which is not affected if the slope of the potential barrier is maintained. This is why a linear $Z-V$ relationship can roughly keep a constant tunnelling current in the high voltage part of the RTS spectrum. However, this linear relationship does not hold in the voltage region close to $\Phi/e$, since the $Z-V$ curve exhibits a step-like behaviour. This can be understood from the fact that the lower order resonance states within the vacuum barrier have a large impact on the electron transmission probability (see equation (2.6) and Figure 2.5), leading to large modulation in the transmission probability when $(Z, V)$ are ramped in RTS.

Because the in- and out-of-resonance occurs alternatively as a result of varying $(Z, V)$, it is fairly difficult to interpret the RTS in a simple way. For instance, it is even not straightforward to identify the order of the eigenstate from the spectrum when the system is in a resonance condition. In order to reach a more quantitative understanding of RTS, however, it is useful to consider a programmed $V-Z$ manipulation applied on the tip-sample junction, while the $dI/dV$ signal is monitored during this procedure. Assuming that $V$ and $Z$ have a simple linear relationship like the one dominating in the high voltage part of $Z-V$ spectrum, ignoring the image potential, and considering that the tip and the sample have the same $\Phi$, then the potential barrier can be expressed by a simple triangular shape given by:

$$V(x) = \frac{V}{Z} \cdot x = Fx ; \text{ for } 0 < x < Z$$  \hspace{1cm} (2.10)

where $F$ is the field strength ($V = FZ$), and $x$ is the position with respect to the tip. $F$ is kept constant when $Z$ is ramped in the RTS spectra. For every set of $(Z, V)$ parameters, the eigenenergies $E_n$ of the potential barrier can be calculated by solving the 1D Schrödinger equation with the potential barrier described by equation (2.10). As shown in Figure 2.13, if the following prerequisite is satisfied:

$$E_n(Z) + \Phi = FZ$$  \hspace{1cm} (2.11)

then a new resonance between the sample and the tip occurs at this $(Z, V)$ condition. This

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Figure 2.14: The eigenenergies ($E_n$) of the resonance states (from $n = 1$ to $n = 7$) at different tip-sample distances ($Z$) (coloured traces), calculated with a $Z$ step of 0.0529 Å (0.1 × Bohr radius); and ($FZ - \Phi$) vs. $Z$ (black trace). The intersections of $E_n$ and ($FZ - \Phi$) are the solutions of $E_n(Z) + \Phi = FZ$, corresponding to the energies of the Gundlach oscillations in the RTS spectrum.

leads to an enhancement of transmission probability, thus a $dI/dV$ oscillation should be observed in the spectrum. An analytical solution of equation (2.11) seems quite difficult to obtain, because the boundary condition for the 1D Schrödinger equation has a variable $Z$ in it. Therefore, numerical calculation was performed to get $E_n(Z)$ associated with equation (2.10), via the MATSLISE package developed by Veerle Ledoux. Figure 2.14 shows the numerical result, in which the eigenenergies $E_n(Z)$ at different $Z$ values were plotted in different colours designating resonance states from $n = 1$ to $n = 7$. The black line denotes ($FZ - \Phi$) as a function of $Z$. The solutions of equation (2.11) hence exist at the points where the coloured lines and the black line intersect with each other. When the bias voltage reaches the corresponding energy of the points marked in Figure 2.14, a Gundlach oscillation appears in the RTS spectrum.

Equation (2.11) can be re-written as:

$$E_n(Z) + \Phi = FZ = eV$$

$$\rightarrow eV_n - \Phi = E_n(Z) > 0$$
where $V_n$ is the voltage of the $n$-th oscillation in the RTS spectrum. It is obvious from equations (2.12) that the resonance peaks have energies higher than the work function.

Here we will discuss the effect of the field strength $F$, which is an essential parameter for the triangular potential barrier. $F$ is directly correlated to the current $I$ in the real measurements, since the current is proportional to the field strength for a specific tip-sample gap. (1) For a larger field strength, $(FZ - \Phi)$ will intersect $E_n(Z)$ at a higher energies, hence leading to an increase of the energies of the Gundlach oscillations. This is in accordance with our experimental observations. Figure 2.15 shows a series of RTS measurements that we performed on a clean Rh(111) surface with different current setpoints. The resonance peaks are observed to shift towards higher voltages with increasing current. (2) For a weaker electric field approaching to zero, equation (2.11) becomes:

$$Z = \frac{(E_n(Z) + \Phi)}{F} \rightarrow \infty.$$
In such case of an infinite $Z$ (i.e. the boundary of the triangular potential well is diminished), $E_{n-1}(Z)$ will become 0. Therefore:

$$eV_{n-1} - \Phi = E_{n-1}(Z) \approx 0$$

$$V_{n-1} \approx \Phi / e.$$  \hspace{1cm} (2.13)

This means that the first resonance state will shift towards the voltage $\Phi/e$ when the field strength is decreased to zero. Although this result itself seems to be very useful for the direct measurement of work function, it is however rendered impractical by inherent technical limitations of STM. Under such a small electric field and consequently large tip-sample distance ($\gg 20$ Å), the tunnelling current is too weak to be detected by the electronics of any STM instrument.

Although the model presented above explains the occurrence of the Gundlach oscillations in RTS, it remains fairly simple. A more thorough description can now be formulated. The assumption of a linear $Z-V$ relationship can be relaxed by adopting a semi-empirical method whereby, instead of using $V = FZ$, we can substitute the experimentally collected $Z-V$ curve into equation (2.11), giving:

$$E_n(Z) + \Phi = V(Z)$$  \hspace{1cm} (2.14)

where $V(Z)$ is directly extracted from the $Z-V$ spectrum. The second assumption we must consider relates to the potential barrier described by equation (2.10), which neglects the image potential and work function difference between tip and sample. The potential can hence be refined by adding to it more terms:

$$V(x) = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{x} + \frac{-1}{4\pi\varepsilon_0} \frac{e^2}{x-(Z-Z_i)} - \frac{V-\Delta\Phi/e}{Z} x$$  \hspace{1cm} (2.15)

where the first and second terms are the image potentials of the tip and the sample, respectively, $Z_i$ is the position of the image plane above the surface and $\Delta\Phi$ is the work function difference between tip and sample. The new $E_n(Z)$ value can be obtained by solving the Schrödinger equation with the potential form (2.15). After substituting $E_n(Z)$ into equation (2.14), the solutions are fitted to the eigenenergies of the Gundlach
oscillations. By doing so, the values of the parameters used in the model can be extracted (Figure 2.13), such as the origin of $Z$ and the work function of the sample. Unfortunately, this semi-empirical method involves a heavy workload of mathematical calculations.

However, from the point of view of experimental surface science, structural parameters like the position of the image plane are not very important. What really makes the RTS technique so promising lies in its ability to measure the local work function variation. That is why it is important to confirm the validity of the empirical observations of Lin et al. which correlate the work function and the RTS spectra. In the following we will further explore how RTS measurements compare at different locations based on the above discussion.

Consider the RTS spectra collected at two different locations A and B exhibit a small work function difference ($d\Phi = \Phi_A - \Phi_B$). We therefore have:

$$E_{A,n}(Z) + \Phi_A = V_A(Z) \quad (2.16)$$

$$E_{B,n}(Z) + \Phi_B = V_B(Z). \quad (2.17)$$

The solution of this set of equations can be described by:

$$E_{A,n}(Z) + \Phi_A = V_{A,n}(Z) \quad (2.18)$$

$$E_{B,n}(Z) + \Phi_B = V_{B,n}(Z) \quad (2.19)$$

where $V_{A,n}$ and $V_{B,n}$ are the $n$-th eigenenergies of the Gundlach oscillations in the RTS spectra on locations A and B. As shown in Figure 2.13, the shape of potential barrier is mainly determined by the field strength. The difference in work function at A and B has mainly an effect of offsetting the potential barrier up or down (according to the sign of $d\Phi$) along the energy axis, bearing no influence on the values $E_{n}(Z)$, as the origin of $E_{n}(Z)$ is set to be the vacuum level of the sample. Therefore, $E_{A,n}(Z) \approx E_{B,n}(Z)$. A subtraction of (2.18) by (2.19) yields:

$$d\Phi = \Phi_A - \Phi_B \approx V_{A,n} - V_{B,n} = dV. \quad (2.20)$$
From this result, it can be concluded that the shift of the Gundlach oscillations ($dV$) reflects the work function difference between the locations A and B, in line with the empirical observations of Lin et al.\textsuperscript{27} This will serve as the basis for our interpretation of the site-specific RTS spectra on graphene/Rh(111) in Chapter 5.

References

(4) Zöphel, S., Freie Universität Berlin, 1996.
(5) http://www.sps-createc.com/mt/general/.
Chapter 2 – Scanning tunnelling microscopy and spectroscopy


3.1 Instruments and methodology

The experimental work presented in this thesis was mainly carried out on a low-temperature STM from CreaTec, a Scanning Probe Microscope manufacturer based in Berlin, Germany. The design of the system follows the instrumental development pursued in the group of Karl-Heinz Rieder, Free University, Berlin. This system was delivered to the Scottish Centre for Interdisciplinary Surface Spectroscopy (SCISS) at St Andrews in early July 2008. I was fully involved in setting up the STM lab which comprised: the commissioning of the instrument upon arrival, the optimisation of all aspects/components of this surface science facility, and the installation of important auxiliary units crucial to the use of the system for the purpose of our measurements on the metal-supported graphene film and carbon clusters.

3.1.1 UHV system

Figure 3.1 presents the overview of our main facility on a concrete block. The UHV (Ultra-High-Vacuum) system is mainly composed of four separated parts: the loadlock (LL) chamber, the preparation (PREP) chamber, the STM chamber and the pumping-stage (TURBO) chamber. (1) The LL chamber is usually used for the fast entry of new STM tips and samples. Besides this, the deposition of the organic molecules with a relatively high vapour pressure can be performed in this chamber, so as to avoid contamination of the PREP chamber. (2) Sample preparation is carried out in the PREP chamber. Single crystals are usually prepared by repeated cycles of Ar⁺ (or Ne⁺) sputtering and annealing. Layered samples can also be cleaved in-situ by a dedicated wobble-stick. The manipulator of the PREP chamber can be cooled down by LN₂ or LHe, hence the temperature of the sample can be adjusted from 20 K to 1300 K. A picture of the inside of the PREP chamber is shown in Figure 3.2A. (3) The STM unit is housed in the STM chamber. A 15 L outer cryostat and a 5 L inner cryostat mounted on top of the STM are used to store LN₂ (liquid nitrogen) and LHe (liquid helium), respectively. The
STM is cooled down by thermal contact to a gold finger extended from the inner cryostat. A double-layer metal shield is further used to protect the STM from being heated up by the outside radiation. (4) The TURBO chamber is pumped by a 240 L/s turbo-molecular pump, backed by a second, small 60 L/s turbo pump and an oil-free two-stage membrane pump. This chamber is designed to provide pumping for the PREP chamber or for the LL chamber during tip/sample entry or molecular deposition. For STM measurements, the turbo and fore pumps are switched off and the TURBO chamber is isolated from the other UHV parts. The vacuum in the PREP and the STM chambers is then maintained by ion pumps. The TURBO chamber has a minimum vacuum loss when pumps are off thanks to two valves installed directly at the exit of the two turbos, minimising the backflow of the air from the high pressure side. Therefore, the vacuum in the TURBO chamber can be recovered in a very short time after switching on the pumping. For instance, the pressure can usually reach $10^{-10}$ mbar in only 2 hours. This design allows for an almost continuous use of the facility without losing too much time on recovering the vacuum.

**Figure 3.1:** Overview of the UHV system including the CreaTec STM. (1) LN$_2$/LHe bath cryostat (CryoVac); (2) variable-gain low-noise current amplifier (FEMTO DLPCA-200); (3) loadlock chamber; (4) linear feedthrough for the tip/sample storage; (5) manipulator (PM25-400); (6) ErLEED (Specs); (7) sputter gun (Specs) with a piezo-controlled leak valve (PV16); (8) gas reservoirs; (9) gas cylinders; (10) cold trap; (11) residual gas analyser; (12) Newport vibration control system; (13) wobble-stick for sample cleavage; (14) CCD camera for tip approach; (15) Magnetic transfer rod. The whole UHV system rests on a 14 tonnes concrete block.
3.1.2 The CreaTec low-temperature STM

Figure 3.2B shows the STM unit when dismounted from the UHV chamber (the radiation shield protecting the STM unit within the UHV chamber prevents good optical access). The STM has a modified Besocke beetle design,² which is known to possess good vibrational and thermal stabilities. The metal plate (8 in Figure 3.2B) resting on the three piezo elements is used to realise the coarse approach of the probe tip. It moves down by rotation around its central axis when an appropriate pulsing voltage (slip-and-stick) is applied to the $x$ and $y$ directions of the piezo tubes. The tip is attached to a fourth piezo tube at the centre of the ramp, which is used to finely coordinate the tip motion. For STM imaging, the three outer piezos are usually adopted to control the $x$ and $y$ movements of the tip, whereas the centre one is used to control the $z$ movement. This judicious choice avoids electronic cross-talk and mechanical instabilities due to the coupling of the $x/y/z$ deformations in a single piezo unit.

![Figure 3.2: Pictures of (A) the inside of the PREP chamber and (B) the STM unit. (1) Sputter gun; (2) LEED; (3) evaporator; (4) residual gas analyser; (5) tip and sample storage; (6) STM unit; (7) central piezo with an STM tip mounted; (8) metal ramp; (9) coarse approach piezos; (10) sample stage.](image)

STM measurements are usually carried out with the cryostats filled with LN$_2$ or LHe. The lowest temperature the STM can reach is about 6 K after it is left in equilibrium with the LHe cryostat for about 24 hours. An advantage of measuring at low temperatures is the
improved stability of the STM system, which is a critical factor for spectroscopy measurements. Moreover, effective strategies have been undertaken to minimise the disturbance from outside vibrations: the UHV system rests on a 14 tonnes concrete block, which is built on the underground floor and well isolated from the rest of the building; the four Newport air-legs can lift up the system to damp the high frequency noise. As a result, the drift during measurements in the $x/y$ directions is about 1 Å per hour, while that in the $z$ direction is less than 1 pm per hour, when the STM is stabilised with LHe. The achieved stability easily meets the requirements of most STS techniques.

For spectroscopy measurements, an internal lock-in amplifier is integrated in the DSP (Digital Signal Processor) board of the CreaTec LT-STM. The lock-in modulates the bias in the voltage channel and measures the signal at the modulation frequency and the second harmonic in the current channel. The modulation frequency can reach a value of up to 6000 Hz.

### 3.1.3 Tip preparation

Acquisition of STM images with atomic resolution relies crucially on an atomically sharp probe tip. Once the sample is transferred into the STM for scanning, a considerable amount of time is spent on the tip to sharpen it by using different voltage pulses. This is unfortunately a repeated trial-and-error job at present. But a good experience will certainly help to identify whether the tip is in a fine state, or to increase the chance of getting a suitable tip for different types of surfaces.

Two different metallic materials, *i.e.* W and Pt/Ir alloy, are used to fabricate the STM tips in our experiments. The W tip is more often used, because it can be made very sharp by electrochemical etching in a relatively controllable way. The etching process is performed with a home-modified device as shown in Figure 3.3. One end of the W wire is fixed on a tip holder, while the other end is placed through the centre of a bubble film surrounded by a Ta loop. The vertical position of the tip holder can be finely adjusted in order to control the precise length of the tip needed to match our coarse-approach criteria (usually $1.5 \pm 0.2$ mm). The bubble film in the loop is made of a high concentration KOH solution (25 wt%). To start the etching, the W wire is positively biased while the Ta loop
Figure 3.3: A home-modified tip etching device. W tips are made by electrochemical etching at the contact between the W wire and a KOH film.

is negatively biased. The small section of the W wire in touch with the KOH film will be etched away by the following reaction:

Anode: \[ \text{W} + 8\text{OH}^- \rightarrow \text{WO}_4^{2-} + 4\text{H}_2\text{O} + 6\text{e} \]

Cathode: \[ 6\text{H}_2\text{O} + 6\text{e} \rightarrow 3\text{H}_2 + 6\text{OH}^- \]

\[ \text{W} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{WO}_4^{2-} + 3\text{H}_2 \] (3.1)

This section becomes thinner and thinner until the lower part of the W wire drops off by gravity, leaving a very sharp W tip fixed on the tip holder. The macroscopic shape of the W tip can be controlled by the etching speed. Usually a slow etching yields a slim shape observed under the optical microscope, which is more likely to possess an atomically sharp tip at the apex. The W tip is rinsed only with de-ionised water several times to remove the ions from the etching solution, and then transferred into the UHV system as soon as possible to avoid oxidation from the ambient air. Sputtering by Ar⁺ and annealing by electron bombardment is further performed in the preparation chamber to clean the freshly-made W tip before it is transferred into the STM chamber.

W metal is relatively reactive in the presence of oxygen. Hence the W tip may sometimes be covered by an oxide layer, which can exhibit a complicated electronic signature in
$dI/dV$ spectra. To avoid this, a Pt/Ir tip is usually favoured for spectroscopy measurements, because it is chemically more inert.\textsuperscript{4} The Pt/Ir tip is made by mechanical cutting of a Pt/Ir (80%/20%) wire. Compared to the electrochemical etching, this method is less controllable. To increase the chance of obtaining a good Pt/Ir tip, the wire is usually cut in a direction almost parallel to its axis, with a fast pull on both ends of the wire.

### 3.1.4 Gas-line system

A dedicated, home-built gas-line system is attached to the UHV system. As can be seen from Figure 3.4, it consists of several gas lines leading to the sputter gun or the individual gas-reservoirs (about 15 cm$^3$). Each reservoir is conditioned to store a specific gas and deliver it to the UHV system via a leak-valve. The gas-line system is designed to have three main functions: (1) Provide Ar gas for the sputter gun. The Ar gas-line is separated from all other lines since the Ar gas is consumed quickly and needs a frequent refill. (2) Supply gas for the reactions in the PREP chamber. The gases can be purified by a cold...
trap cooled down by LN$_2$ (or a mixture with ethanol) before being stored in the gas reservoirs. Chemical reactions carried out in the PREP chamber may require more than one gas simultaneously; hence the UHV part after the gas reservoir is designed to be able to provide mixed gases with different ratios. This is realised by controlling the leak rate of the valve behind each gas reservoir. All gas exposures are performed by back-filling the PREP chamber to the desired pressure. (3) Allow for in-situ gas dosing directly in the tunnel junction of the STM. The gas is introduced through a CF36 flange that has its axis oriented with a grazing-incidence angle to the sample surface in the STM unit.

3.1.5 Evaporators

Different types of evaporators were made for dosing different chemical species to the sample surface in the PREP chamber. For an organic molecule doser (Figure 3.5A), the molecule powder is stored in a glass tube because the organics usually have a low

![Figure 3.5: Pictures of two home-made evaporators. (A) An organic molecule evaporator; (B) a metal evaporator with two metal sources separated by a Ta shield. This was used in a collaboration project with SASOL, UK, not discussed in this thesis.]()
evaporation temperature. A Ta wire wrapped around the tube is used to heat the molecules to their sublimation temperature, which can be precisely monitored by a K-type thermocouple sealed inside of the glass tube. For a metal doser (Figure 3.5B), the metal source is attached closely to a W filament. The evaporation starts when the W filament is resistively heated up to high temperatures. Calibration of the deposition rate is achieved by STM measurements of the coverage.

3.1.6 LEED and AES

An ErLEED from Specs is mounted on a DN 150 CF flange of the preparation chamber. This optics has a back-view design with a transparent fluorescent screen. For a LEED (Low Energy Electron Diffraction) measurement, a focused electron beam of a well-defined energy (20–200 eV) is emitted from a cathode filament at normal incidence on the sample surface. While the inelastically back-scattered electrons are mainly screened out by the hemispherical concentric grids, the elastically scattered ones will reach the fluorescent screen, forming a bright diffraction pattern. The electron energy used in LEED is close to the minimum of the universal mean free path curve in solids, allowing for high surface sensitivity. The LEED pattern can be understood by the Ewald sphere construction for diffraction by a 2D surface lattice. The periodicity in the direction normal to the surface is lost due to the solid/vacuum interface and a low mean free path of the electron in solid. Hence the surface in the reciprocal space is represented by a 2D array of rods. Diffraction is allowed when the Ewald sphere intersects the lattice rods, requiring that the wavelength of the electron must be smaller than the lattice constant. Due to the conservation of the momentum parallel to the surface and the conservation of energy in elastic scattering, the relationship between the incident and scattered electron beams is defined by:

\[ k_i = k_0 + g_{hk}, \quad (g_{hk} = ha_1 + ka_2) \]  

\[ |k_i| = |k_0| \]  

where \( k_0 \) and \( k_i \) are the momentum vectors of the incident and scattered electrons, \( a_1 \) and \( a_2 \) are the periodicities of the 2D reciprocal lattice, and \( h \) and \( k \) are integers. Figure 3.6B,
which graphically illustrates equations (3.2) and (3.3), allows for an important conclusion to be reached: the observed LEED pattern is a scaled representation of the reciprocal lattice of the 2D surface structure. Based on this, the real space symmetry and dimensions of the surface structure can be extracted from the LEED pattern.

Figure 3.6: Schematics of LEED in the real space and the Ewald sphere construction in the reciprocal space for an electron beam incident normal to a 2D surface.

Additionally, the 4 grid optics in ErLEED can also be used as a retarding field analyser; hence the device can be used for AES (Auger Electron Spectroscopy) measurements. The Auger process in our ErLEED is initiated by excitation of the surface atoms with a high-energy electron beam (up to 3 keV). A core hole is generated by removing an electron from the atom. Such a hole can then be filled by an outer shell electron, meanwhile its transition energy is coupled to a second shell electron emitting from the atom. Hence, the kinetic energy of an Auger electron is equal to the energy difference of the singly ionised initial state and the doubly ionised final state. Since the orbital energies are unique to the ionised atom, the analysis of the Auger electrons can give information of the chemical components of the measured sample.

During the AES measurements with ErLEED, the Auger electrons with different energies are collected by the screen. The gate voltage is scanned in a linear ramp, and the second
derivative of the electron current is obtained by a lock-in amplifier. Therefore, AES with an energy resolution of a few eV can be acquired. This is usually employed in our experiments to check for the possible contamination on the sample surface.

3.2 Preparation of Rh(111)

3.2.1 Cleaning procedures

The two subjects (graphene film and carbon clusters) studied in this thesis are both supported on the Rh(111) surface. Like many other transition metals, as purchased Rh(111) single crystal always contains some carbon residues in the bulk, although evaluated at concentrations less than 0.01% by the manufacturer (MaTeck GmbH). Such carbon is in a form of a carbide (or carbon-metal alloy), which makes it hard to remove from the crystal. After many repeated cycles of Ar\(^+\) sputtering (P[Ar] = 1.5 \times 10^{-5}\) mbar, 1.5 keV, 2–4 µA/cm\(^2\), 10 minutes), annealing (1170 K, 10 minutes) and oxidation (P[O\(_2\)] = 2 \times 10^{-7}\) mbar, 1000 K, 40 minutes), the carbon impurities are significantly reduced. However, when the Rh(111) crystal is subjected to prolonged annealing at extremely high temperatures (e.g. 30 minutes at 1200–1300 K), carbon is still found to segregate into small low-quality graphene flakes at the step edges of Rh(111). To avoid such carbon segregation, a clean Rh(111) surface is usually prepared by mildly annealing the sample at 800–1000 K for 5–10 minutes after the sputtering procedure (P[Ar]=1.0 \times 10^{-5}\) mbar, 1.5 keV, 2–4 µA/cm\(^2\), 5 minutes). This procedure is enough to guarantee a good-quality Rh(111) surface with extended terraces (up to several µm) for STM applications.

3.2.2 General features of Rh(111)

A rhodium crystal is known to have a FCC (Face Centred Cubic) structure. Hence the Rh(111) surface has a hexagonal symmetry, and a ABC-type stacking of its layers along the [111] direction, as illustrated in Figure 3.7. When considering not only the first but also the second layer of rhodium atoms, the symmetry of Rh(111) downgrades from 6-fold to 3-fold. As a result, two different dense-packed steps exist, namely A-type and B-type steps.\(^7\)
Figure 3.7: Model of the top three layers of the Rh(111) surface. The inset shows the relative positions of the two different hollow sites with respect to the centre of a rhodium atom.

STM images of a freshly prepared Rh(111) surface are presented in Figures 3.8, showing clean terraces and an ordered hexagonal rhodium lattice. The purpose of imaging the original Rh(111) surface is manifold: (1) allowing for the identification of the locations of the fcc/hcp hollow sites with respect to the rhodium atoms and the A-/B-type steps. This is performed by imaging across a rhodium step edge with atomic resolution (not shown here). This structural information will be needed later when analysing the atomic-scale registry of the graphene layer and the carbon clusters on Rh(111); (2) a reference for the rhodium step edge reconstruction accompanying the formation of graphene, as will be detailed in section 4.5; (3) A routine procedure to check the sample cleanliness before the graphene growth. This is usually done along with LEED (Figure 3.8C) and AES measurements.
Figure 3.8: STM images of (A) a large-scale Rh(111) surface (800 Å × 800 Å, 0.41 V, 0.75 nA) and (B) a Rh(111) lattice atomically resolved (38 Å × 38 Å, 0.10 V, 3.0 nA). (C) LEED pattern of Rh(111). Electron energy: 72 eV.

Figure 3.9: (A) STM images (28.6 Å × 16.5 Å) of Rh(111) surface acquired using a Pt/Ir tip with different tunnelling parameters. (B) Height profiles along the lines indicated in the corresponding STM images.
The rhodium steps generally adopt the two inequivalent close-packed orientations (A- and B-steps), although they are usually not perfectly straight. More B-steps are observed than A-steps based on more than 100 STM images on this Rh(111) sample. The rhodium atoms in the STM images with high magnifications usually appear as bright protrusions. On rare occasions, when the probe tip is in a peculiar electronic state, the rhodium atoms can also be observed as depressions, as illustrated in Figure 3.9 where a contrast reversal of the rhodium lattice is witnessed at different tunnelling parameters (using a Pt/Ir tip).

The Rh(111) surface has a high propensity to form step dislocations (as seen in Figure 3.8A) and vacancy island defects. Figures 3.10A and 3.10B present two dislocations on Rh(111) recorded with high magnification. These dislocations are accommodated in a very small surface area, yielding a strong distortion of the local rhodium lattice. The structural stress is likely to result in high chemical reactivity around the dislocation. Indeed, such sites are usually a preferential location for the graphene growth, as will be mentioned later. Interestingly, small triangular vacancies are sometimes observed on the large flat terraces of Rh(111). The three edges of the triangular defect exclusively adopt

**Figure 3.10:** STM images (A) (150 Å × 82 Å, 0.10 V, 0.5 nA) and (B) (55 Å × 40 Å, 0.10 V, 0.5 nA) of typically encountered dislocations on Rh(111). (C) 3D STM image (55 Å × 55 Å, 0.05 V, 1.5 nA) of a triangular vacancy on a Rh(111) terrace.
B-step configurations. These defects may be intermediate structures which did not manage to heal during the annealing process.

Rh(111) is quite reactive, for instance, it binds strongly with CO molecules\(^9\), and it can dehydrogenate hydrocarbon molecules at low temperatures\(^6\)\(^-\)\(^7\). The residual gas in a UHV system is mainly composed of H\(_2\), CO and H\(_2\)O.\(^10\) If the Rh(111) sample stays in the preparation chamber (~ 1–5 × 10\(^{-10}\) mbar, room temperature) too long (\(i.e.\) 1 hour), it has a high probability to absorb some of these molecules (note: the expected coverage is 0.4–2 ML, if the sticking coefficient of the molecules is unity). This is in contrast to the Au(111) and Ag(111) samples, which can remain uncontaminated in the preparation chamber for a much longer time. To avoid such possible contamination, the freshly prepared Rh(111) sample is usually transferred within 20 minutes into the STM chamber (< 10\(^{-11}\) mbar, at LN\(_2\) or LHe temperature) for measurements.

### 3.3 DFT calculations

Density Functional Theory (DFT) calculations were utilised by our collaborators to investigate the subjects we aim at in this thesis. The calculations for monolayer graphene/Rh(111) included in Chapter 5 are provided by Herbert Früchtl and Catherine Bromley at the University of St Andrews, UK, and those for carbon-clusters/Rh(111) in Chapter 6 are from Weixue Li and Xiufang Ma at Dalian Institute of Chemical Physics, China. Since the theoretical approach is crucial for a better understanding of our experimental results, a very brief overview of the DFT calculations will be presented in what follows.

For any given system, the wavefunction \((\Phi(r_1, r_2, \ldots, r_N))\) describing its electronic structure can in principle be completely derived by solving the Schrödinger equation within the Born-Oppenheimer approximation:

\[
H\Phi = (T + V + U)\Phi = E\Phi
\]  

(3.4)

where the Hamiltonian \((H)\) consists of the kinetic energy \((T)\), the electrostatic potential from the nuclei \((V)\) and the internal interaction between the electrons \((U)\). Due to the electron-electron interaction \((U)\), the wavefunctions of the electrons in the system are correlated to each other. Therefore, solving equation (3.4) becomes challenging when
treating systems with a large number of particles. DFT offers an alternative way to tackle this many-body problem, since it adopts the electron density \( n(r) \) rather than the wavefunction \( \Phi(r_1, r_2, \ldots, r_N) \) as the basic variable, presenting a real space perspective of the physical situation. The basis of DFT was laid in 1964 by Pierre Hohenberg and Walter Kohn, who demonstrated that the electronic ground state of a system is a unique functional of the electron density. Based on this, an approach was further developed by Walter Kohn and Lu Jeu Sham to calculate the electron density and electronic ground state. The electrons are treated by the Kohn-Sham approach as a combination of non-interacting particles in an effective potential, and the total wavefunction can be split into single-particle wavefunctions defined by:

\[
(T + V_{\text{eff}}) \phi_i(r) = \epsilon_i \phi_i(r) \quad \text{(3.5)}
\]

\[
V_{\text{eff}} = V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}} \quad \text{(3.6)}
\]

where \( V_{\text{eff}} \) is the effective potential containing the external potential \( V_{\text{ext}} \), the electron-electron Coulomb repulsion \( V_{\text{H}} \) and the exchange-correlation potential \( V_{\text{xc}} \). Since \( V_{\text{eff}} \) depends on the electron density, equation (3.5) is solved by means of iteration. To initialize the calculation, a guess of the electron density of the system has to be made. The corresponding Hamiltonian is then derived, and used to relax the electronic structure. Consequently, a new electron density and a new Hamiltonian can be obtained. This cycle is further continued until reaching a convergence criterion.

Notably, the exchange-correlation potential \( V_{\text{xc}} \) is not known exactly in equation (3.6). Hence an approximation has to be introduced to describe \( V_{\text{xc}} \) for the self-consistent calculation. Two commonly used approximations are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). In the LDA the exact exchange and correlation energy per particle calculated for a homogeneous electron gas is used. This approximation is suitable for the slowly varying electron densities. But for non-uniform charge densities, the exchange-correlation energy can deviate significantly from the uniform result. In order to correct for this deviation, the more advanced GGA was derived by adding an extra term depending on the gradient of electron density. With these approximations, DFT has become the most successful approach to compute the
Chapter 3 – Experimental section

electronic structure and the total energy of a given many-particle system in its ground state. Compared to solving the Schrödinger equation (3.4), the computational cost associated with DFT calculations scales significantly lesser with the number of atoms, allowing for an ab initio description of systems with a moderate size.

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Chapter 4 – Superstructures of epitaxial graphene on Rh(111)

4.1 Introduction

Graphene has attracted considerably increasing interest since Geim et al. extracted a single graphene sheet by micromechanical cleavage in 2004.\textsuperscript{1} Due to the unique properties of this carbon material and its promising applications for nanoelectronics\textsuperscript{2,3}, the study of graphene is not restricted to the exfoliated carbon flakes from HOPG. Epitaxial graphene grown on transition metal surfaces is becoming an important branch of graphene research, since high-quality monolayer carbon films can be synthesised by pyrolytic decomposition of hydrocarbon molecules. Moreover, graphene/TM constitutes an ideal model system for studies pertaining to coke formation, that is, one of the main deactivation factors in heterogeneous catalysis.\textsuperscript{4} Studies in this respect can help to understand how the catalysts become passivated by carbon species under high temperature conditions. From the materials science point of view, the graphene/TM system shows potential as a template (nanomesh) for nanotechnology, e.g. polarization-induced surface trapping of laterally-organized atoms or molecules was recently demonstrated.\textsuperscript{5-10}

Unlike free-standing graphene, epitaxial graphene supported on the close-packed surfaces of the 4d and 5d transition metals exhibits various Moiré superstructures, as mentioned in Chapter 1. It is hence crucial to understand the concept of Moiré before discussing the structural features of graphene/TM.

4.1.1 Fundamentals of Moiré patterns

Moiré in Physics is an interference pattern created by overlying two grids either at a certain angle, or having different lattice constants. Such patterns are commonly seen in our everyday life, for instance, in the ripple-like stripes we observe on some birds’ feathers. Moiré patterns are not a new concept for surface scientists, especially in the field of epitaxial film growth.\textsuperscript{11} These can provide valuable insights on the registry of the top layer with respect to the “invisible” second layer beneath. The most famous example
of Moiré patterns in surface science is probably the \((23 \times \sqrt{3})\) herringbone pattern of Au(111), which is induced by a reconstructed first layer of the single crystal. Its identification\(^{12-13}\) demonstrated the powerful capability of the STM technique in tackling surface science problems.\(^{14-15}\)

Figure 4.1: (A) Moiré pattern formed by two mismatched lattices. (B) Overlap of two lattices with a large mismatch angle. The corresponding lattice vectors in reciprocal space are given on the right side of the Moiré patterns.

Figure 4.1A illustrates a Moiré pattern created by the overlap of two mismatched lattices \(L_1\) (in red) and \(L_2\) (in blue). The Moiré vector is defined in reciprocal space by:

\[
\vec{k}_{\text{Moiré}} = \vec{k}_2 - \vec{k}_1
\]

\[(4.1)\]
where \( \vec{k}_1 \) and \( \vec{k}_2 \) are the reciprocal vectors of \( L_1 \) and \( L_2 \), respectively. The periodicity of the Moiré pattern, \( i.e. \) the absolute value of \( \vec{k}_{Moiré} \), can be calculated from equation (4.1):

\[
d_{Moiré} = \left( \frac{1}{d_1} \right)^2 + \left( \frac{1}{d_2} \right)^2 - \left( \frac{2}{d_1 d_2} \right) \cos(\phi_{1,2}) \right)^{-1/2}
\]

where \( d_1 \) and \( d_2 \) are the lattice constants of \( L_1 \) and \( L_2 \), respectively, and \( \phi_{1,2} \) is the mismatch angle between the two lattices.

The concept of Moiré does not obey a very strict definition from a mathematical point of view, for the following reasons. Considering the three different vectors \( (\vec{k}_1, \vec{k}_2, \vec{k}_{Moiré}) \) in reciprocal space, we usually say that a Moiré pattern occurs only when \( |\vec{k}_{Moiré}| \) is significantly smaller than \( |\vec{k}_1| \) and \( |\vec{k}_2| \), which makes the Moiré superstructure easy to distinguish from the two constituting lattices in real space. If \( |\vec{k}_{Moiré}| \) is comparable to \( |\vec{k}_1| \) and \( |\vec{k}_2| \), the superstructure is not visibly obvious in real space (as shown in Figure 4.1B), and is usually not referred to a Moiré pattern by common sense. Hence the so-called Moiré occurs only if \( |\vec{k}_{Moiré}| \) has a relatively small value in reciprocal space, requiring that \( \vec{k}_1 \) and \( \vec{k}_2 \) have close absolute values. This seemingly non-rigid restriction \( (|\vec{k}_1| \sim |\vec{k}_2|) >> |\vec{k}_{Moiré}| \), or \( d_1 \sim d_2 << d_{Moiré} \) is critical to the understanding of Moiré superstructures and will be used frequently in the following discussions.

A Moiré pattern is very sensitive to both the lattice mismatch and the angular mismatch of the constituting lattices. First, the effect of the lattice mismatch on the Moiré pattern is discussed. For simplification, we consider a Moiré pattern formed by lattices \( (L_1 \) and \( L_2 \) without any angular mismatch \( (\phi_{1,2} = 0) \). The Moiré periodicity is given by:

\[
d_{Moiré} = \left( \frac{1}{d_1} \right)^2 + \left( \frac{1}{d_2} \right)^2 - \left( \frac{2}{d_1 d_2} \right) \right)^{-1/2}
\]
\[ d_{\text{Moiré}} = \left| \frac{d_{1}d_{2}}{d_{1} - d_{2}} \right| \quad (4.3) \]

Assuming that lattice L₂ has a slight change in its periodicity from \( d_{2} \) to \( d_{2}' = d_{2} + \Delta d_{2} \) \((\Delta d_{2} \ll d_{2})\), the new Moiré pattern has a periodicity given by:

\[ d_{\text{Moiré}}' = \frac{d_{1}d_{2}'}{d_{1} - d_{2}'} = \frac{d_{1}(d_{2} + \Delta d_{2})}{d_{1} - d_{2} - \Delta d_{2}}. \]

The relative variation of the Moiré periodicity is:

\[ \frac{\Delta d_{\text{Moiré}}}{d_{\text{Moiré}}} = \frac{d_{\text{Moiré}} - d_{\text{Moiré}}'}{d_{\text{Moiré}}} = \frac{(d_{1} - d_{2})(d_{2} + \Delta d_{2})}{d_{2}(d_{1} - d_{2} - \Delta d_{2})} - 1 = \frac{d_{1}}{d_{1} - d_{2}'} \frac{\Delta d_{2}}{d_{2}}. \]

Since \( d_{1} \gg d_{1} - d_{2} \approx d_{1} - d_{2}' \), we have:

\[ \left( \frac{\Delta d_{\text{Moiré}}}{d_{\text{Moiré}}} \right) / \left( \frac{\Delta d_{2}}{d_{2}} \right) = \frac{d_{1}}{d_{1} - d_{2}'} \gg 1. \quad (4.4) \]

Equation (4.4) indicates that the relative variation of the Moiré periodicity is much larger than that of the lattice constant. In other words, the size variation of the constituting lattices is amplified in the variation of the Moiré periodicity. To see this effect more specifically, a superstructure formed by overlapping free-standing graphene on Rh(111) will be used as an example. According to equation (4.3), the Moiré pattern of free-standing graphene and a Rh(111) surface has a periodicity of \( \frac{2.69 \times 2.456}{2.69 - 2.456} = 28.23 \text{ Å} \), containing about 10.7 rhodium or 11.7 graphite units. If graphene has a 1% expansion in its lattice, the new Moiré pattern will have a periodicity of \( \frac{2.69 \times 2.456 \times 1.01}{2.69 - 2.456 \times 1.01} = 31.86 \text{ Å} \). The relative variation of the Moiré pattern is 12.84%, which is larger by one order of magnitude than the 1% variation of graphene. This is very useful for STM imaging: a 1% variation in the lattice constant is usually difficult to distinguish directly by STM imaging. By measuring, however, the variation of
the Moiré periodicity, such a small lattice variation can be resolved with an enhanced accuracy.

Besides the variation of the lattice dimensions, a Moiré pattern can also amplify the variation of the lattice misalignment. Assuming that lattice $L_2$ is rotated by an angle $\phi_{1,2}$ with respect to lattice $L_1$. The angle between the Moiré superlattice and lattice $L_2$ ($\phi_{Moiré,2}$) is described by:

$$\sin(\phi_{1,2}) = \left( \cos(\phi_{1,2}) - \frac{|k_2|}{|k_1|} \right) \tan(\phi_{1,2}).$$  \hspace{1cm} (4.5)

If the rotation is assumed small ($\phi_{1,2} \rightarrow 0$), the above equation can be simplified to:

$$\phi_{Moiré,2} \approx \frac{|k_1|}{|k_1| - |k_2|} \cdot \phi_{1,2}.$$  \hspace{1cm} (4.6)

Since $|\vec{k}_1| \sim |\vec{k}_2| >> |\vec{k}_1| - |\vec{k}_2|$, we have:

$$\phi_{Moiré,2}/\phi_{1,2} \approx \frac{|k_1|}{|k_1| - |k_2|} >> 1$$  \hspace{1cm} (4.7)

and:

$$\phi_{Moiré,1}/\phi_{1,2} = (\phi_{Moiré,1} + \phi_{1,2})/\phi_{1,2} >> 1.$$  \hspace{1cm} (4.8)

These last two relations show that the angular rotation of the Moiré pattern is much larger than that of the constituting lattice.

### 4.1.2 Moiré patterns of graphene/TM

Typical STM images of graphene supported on four different VIIIB-group transition metals (i.e., Ru(0001)$_{16}$, Ir(111)$_{17}$, Pt(111)$_{18}$ and Pd(111)$_{19}$) reported in the literature are shown in Figure 4.2. Hexagonal Moiré patterns with an obvious contrast modulation can be easily recognised. The [11\overline{2}0] direction of the graphene layer is parallel to the close-packed directions of the Ru(0001), Pd(111) and Ir(111) substrates (i.e., [\overline{1}0\overline{0}] for Ir(111).
and Pd(111), and [11\20] for Ru(0001)), whereas graphene supported on the Pt(111) substrate does not have a fixed, unique orientation with respect to the metal surface.\textsuperscript{18,20}

Figure 4.2: STM images of (A) graphene/Ru(0001), (60 Å × 42 Å), modified from reference\textsuperscript{16}, (C) graphene/Ir(111), (75 Å × 57 Å), modified from reference\textsuperscript{17}, (E) graphene/Pt(111), (200 Å × 200 Å), modified from reference\textsuperscript{18}, (G) and (H) graphene/Pd(111), modified from reference\textsuperscript{19}. LEED patterns of (B) graphene/Ru(0001), (D) graphene/Ir(111) and (F) graphene/Pt(111), modified from reference\textsuperscript{21}.
This is indeed confirmed by the LEED results accompanying Figure 4.2 (Note: LEED patterns for graphene/Pd(111) are not available from the literature). Clearly, the diffraction spots of the carbon and metal surface are well aligned with each other for graphene/Ru(0001) and graphene/Ir(111), whereas the diffraction pattern of graphene is quite diffuse for graphene/Pt(111), indicating multiple angular orientations.

We will now look further into the Moiré superstructures of graphene/Ru(0001) and graphene/Ir(111), since they have a single orientation on the metal substrate and have been extensively investigated by different research groups. The Moiré of graphene/Ru(0001) is usually reported to have a superstructure of approximately $(12 \times 12)\ C\ on\ (11 \times 11)\ Ru(0001)^{22}$ or $(11 \times 11)\ C\ on\ (10 \times 10)\ Ru(0001)^{23}$ (note: C represents the unit cell of graphene). However, other superstructures were also observed by various techniques. For example, a $(10 \times 10)\ C\ on\ (9 \times 9)\ Ru(0001)$ was reported by Grant et al. based on LEED measurements.$^{24}$ Recently, Surface X-Ray Diffraction (SXRD) was applied by Martoccia et al. to characterise graphene/Ru(0001), yielding a more precise evaluation of the superstructure, $i.e.$ $(25 \times 25)\ C\ on\ (23 \times 23)\ Ru(0001)$.\textsuperscript{25} For the Moiré pattern of graphene/Ir(111), it is usually regarded to have an incommensurate superstructure, which is described as $(10.32 \times 10.32)\ C\ on\ (9.32 \times 9.32)\ Ir(111)$.\textsuperscript{17} The discrepancies in the Moiré periodicities of the graphene/TM systems may relate to the characterisation technique itself. Generally, averaging techniques are more efficient than local ones (such as STM) to measure the supercell with such a large periodicity. Moreover, defects are known to locally influence the graphene lattice (e.g. Figure 2 from reference\textsuperscript{26} and Figure 1 from reference\textsuperscript{22}), and hence complicate the interpretation of STM data. This is less problematic for the averaging techniques, as the accuracy of the statistical measurements is not much affected by local inhomogeneities.

Although epitaxial graphene generally aligns with the metal lattices in graphene/Ru(0001) and graphene/Ir(111), a small angular scattering of the Moiré patterns was commonly observed by STM at the local scale.\textsuperscript{17,22} Figure 4.3A shows an STM image of two neighbouring Moiré supercells of graphene/Ru(0001) from the work of Marchini et al.\textsuperscript{22} By extrapolating the graphene lattice to the neighbouring Moiré supercell, an angular mismatch of about $10^\circ$ between the two Moiré supercells can be estimated. A similar
local angular mismatch was also observed in the STM images of graphene/Ir(111), and a distribution of the Moiré misorientation was plotted by N’Diaye et al.,\textsuperscript{17} as shown in Figure 4.3B. The standard deviation of the distribution is 2.6° for the Moiré misorientation, which corresponds to an angular scattering of the graphene lattice of about only 0.25°. However, we will present a new interpretation on such an apparent angular misorientation in section 4.4.2.

\[\text{Figure 4.3: (A) High-resolution STM image (40 Å × 80 Å) of the Moiré pattern of graphene/Ru(0001). From reference\textsuperscript{22}. (B) Distributions of the Moiré orientations around the average for graphene/Ir(111) islands. The standard deviation of the distribution is 2.6° corresponding to a standard deviation of the angular scattering of the carbon rows of only 0.25°. From reference\textsuperscript{17}.}\]

In this chapter the epitaxial graphene that we investigated is grown on the Rh(111) surface. We chose rhodium as a substrate because it is located in the centre of the VIIIB group of the periodic table. As mentioned in Chapter 1, metals located on the upper-left side of Rh, such as Fe, Co, Ni and Ru, have a strong chemical interaction with carbon, whereas metals on the right-hand side of Rh, that is Pt, Ir, and Pd, are known to have a
relatively weak carbon-metal interaction. This trend follows expectations from the d band model, and further predicts that rhodium is characterised as the intermediate metal in terms of carbon-metal bond strength.

A comparison of graphene adsorbed on Rh(111) with other transition metals, regarding issues related to chemical bonding, will be presented in Chapter 5. This chapter only focuses on the structural features of graphene/Rh(111), studied by low-temperature Scanning Tunnelling Microscopy (STM) and Low Energy Electron Diffraction (LEED). We start by reviewing the synthesis methods that lead to epitaxial graphene. The graphene/Rh(111) Moiré will be carefully analysed with respect to its periodicity, local registries and corrugation. A discussion about the “commensurate vs. incommensurate” nature of this type of Moiré superstructure will be presented. Finally, the configurations of various boundaries and step edges observed in graphene/Rh(111) will be analysed and compared.

4.2 Experimental section

Epitaxial graphene on transition metals can be prepared by two different chemical approaches, depending on the nature of the carbon source. On one hand, the carbon impurities in the bulk can be forced to segregate at the surface, and on the other hand carbon-containing molecules (such as a hydrocarbon or CO) can be exposed from the gas-phase to the surface. A comparison of these two approaches will be discussed for the case of Rh(111).

(1) Carbon segregation from the bulk of Rh(111)

Carbon segregation on Rh(111) is observed after length annealing (> 20 min) at high temperatures (1000–1200 K). For a new Rh(111) single crystal, usually it takes only a few minutes to reach a high coverage of graphene (i.e. 0.4 ML), as a consequence of the high concentration of carbon impurities. The disadvantage of this preparation method is that the graphene product has a low structural quality. Many defects and dislocations can be observed in the carbon film, as shown in Figure 4.4. Moreover, a long annealing time may also lead to the segregation of other possible impurities (e.g. boron). The LEED pattern (not shown) exhibits quite diffuse diffraction spots of carbon, from which it is
difficult to extract structural information of graphene/Rh(111). Therefore this is not an ideal method for our study of graphene/Rh(111).

Figure 4.4: STM images (A) (470 Å × 304 Å, 1.07 V, 0.13 nA) and (B) (931 Å × 707 Å, 1.07 V, 0.16 nA) of graphene formed by carbon segregation from the Rh(111) bulk.

(2) Dehydrogenation of ethylene on Rh(111)

Two slightly different procedures can be adopted to prepare graphene/Rh(111) by pyrolytic decomposition of small hydrocarbon molecules (e.g. ethylene, > 99.95%).

The first procedure consists in depositing ethylene molecules on Rh(111) at room temperature and then anneal the adsorbate/substrate system to high temperatures. This procedure was termed Temperature Programmed Growth (TPG) of graphene by Coraux et al.29 The other procedure is conventional Chemical Vapour Deposition (CVD), whereby a hot Rh(111) surface is directly exposed to a background pressure of ethylene. Here are the experimental details for these two procedures:

TPG procedure: The ethylene is deposited on a clean Rh(111) sample at room temperature with a gas pressure of $2 \times 10^{-7}$ mbar for 2 minutes. This condition is enough to reach a saturation coverage, since ethylene has a high sticking coefficient on the rhodium surface at about 300 K.32 The sample is then slowly heated up to a high temperature (870–1070 K) with a controlled rate less than 100 K/min. It is important to note that a low rate of temperature ramp is critical in the TPG method to obtain a high-quality graphene sample. We keep the sample at the maximum temperature for 10
seconds to make sure the carbonisation is complete. After that, the graphene/Rh(111) sample is cooled down by directly switching off the heating power.

CVD procedure: The clean Rh(111) crystal is initially heated up to a desired temperature (970–1100 K). 1100 K is the maximum temperature we used, in order to minimise the segregation of carbon from the rhodium bulk. Ethylene gas is then introduced into the preparation chamber at a pressure of 1–5 × 10⁻⁷ mbar for 1–3 minutes. The sample is subsequently cooled down after pumping out the unreacted ethylene from the vacuum system.

The TPG procedure is usually employed in our experiments to grow graphene islands, as the obtained coverage is limited by the amount of ethylene molecules deposited on Rh(111) at room temperature. A saturation coverage of ethylene on Rh(111) at room temperature leads to a maximum coverage of graphene of about 0.20 ML after dehydrogenation. Higher coverages of up to 1 ML of graphene/Rh(111) are prepared by the CVD procedure, in which the graphene coverage increases with the ethylene pressure and the reaction time until a saturation coverage is reached. The Rh(111) surface becomes fully passivated once it is coated with a monolayer carbon film. Therefore, no double or multiple layers of graphene have been observed in our STM measurements.

4.3 General characteristics of graphene/Rh(111) Moiré

4.3.1 Moiré periodicity

Figure 4.5A shows a larger-scale STM image of graphene/Rh(111) with a 1 ML carbon coverage prepared by the CVD method. We found that the density of structural defects/dislocations is quite small. The periodicity of the graphene superstructure is hence well maintained and the coherence length can approach 1 µm on the rhodium substrate. The LEED pattern in Figure 4.5B shows that the bright diffraction spots of carbon and rhodium are in line with each other, confirming the epitaxial growth of graphene on Rh(111).
Interestingly, the periodicity of the Moiré pattern is found to vary by about 10% when collecting STM images at different locations on the graphene/Rh(111) surface. For instance, the Moiré periodicities in Figures 4.6A and 4.6B are 29.3 Å and 26.0 Å, respectively. These two values correspond closely to the expected periodicities resulting from 12C/11Rh and 11C/10Rh (note: due to the hexagonal symmetry of the Moiré lattice, the \((m \times m)\) C / \((n \times n)\) TM superstructure is abbreviated as \(mC/nTM\) in the following discussion). The analysis of many images shows that the periodicity of the Moiré can in fact vary within the range 26.0 Å and 29.3 Å. Figures 4.6A and 4.6B are hence representative of two limiting cases. As it has been mentioned in section 4.1.1, the superposition of free-standing graphene on Rh(111) yields a superstructure of 11.7C/10.7Rh, with a periodicity of 28.8 Å. Compared to the 11.7C/10.7Rh supercell, the average C-C bond in Figure 4.6A is very likely expanded (0.2%) whereas that in Figure 4.6B is contracted or tilted (0.9%). In agreement with our topographic observations,
LEED patterns (Figures 4.5B and 4.5C) show slightly diffuse, hexagonally arranged satellites around the Rh(111) substrate spots, indicative of a superstructure with a periodicity of $11.6 \pm 0.2$ graphene lattice constants. Our observations suggest that graphene/Rh(111) does not adopt a simple commensurate structure (further discussed in section 4.4). The main reason for this is probably the relative weak interaction between graphene and Rh(111) (similar to Ir(111)\textsuperscript{17}, as will be discussed in Chapter 5), which is not strong enough to force the carbon overlayer into a simple commensurate structure on the metal substrate.

### 4.3.2 Local registries

We find that the STM topographic appearance of graphene adsorbed on Rh(111) is unique when compared to other transition metal substrates (Figure 4.2). The Moiré pattern of graphene/TM (TM = Ru(0001), Pd(111), Ir(111) and Pt(111)) is simply an alternative arrangement of large bright and dark regions,\textsuperscript{17-18,22-23} whereas the graphene/Rh(111) supercell exhibits three extra dark zones, located exactly in the middle of two neighbouring bright regions. These distinctive site-specific features of graphene/Rh(111) suggest rich topographic or electronic variations within the unit cell, and calls for an
explicit identification of the local registries.

To discuss the atomic registry within a supercell, we consider a 12C/11Rh commensurate relation for which a ball model is sketched in Figure 4.7. Locally, three C-Rh high-symmetry configurations can be distinguished within the supercell, hereafter labelled as ring-top, ring-hollow and ring-bridge, the name referring to the position of the centre of a carbon ring with respect to the substrate. These abbreviations for the local registries within the Moiré supercell will be used throughout the following discussion. The occurrence of these configurations within a unit cell follows the ratio ring-top : ring-hollow : ring-bridge = 1 : 2 : 3.

![Figure 4.7](image)

**Figure 4.7:** Model of a 12C/11Rh superstructure. The highlighted areas indicate local high-symmetry configurations. The green balls denote rhodium atoms, while the red and blue balls denote the two different carbon atoms (A and B) in the graphene unit cell. T = ring-top; B = ring-bridge; F = ring-fcc; H = ring-hcp.

Now we return to the STM images of graphene/Rh(111) in Figure 4.6. These Moiré patterns are found to have one feature in common: there exist three small zones exhibiting a minimum in the tunnelling contrast within each supercell. These zones correspond to the ring-bridge sites, in light of the ratio of the high-symmetry sites.
recognised in the structural model presented in Figure 4.7. Based on this, the other local registries can be identified very easily. (1) The large triangular zones are assigned to ring-top sites. One can see that the ring-top site is characterised by the maximum in the tunnelling contrast within the Moiré supercell. (2) The ring-hollow sites are located at the centre of every three neighbouring ring-bridge sites. Their assignment to ring-hcp and ring-fcc is achieved by identifying the relative locations of the fcc and hcp hollow sites in the first layer of Rh(111) via high-resolution imaging. These usually have similar intermediate tunnelling height in the Moiré supercell of graphene/Rh(111). As will become apparent in the next chapter, the unambiguous assignment of the STM topographic features with the local high-symmetry configurations is central to the analysis of our spectroscopic results.

Different local registries represent different C-metal configurations, hence we can compare the different contrast zones in the STM images with their corresponding atomic configurations. For instance, the ring-hollow registry has the two carbon atoms of the graphene unit cell located on the top and the hollow sites of the rhodium atoms. Therefore the atomic-like protrusions observed in the ring-fcc (or ring-hcp) zone should correspond to the carbon A (or the carbon B) in the model of Figure 4.7. Indeed, the ring-fcc and ring-hcp zones are observed to have a reversed structural contrast in our STM images (see Figure 4.6). The protrusions appearing in the non-symmetric local registries correspond to even more complicated C-Rh configurations. As a consequence, the “apparent lattice” of graphene/Rh(111) in the STM images deviates significantly from the ones observed for free-standing graphene and HOPG. In other words, the atomically resolved features cannot straightforwardly be ascribed to atomic positions.

4.3.3 Corrugation of topographic images

A large contrast modulation between different local registries within the supercell is evident in the STM topographic images. In order to illustrate this, we acquired data at the boundary between graphene and the rhodium surface, allowing for a direct comparison of the corrugation on these two different regions. The graphene lattice has its [1\overline{1}00] direction parallel to the [\overline{1}10] direction of the rhodium surface, consistent with the
Figure 4.8: (A) STM image (64 Å × 82 Å, 0.2 V, 0.4 nA) of the graphene-Rh(111) boundary. (B) Height profile across the Moiré supercell and Rh(111) indicated in (A). (C) Height histogram of image (A).

epitaxy observed in the LEED patterns and in line with observations made on graphene grown on Ir(111) and Ru(0001). A line-profile acquired across the graphene-Rh(111) boundary is shown in Figure 4.8B. We see that graphene exhibits a large topographic modulation in the $z$ direction, as opposed to the gentle lattice corrugation of Rh(111). The height histogram in Figure 4.8C, extracted from the corresponding STM image, further demonstrates that the height distribution of the carbon layer has a FWHM (Full Width at the Half-Maximum) of 0.35 Å, whereas that of the rhodium surface is only 0.08 Å. We need to keep in mind that such a measurement is just a qualitative description of the graphene/Rh(111) system, because the STM data is necessarily bias dependent.

A similar large corrugation has also been reported to exist for graphene epitaxially grown on other transition metals. Since the STM topographic images result from a combination of topographic and electronic effects, there is a debate about which factor dominates the large corrugation commonly observed. In the graphene/Rh(111) case, the contrast of the Moiré supercell in the STM images is found to depend not only on the tip state, but also on the tunnelling parameters. Figures 4.9A and 4.9C show the STM images collected before and after a tip change, respectively. We see from the line-profile
Figure 4.9: (A-C) STM images (width: 150 Å) of the same region of graphene/Rh(111) with different tip states. A tip change occurs in (B) during the scanning. (D-F) STM images (81 Å × 59 Å) of the same region of graphene/Rh(111) with different tunnelling parameters. The small topographic differences between the three neighbouring ring-bridge zones are marked by green circles.
Figure 4.10: (A) and (B) line-profiles across the long symmetry axis of the Moiré supercells in Figures 4.9 (A, C) and (D-F), respectively. (Note: the line-profile of Figure 4.9B is not included, since it is the same as either Figure 4.9A or Figure 4.9C.) Although the contrast variation within the supercell is not the same in all cases, the bridge zone always has the minimum height.

Although the contrast variation within the supercell is not the same in all cases, the bridge zone always has the minimum height.

along the long diagonal of the supercell that a contrast reversal occurs between ring-fcc and ring-hcp (Figure 4.10A). Figures 4.9D-F present STM images acquired on the same region of graphene/Rh(111) at different voltages. The contrast between different registries is enhanced at lower absolute voltages, and the apparent shrinking of the lateral dimensions of bright regions seen in Figures 4.9E to 4.9F is probably due to a strong tip-sample interaction, considering the harsh parameters (i.e. small bias and large tunnelling current) used for the imaging. Nevertheless, we have to emphasise that the ring-bridge site always has the lowest contrast within the graphene/Rh(111) supercell, no matter what tip state and tunnelling parameters we used. Indeed, this is demonstrated in the line-profiles across the unit cells in Figure 4.10.

The ring-bridge site in the case of graphene/Rh(111) is rather special. The ring-hollow site was reported to have the lowest topographic height when graphene is supported on other transition metals (i.e. Ru(0001) and Ir(111)). The ring-bridge configurations,
Figure 4.11: Contour map of the STM image (150 Å × 150 Å) in Figure 4.9A. It can be seen that every three neighbouring ring-bridge sites have slightly different heights in the topographic image.

seen as STM contrast minima on Rh(111) substrate, have so far largely been ignored in previous experimental and theoretical studies. This is unsurprising due to their lack of distinctiveness on other TM substrates. The special character of the ring-bridge configuration in the graphene/Rh(111) system will be revealed by spectroscopy measurements and theoretical calculations presented in Chapter 5. Notably, here we found that the three ring-bridge sites within a Moiré supercell are always not exactly equivalent, irrespective of the tip state. They have slightly different heights in the topographic images as shown in Figures 4.9 and 4.11. This is correlated to the non-simple-commensurate structure of graphene/Rh(111), as will be discussed in the following section.

4.4 Non-simple-commensuration of graphene/Rh(111) Moiré

In this part, we will further look into a fundamental feature of the graphene/Rh(111) Moiré. Figure 4.12 shows an atomically resolved STM image of graphene/Rh(111). A close inspection reveals that the Moiré supercell is not perfectly repeating itself. To illustrate this, we consider the ring-hcp zone highlighted by a triangle delimiting 6 atomic-like features in the Moiré supercell. When comparing the locations of the ring-hcp
Figure 4.12: High-resolution STM image (81 Å × 59 Å, -0.17 V, 1.0 nA) of graphene/Rh(111). The blue lines indicate the [1010] direction of the Moiré superlattice. The edges of the orange triangles follow the “apparent lattice” of the ring-hcp zones. The two yellow arrows indicate the phase shifts of the ring-hcp zones with respect to those in the neighbouring supercells.

zones with the Moiré superlattice (in blue colour), these triangles are found to have different lateral offsets with respect to each other, as marked by the different lengths of the arrows. Such lateral offsets are ubiquitous in all STM images acquired on graphene/Rh(111). Since the Moiré units are not identical even at a local scale, it seems difficult to define the superstructure of graphene/Rh(111) solely based on our STM images. To interpret this type of superstructure, a precise discussion about the concepts of commensuration and incommensuration is needed.

4.4.1 Commensurate vs. incommensurate superstructures

Figure 4.13 shows two Moiré patterns with different supercells, namely, 12C/11Rh and 11.7C/10.7Rh. The 11.7C/10.7Rh represents the Moiré pattern formed by the overlap of free-standing graphene and Rh(111) (see section 4.1.1). These two Moiré patterns are
Figure 4.13: Structural models for graphene/Rh(111) with two different supercells (A) 12C/11Rh and (B) 11.7C/10.7Rh. T = ring-top; B = ring-bridge; F = ring-fcc; H = ring-hcp.

similar at the first glance, despite the small difference in their periodicities. However, a close inspection reveals that every Moiré supercell is exactly the same in the 12C/11Rh superstructure, whereas the Moiré supercells are different for 11.7C/10.7Rh. These two different types of Moiré patterns are usually referred to as commensurate and incommensurate superstructures, respectively, because the latter Moiré has a coincidence lattice comparable to or larger than the surface domains (~μm, limited by the step edges) of the single crystals. To further this discussion, we need understand the relationship between the Moiré periodicity and the coincidence lattice.
(1) Moiré periodicity

The Moiré periodicity described by equation (4.2) can be interpreted in an alternative way using a 1D analogous model. We consider two sinusoidal functions with different periodicities \((d_1 \text{ and } d_2)\). Their overlap (addition) yields:

\[
\sin\left(\frac{2\pi}{d_1} \cdot x\right) + \sin\left(\frac{2\pi}{d_2} \cdot x\right) = 2\sin\left(\pi \cdot \left(\frac{1}{d_1} + \frac{1}{d_2}\right) \cdot x\right) \cos\left(\pi \cdot \left(1 - \frac{1}{d_1} - \frac{1}{d_2}\right) \cdot x\right).
\]

The second part in the last expression has a periodicity given by:

\[
d_{\text{envelop}} = \left|\frac{d_1 d_2}{d_1 - d_2}\right|
\]

Figure 4.14 illustrates several different Moiré superstructures formed by the overlap of different sinusoidal functions. It can be seen that the average periodicity of the wave’s envelop is determined by the term \(\sin\left(\pi \cdot \left(1 - \frac{1}{d_1} - \frac{1}{d_2}\right) \cdot x\right)\). Hence the Moiré periodicity that we used for the description of the superstructures of graphene/TM (see equation (4.3)) corresponds to the average periodicity of the wave’s envelop in this case (i.e. \(d_{\text{envelop}} = d_{\text{Moiré}}\)).

(2) Coincidence lattice

From a mathematical point of view, the coincidence lattice (or coincidence length in a 1D analogous model) of a superstructure formed by two different lattices \((L_1 \text{ and } L_2)\) differs from the Moiré periodicity. The ratio of the lattice constants \((d_1 / d_2)\) can be written as:

\[d_1 / d_2 = p / q\]

where \(p\) and \(q\) are two irreducible integers. Therefore the coincidence length can be simply described by:

\[d_{\text{coincidence}} = d_1 \cdot q \text{ or } d_2 \cdot p\]

(4.10)
A comparison of the Moiré periodicity (4.9) and the coincidence length (4.10) gives:

\[
d_{\text{coincidence}}/d_{\text{Moiré}} = \left| \frac{d_1 \cdot q}{d_1 - d_2} \right| = \left| q(d_1 - d_2) \right| = q \left| \frac{d_1}{d_2} - 1 \right| = q \left| \frac{p}{q} - 1 \right| = |p - q|
\]

which means \(d_{\text{coincidence}}\) contains \(|p-q|\) units of \(d_{\text{Moiré}}\). To illustrate the relationship between the coincidence length and the Moiré periodicity, three different Moiré superstructures formed by two different 1D lattices are shown in Figure 4.14. Lattice \(L_2\) has a period of \(2.69 \text{ Å}\) (corresponding to the lattice constant of Rh(111)), while the lattice \(L_1\) has a period of \(2.69 \times \frac{11}{12}, 2.69 \times \frac{23}{25}\) and \(2.456 \text{ Å}\), respectively. The resulting superstructures A, B and C in Figure 4.14 represent examples of 12C/11TM, 22 23C/25TM, and incommensurate graphene/TM, respectively. It can be seen that: (1) Moiré A has a \(12L_1/11L_2\) supercell. Since \(p - q = 12 - 11 = 1\), the coincidence length and the Moiré periodicity are exactly the same. (2) Moiré B has a \(25L_1/23L_2\) supercell. Its coincidence

**Figure 4.14**: Comparison of the coincidence length and Moiré periodicity in the three different 1D Moiré models (A: \(12L_1/11L_2\); B: \(25L_1/23L_2\); C: \(1345L_1/1228L_2\)). The three different Moiré patterns are formed by the overlap of the sinusoid functions \(L_1\) (\(d_1 = 2.69 \text{ Å}\)) and \(L_2\) (A: \(d_2 = 2.69 \times \frac{11}{12} \text{ Å}\); B: \(d_2 = 2.69 \times \frac{23}{25} \text{ Å}\); C: \(d_2 = 2.456 \text{ Å}\)).
length consists of $p - q = 25 - 23 = 2$ slightly different Moiré units. (3) Moiré C has a quite large coincidence length $(1228 \times 2.69 = 3303.32 \text{ Å})$. Hence its coincidence length is composed of a larger number of slightly different Moiré units. One important feature of Moiré B and C is that, the difference between the neighbouring Moiré units is very small. The real-space imaging techniques such as STM usually have difficulties to resolve such differences. Hence if only based on STM results, it can be hard to distinguish the commensurate superstructure with a large coincidence length. Indeed, the 25C/23Ru superstructure of graphene/Ru(0001) identified by SXRD can hardly be resolved by STM. The information STM imaging can realistically provide is whether the Moiré superstructure has a simple commensuration, like 12C/11TM and 11C/10TM. For non-simple-commensurate superstructures including incommensurate superstructures, STM is not an ideal technique to resolve the exact coincidence length. In this case, however, STM can measure the local averaged Moiré periodicity, since it can be extracted by performing a 2D FFT (Fast Fourier Transform) on the STM images of graphene/TM.

### 4.4.2 Non-simple-commensuration – accounting for “apparent angular scattering”

Here we return to the structural analysis of the graphene/Rh(111) Moiré. Based on the above discussion, we can conclude that graphene/Rh(111) has a non-simple-commensurate superstructure, due to the fact that neighbouring Moiré supercells exhibit a slight offset with small variations in dimension in the STM images. Interestingly, similar local variations of the Moiré supercell were also observed in graphene/Ru(0001) and graphene/Ir(111), and were explained by the angular scattering of the local structural defects that may commonly exist in the carbon film on transition metals. We believe that the introduction of the defect effect is not necessary, because the non-simple-commensuration can lead to such “apparent angular mismatch” appearing in the STM images. To support our interpretation, an estimation of the “apparent angular mismatch” will be made in the following.

Figure 4.15 shows a model of graphene/TM viewed from the [11\(\bar{2}0\)]\text{graphene} direction. Assuming that the two neighbouring Moiré supercells have different ring-top configurations I and II, the red arrows indicate the real centre of the ring-top site, whereas
Figure 4.15: Schematics of (A) the error estimation in measuring the local Moiré periodicity of graphene/TM, and (B) the estimation of the “apparent mismatch” angle in a 12C/11TM Moiré supercell. The violet balls denote the unit cells of graphene, while the cyan balls denote the transition metal atoms.

the blue arrows indicate approximately the centre of the ring-top site appearing in STM images. The real ring-top centre and the apparent centre are at the same location in configuration I. However, they are separated by approximately $\pm 0.5d_{\text{graphene}}$ in configuration II. Therefore this would introduce an error of about $\pm 0.5d_{\text{graphene}}$ when measuring the dimension of a Moiré supercell extending from configuration I to configuration II. Such an error corresponds to an “apparent angular mismatch” of up to $360^\circ / (2\pi \times 12) = 4.8^\circ$ in the Moiré pattern and an “angular mismatch” of $\pm 0.5^\circ$ between graphene and the underlying metal lattice. This result is comparable to the angular misorientations reported for the graphene/Ir(111) system (see Figure 4.3B).17
Notably, the non-simple-commensurate nature of graphene/Rh(111) has more effects on the Moiré patterns. For instance, the Moiré superlattice usually deviates from a perfect hexagonal lattice. This is because the two constituting lattices (see Appendix I) of graphene and Rh(111) \( i.e., \) the \([10\bar{1}0]_{\text{graphene}}, [0\bar{1}0]_{\text{graphene}} \) directions and the \([10\bar{1}]_{\text{Rh}}, [0\bar{1}1]_{\text{Rh}} \) directions) may locally have different “apparent angular mismatches”. As a result of this symmetry reduction, the three ring-bridge sites have slightly different configurations within a supercell. This is in agreement with the inequivalence of the three ring-bridge zones observed in the STM images of graphene/Rh(111), as mentioned in section 4.3.3.

4.5 Boundaries and step edges of graphene/Rh(111)

So far we have investigated the periodical Moiré patterns of graphene/Rh(111). In fact a flat 2D carbon layer in our system has a finite size, which is usually limited by the terraces of Rh(111). Free-standing graphene is known to have two typical step edges \( e.g., \) zigzag type and armchair type, see Figure 4.16), which are characterised by different

![Figure 4.16: Schematics of the zigzag and armchair edges of graphene. Modified from reference 39.](image)

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electronic properties. In the graphene/Rh(111) system, the introduction of the metal interface constitutes an additional boundary for the graphene network. In what follows, three different boundary structures of graphene/Rh(111) will be presented.

### 4.5.1 Graphene islands on the terraces of Rh(111)

Graphene islands on the rhodium terraces can be observed in a low-coverage graphene/Rh(111) sample usually prepared by the TPD method (see the experimental section 4.2). Figure 4.17 shows a graphene island with a truncated hexagonal shape on a rhodium terrace. The graphene steps are aligned with the \([1\bar{1}20]_{\text{graphene}}\) directions hence the carbon island adopts zigzag type edges, as reported for graphene islands on iridium and ruthenium substrates. Compared to the armchair edge, the zigzag one has fewer 2-fold coordinated carbon atoms, hence it is more stable in terms of energy. A further inspection reveals that the B-steps of the graphene islands have a length larger than the A-steps. Interestingly, both steps are terminated with a similar feature: an alternating arrangement of bright and dark zones, irrespective of the state of the probe tip. By mapping the graphene boundaries with a Moiré superlattice, with reference to the local C-Rh registries established earlier, the step edges are found to cut through the ring-top and the ring-bridge zones. Compared to the other possible \([11\bar{2}0]\) step edges crossing the Moiré supercell, this one has the largest geometric buckling because the ring-top and the ring-bridge sites are the topographic maximum and minimum of the Moiré supercell, respectively (as will be demonstrated in Chapter 5). Such a step configuration may maximise the relaxation of the zigzag boundaries, which are stressed by the mismatch between graphene and the Rh(111) substrate.
Figure 4.17: (A) and (B) STM images (250 Å × 232 Å, 0.4 V, 0.4 nA) of a graphene island on the terrace of Rh(111) acquired with different tip states. High-resolution STM images (C) (101 Å × 101 Å, 0.4 V, 0.4 nA) and (D) (121 Å × 121 Å, 0.6 V, 0.2 nA) of the island edges. The STM tip in (A) and (C) has the same state.

4.5.2 Graphene islands at the step edges of Rh(111)

For the graphene/Rh(111) sample with low carbon coverages, most of the graphene islands are located at the step edges instead of on the rhodium terraces (the growth of graphene will be discussed in Chapter 6). Figure 4.18 shows a typical graphene island at the step edge of Rh(111), which indicates that the carbon island is almost completely surrounded within the upper rhodium terrace. This can be understood by a reconstruction...
of the Rh(111) step edges during the graphene growth process. At the high temperatures required for carbonisation, the step edges of Rh(111) are mobile due to Ostwald ripening. Hence, rhodium atoms constantly evaporate from and condense back on the metallic step edges resulting in the fluctuation of the location of the rhodium step edges. The observation of partially embedded carbon islands is a clear indication that it is energetically favourable for the graphene/Rh(111) system to minimise the density of naked graphene step edges by a 2D encapsulation, whereby the coordination of the carbon atoms at the edges of graphene to the atoms at a rhodium terrace edge is maximised. Support for this conclusion can be found in high-resolution images of the boundaries between graphene and the upper rhodium terrace. Figures 4.18B and 4.18C show that the C-Rh interface is regular and straight when compared to the step edges of a clean Rh(111) surface in Figure 3.8A. Interestingly, the graphene islands are in contact with the Rh(111) upper terrace at the ring-bridge zones. We know that the carbon atoms in the ring-bridge zones lie closer (2.2 Å) to the underneath rhodium terrace (see the results of DFT calculations in Chapter 5), while the step height of Rh(111) is also around

**Figure 4.18:** STM images (A) (434 Å × 369 Å, 1.06 V, 0.047 nA) (B) (149 Å × 135 Å, 0.28 V, 0.22 nA) and (C) (101 Å × 88 Å, 0.28 V, 0.22 nA) of graphene islands at the step edges of Rh(111).
2.2 Å. Hence the carbon atoms at ring-bridge have a comparable height with the rhodium atoms in the upper terrace, which represents a geometrically favourable situation for C-Rh bonding. Instead, if the graphene island was terminated with an alternation of ring-top and ring-bridge sites (similar to the free boundary of graphene shown in Figure 4.17), the carbon atoms in the ring-top zones and the rhodium atoms in the upper terrace would have a height mismatch of about 1 Å in the direction perpendicular to the graphene surface. Such a configuration cannot provide the necessary stabilisation for this shoulder-by-shoulder boundary between the graphene and rhodium surfaces.

**Figure 4.19:** STM images (A) (3D, 250 Å × 250 Å, 0.40 V, 0.32 nA) and (B) (600 Å × 600 Å, 0.62 V, 0.20 nA) of the graphene islands at the dislocations of Rh(111). High-resolution STM images (C) (142 Å × 142 Å, 0.62 V, 0.06 nA) and (D) (112 Å × 105 Å, 0.60 V, 0.20 nA) of the graphene-Rh boundaries.
As mentioned in section 3.2, step dislocations are commonly observed on the clean Rh(111) surface. Figure 4.19 shows that the rhodium dislocations are also preferential sites for the growth of graphene islands, due to the high chemical reactivity of the strained metal surface.\textsuperscript{40} Similarly, the edges of the rhodium dislocations are also reconstructed and a well-defined graphene-Rh boundary can be resolved in Figures 4.19C and 4.19D.

### 4.5.3 Graphene layers over the step edges of Rh(111)

We now discuss the step edges of graphene when the carbon layer grows to a complete monolayer on the metal surface. It was reported by Coraux \textit{et al.} that the graphene film maintains a structural coherency over the iridium step edges in graphene/Ir(111), and the local radius of curvature at the transition region is similar to those of thin single wall carbon nanotubes.\textsuperscript{26} In what follows we will study how graphene crosses over the step edges of Rh(111) by carefully analysing the Moiré patterns at the terrace boundaries.

Figure 4.20A shows that all the step edges of graphene are remarkably well defined, in contrast to the irregular step edges of a clean Rh(111) surface. This is a strong indication that the steps of Rh(111) beneath the graphene layer are severely reshaped during the growth process. Interestingly, all the step edges of the carbon layer are terminated with identical graphene-Rh registries, depending on their orientations. The STM images reveal that the graphene terraces exhibit lengths corresponding to an integer number of Moiré units along the directions perpendicular and parallel to the step edges, so do the rhodium terraces below the graphene layer. These quantised structures indicate that the growth of graphene on Rh(111) is a complicated self-assembly process, which involves mass transport (by diffusion) of the rhodium atoms and carbon species, and is regulated by the C-Rh interactions at the boundaries.

Two different types of step edges for the graphene layer are presented in Figures 4.20C and 4.20D, respectively. One is crossing over the A-step of Rh(111), while the other one is over the B-step. Hence these will be abbreviated as A\textsubscript{g}-step and B\textsubscript{g}-step, respectively, in the following discussion. Like the rhodium steps on Rh(111), B\textsubscript{g}-steps are much more commonly observed than A\textsubscript{g}-steps on graphene/Rh(111). A close inspection on Figures
Figure 4.20: Large-scale STM images (A) (801 Å × 801 Å, 0.5 V, 0.1 nA) and (B) (720 Å × 558 Å, 2.0 V, 0.1 nA) of the step edges of graphene/Rh(111). (C) B₉-steps (263 Å × 220 Å, 2.0 V, 0.1 nA) and (D) A₉-steps (202 Å × 205 Å, 0.20 V, 0.04 nA) of graphene/Rh(111). $d_M$ denotes Moiré periodicity.

4.20C and 4.20D reveals that $A_9$-step and $B_9$-step have one feature in common: the lower terraces of graphene are all terminated with the ring-bridge zones. This is the same as the shoulder-by-shoulder graphene-Rh boundary at the step edges of Rh(111) in Figure 4.18, because such a configuration can facilitate a stronger interaction between graphene and the upper rhodium terrace. However, the $A_9$-step and $B_9$-step have clearly different configurations in their upper terraces: the $B_9$-step is terminated with ring-hcp zones while the $A_9$-step is terminated with ring-bridge and ring-top zones.
The B_{g}-step of graphene is discussed first, since it is the dominating step structure observed. The Moiré patterns in the upper and the lower terraces of the graphene layer have a phase shift with respect to each other as seen in the STM image presented in Figure 4.20C. Based on this observation, an atomic model (shown in Figure 4.21) can be built, representing both upper and lower terraces separately and matching the observed

**Figure 4.21**: Structural model of the B_{g}-step of graphene/Rh(111). The upper and lower terraces of the graphene layer are configured to match the B_{g}-step observed in Figure 4.20C. A gap exists in between of the upper and the lower graphene layers, which will be completed in Figure 4.22.
Moiré patterns appearing in the STM images. The missing link in this model is the atomic configurations adopted by the carbon atoms right over the rhodium B-step. Figure 4.22A shows a 3D image of this graphene edge gap viewed from the [212]$_{Rh}$ direction that needs to be structurally elucidated. The carbon gap has a size comparable to a unit cell of graphene. Considering the large C-C bond energy (about 4.8 eV$^{41}$) and the average C-TM bond energy of about 8 meV (in graphene/Rh(111), see Chapter 5), in addition to the fact that both carbon and rhodium atoms in this gap region are under-coordinated, it is energetically unfavourable for such a structural gap to exist. The graphene layer will necessarily maintain its structural coherency over the rhodium B-step edges. Considering the phase difference between the upper and the lower Moiré patterns and the dimension of the gap, a two-carbon-atom configuration, as shown in Figures 4.22B and 4.22C, is the only possible structure that can account for filling the gap at the B$_g$-step. The C-C bond in this configuration maintains a length comparable to relaxed graphene, thus minimising any disturbance (tensile stress) to the upper and the lower graphene structures. This is substantiated by the fact that the Moiré patterns remain perfectly modulated in both upper and lower graphene layers when extending to the B$_g$-step in the STM image (Figure 4.20C).

We note that graphene on Rh(111) and Ir(111) have similar C-TM configurations on the terraces around the B$_g$-type steps, by comparing our Figures 4.21-4.22 with Figure 4 from reference$^{26}$. However, our structural model adopts a relatively smaller C-TM distance at the B$_g$-type step. This is a more reasonable description, considering that the local registries around the B$_g$-type step are the ring-bridge and ring-hcp sites, which have small C-TM lengths among all local registries.
Figure 4.22: 3D structural models (viewed from the $[\bar{2}\bar{1}2]_{Rh}$ direction) of the $B_g^*$ step of graphene/Rh(111) (A) without and (B) with the two-carbon-atom bridging the upper and the lower graphene layers. (C) Side view of $B_g^*$-step of graphene/Rh(111) (viewed from the $[10\bar{1}]_{Rh}$ direction).
A similar structural analysis can be performed on the $A_g$-step of graphene. The C-TM configurations on the rhodium terraces around the A-type step are shown in Figure 4.23. A structural gap is also found to exist in this model due to the phase mismatch between the two carbon layers. The carbon atoms A and B in Figure 4.23, at the edge of the upper and the lower graphene layers, respectively, have a small lateral separation ($\sim 0.5$ Å) when viewed from the $[0001]_{\text{graphene}}$ direction. However, the vertical mismatch between these two carbon atoms amounts to more than 2.2 Å, as viewed from the $[100]_{\text{Rh}}$ direction in Figure 4.24. Therefore, a direct chemical bonding between carbon A and B is not likely to occur ($d_{C-C} \sim 1.4$ Å in free graphene). We observe that the contrast at the $A_g$-step in the STM image is unusually high, even when compared to the normal ring-top site at the terraces. This suggests that some structural relaxation or reconstruction of carbon network over this rhodium A-type step may occur. Unfortunately, we can hardly extract further structural information, because (1) it remains unknown whether the high contrast comes from an electronic effect or a topographic effect, and (2) it is fairly difficult to achieve atomic resolution at this location. A clear elucidation of this $A_g$-step of graphene requires further work in the future.
Figure 4.23: Structural model of the A\textsubscript{G}-step of epitaxial graphene on Rh(111). The upper and the lower terraces of the graphene layer are configured to match the A\textsubscript{G}-step observed in Figure 4.20D. A gap exists in between of the upper and the lower graphene layers.

Figure 4.24: 3D structural model (viewed from the [100]\textsubscript{Rh} direction) of the A\textsubscript{G}-step of graphene/Rh(111).
In summary, we have systematically investigated the structural characteristics of graphene/Rh(111) by high-resolution STM. The local Moiré periodicity is found to vary in the range of 26.0–29.3 Å. The high-symmetry registries within the supercell were explicitly identified, based on their distinctive contrast appearance in the STM images. Independent of the imaging parameters, the ring-bridge sites are always the minima of the tunnelling contrast among all local registries, which is a unique feature for graphene/Rh(111) when compared to the other TM-supported graphene systems (an explanation of this observation will be presented in Chapter 5). We further made a thorough discussion about the “commensurate vs. incommensurate” nature of the Moiré patterns, whereby the graphene/Rh(111) is concluded to have a non-simple-commensurate superstructure. Finally, quantised Moiré superstructures were commonly observed in the boundaries and step edges in graphene/Rh(111), and the metal substrate is accordingly reshaped to match the quantised dimensions in the high coverage graphene samples. These facts indicate that the graphene growth is a self-assembly process regulated by C-TM interactions. A further study towards this aspect will be presented in Chapter 6.

References:


Chapter 5 – Coupling surface geometry and electronic properties of graphene/Rh(111)

5.1 Introduction

Graphene is by definition a planar network of sp$^2$ bonded carbon atoms. This carbon sheet in its free-standing state is often used as a model to calculate the electronic structures of graphene or other graphitic materials.$^{1-2}$ However, the graphene film experimentally studied so far is either suspended$^{3-4}$ or supported on solid surfaces$^{5-6}$. Periodical Moiré patterns are generated when graphene and its substrate (SiC or transition metals) have a large lattice mismatch.$^{7-9}$ For example, graphene grown on the closed-packed surfaces of 4d and 5d transition metals are characterised by hexagonal Moiré with a supercell of about 3 nm. The overall modulation of the Moiré supercell of graphene/TM observed in the STM topographic images is usually larger by one order of magnitude than the local corrugation of the neighbouring carbon atoms.$^{10-11}$ Unfortunately, this fact cannot directly lead to the conclusion that epitaxial graphene is strongly buckled on the transition metal surfaces (i.e., Ru(0001), Rh(111), Pd(111), Ir(111) and Pt(111)) since STM images are the result of a complicated convolution of topographic and electronic effects, as detailed in Chapter 2.

The electronic structures of graphene/TM play an important role in determining the contrast of the topographic images. A strong evidence is that a contrast reversal can occur between two different zones within a Moiré supercell when the bias voltage is varied, as reported for graphene/Ir(111) in Figure 8 of the paper by N’Diaye et al.$^{11}$ The local electronic structures of graphene/Ru(0001) were initially studied by Vazquez de Parga et al. through scanning tunnelling spectroscopy.$^{10}$ The $dI/dV$ images of the Moiré supercells, varying as a function of bias voltage in Figure 5.1, present a spatial map of the electronic structure of graphene/Ru(0001). An important conclusion drawn from these spectroscopic data is that the two main zones within the Moiré supercell are characterised by quite different LDOS at energies around the Fermi level. Due to the difficulties in separating the electronic and the topographic effects, it still remains a debate whether the large
Figure 5.1: (A) $dI/dV$ curves recorded at 300 K on the higher (black curve) and lower (red curve) areas of graphene/Ru(0001). The inset shows the topographic image measured simultaneously. $dI/dV$ images of graphene/Ru(0001) acquired at (B) 100 meV and (C) 200 meV. From reference\textsuperscript{10}.

contrast variation observed in the STM images of graphene/Ru(0001) is dominated by the geometric buckling or the electronic effects.\textsuperscript{12-13}

The discrepancies in the interpretation of experimental observations often call for theoretical approaches. For the case of graphene/TM, large-scale DFT (Density Functional Theory) calculations of a full Moiré supercell have been undertaken recently by several research groups.\textsuperscript{10,14-16} The 3D structure of the relaxed (12 × 12) C on (11 × 11) Ru(0001) obtained by Wang \textit{et al.} is presented in Figure 5.2. The side view of the graphene layer displays a strong deformation in the direction perpendicular to the surface. The carbon atom at the centre of the high-zone is 3.7 Å above the ruthenium layer, whereas the carbon atom at the centre of the low-zone is located at a distance of only 2.2 Å. Therefore, a geometric buckling of 1.5 Å is found to exist within a 30 Å Moiré supercell.\textsuperscript{15} Similar calculations have also been performed on graphene/Ir(111) by N’Diaye \textit{et al.}, which revealed that the relaxed (10 × 10) C on (9 × 9) Ir(111) exhibits a
similar buckling in the carbon layer. Nevertheless, the overall height modulation is only about 0.27 Å, much less than that of graphene/Ru(0001). These studies imply that the buckling of the epitaxial graphene layer is related to the C-TM interactions.

The C-TM bonding in graphene/TM has been experimentally investigated by non-local spectroscopy techniques (photoemission spectroscopy). Figure 5.3 shows the C 1s NEXAFS (Near-Edge X-ray Absorption Fine Structure) spectra of graphene/TM (TM = Pt(111), Ir(111), Rh(111) and Ru(0001)). The orbital hybridisation between carbon and platinum is found to be rather weak, consistent with the fact that the C-Pt bonding is not strong enough to force the graphene layer into adopting a single orientation with respect to the Pt(111) substrate (see Figure 4.2). Interestingly, a broadening of the $\sigma^*$ and $\pi^*$ bands is observed in the series: graphene/Pt(111) – graphene/Ir(111) – graphene/Rh(111) – graphene/Ru(0001). This trend indicates a strong chemical bonding and electron sharing at the interfaces of graphene/Rh(111) and graphene/Ru(0001). Moreover, the photoelectron spectra in Figure 5.3B show that the chemical bonding is not
homogeneously distributed on graphene/Rh(111) and graphene/Ru(0001), because the C 1s peak splits into two distinct components, corresponding to the elevated (non-bonding) parts and the strongly bonded parts of the carbon layer. Based on these results, Preobrajenski et al. concluded that epitaxial graphene grown on Rh(111) and Ru(0001) should be strongly corrugated in real space.\textsuperscript{17}

**Figure 5.3:** (A) C 1s NEXAFS spectra of HOPG (Highly Oriented Pyrolytic Graphite) and graphene/TM (TM = Pt(111), Ir(111), Rh(111) and Ru(0001)). The peaks A, B and C correspond to the promotion of core electrons into $\pi^*$, $\sigma_1^*$ and $\sigma_2^*$ orbitals, respectively. (B) C 1s photoelectron spectra taken at normal emission for HOPG and graphene/TM. Photon energy: 400 eV. The Ru 3d signal is subtracted from the spectrum of graphene/Ru(0001). MG denotes monolayer graphene. From reference\textsuperscript{17}.

Despite considerable efforts devoted to investigate the topographic and the electronic structures of graphene/TM, there are still no direct experimental measurements on the correlation between the geometry buckling and electronic structures at the local scale of epitaxial graphene. This information is crucial because it can provide important information on how the local electronic structure of graphene is affected by the C-TM
interaction at different C-TM registries. In this chapter, the graphene/Rh(111) system is investigated by RTS (Resonance Tunnelling Spectroscopy) and DFT calculations. Spectroscopic measurements show that the modulation of the electronic surface potential (or work function $\Phi$) across the unit cell of the graphene superlattice amounts to 220 meV. By combining microscopy and spectroscopy data, with the support of extended DFT calculations, the electronic coupling of the various local C-Rh registries is examined in detail, whereby we identify experimentally and confirm theoretically the atomic configurations of maximum and minimum chemical bonding to the metal substrate. Our observations are at odds with reported trends for other transition metal substrates. We will explain why this is the case by analysing the various factors that contribute to the local bonding at the graphene/TM interface.

5.2 Experimental section

The procedures for the preparation of graphene/Rh(111) are described in section 4.2 of Chapter 4. The RTS technique is discussed in detail in Chapter 2. STM and RTS measurements were performed at LN$_2$ and LH$_e$ temperatures, respectively.

Periodic DFT calculations were carried out, in collaboration with Dr Herbert Früchtl (School of Chemistry, University of St Andrews) using the VASP code,$^{19-21}$ with the gradient corrected PW91 functional$^{22}$ and Projector Augmented Wave (PAW) potentials$^{23}$. Our simulations employed a plane wave basis with a kinetic energy cutoff of 300 eV for geometry optimisation, and 400 eV for subsequent charge density differences and density of states calculations. Sampling of the Brillouin zone was made using only the $\Gamma$-point, which can be justified through the size of the unit cell of the graphitic superstructure (29.9 Å in the plane of the surface). To model the geometry and electronic structure of the graphene/Rh(111) system, we constructed a unit cell with a 12C/11Rh coincidence lattice. The simulated system consists of a graphene sheet adsorbed on three rhodium layers. The unit cell of the graphitic superstructure contains 288 carbon and 363 rhodium atoms. The lower two rhodium layers were frozen at the bulk geometry, while the uppermost layer of metal atoms and the carbon layer were optimised with an energy tolerance set at 0.02 eV. Surface dipole correction in the direction orthogonal to the surface was applied. The size of the unit cell orthogonal to the surface was set to 33.31 Å.
The optimised lattice constants for graphene and rhodium are 2.466 Å and 2.718 Å, respectively, in good agreement with experimental values (2.46 Å and 2.69 Å, respectively). Our DFT calculations follow the procedures reported by other groups for graphene on fcc/Co(111), Ru(0001) and Ir(111), allowing for meaningful comparisons to be drawn.

5.3 RTS results

Resonance tunnelling spectra were collected at various local graphene/Rh(111) registries associated with the high-symmetry configurations described in Figure 4.9, and on the clean Rh(111) surface for comparison. The $dZ/dV$ spectra are obtained from numerical differentiation of the $Z-V$ data, and every spectrum shown in Figure 5.4 is an average of 5 measurements (the error in energy is estimated to be ±10 meV). We can identify two different series of resonances in the spectra: A first series (labelled $m$) is located in the low voltage range (2–5 V) and distinguished by broad peaks of low intensity. A second series (labelled $n$) occurs in the higher voltage range (4–10 V) and is characterised by sharper, intense peaks. The $n$ series corresponds to the Gundlach oscillations induced by

![Figure 5.4: dZ/dV spectra acquired at different high symmetry sites within the graphene/Rh(111) supercell and on Rh(111) for reference. I = 1.0 nA. The $n = 1$ oscillation is highlighted.](image)
resonance tunnelling in the junction between the STM probe and the substrate, as detailed in Chapter 2.26-27 The \( m \) series is, however, induced by resonance states located between graphene and the metal substrate.\(^{28}\) Accordingly, the spectrum of Rh(111) exhibits only the \( n \) series, which has its first oscillation at an energy of 5.84 eV, slightly higher than its \( \Phi \) of 5.6 eV.\(^{29}\)

The \( n \) series of oscillations is first analysed. An important conclusion from the RTS discussion in Chapter 2 is that the energy shift of the Gundlach oscillations reflects the \( \Phi \) difference between two sites on a surface. Nevertheless, we choose the second Gundlach oscillation (\( n = 1 \)) to calculate the local work function variation, following the method used in the work of Lin \textit{et al.}\(^{30}\) There are two reasons for this: (1) the \( n = 1 \) oscillation is less affected by the image potential of the surface, as explained by Lin \textit{et al.}\(^{30}\); (2) in our case, the \( n = 1 \) oscillation is energetically well separated from the \( m \) resonance series, whereas the \( n = 0 \) oscillation overlaps with the \( m = 1 \) oscillation. It can be seen from Figure 5.4 that ring-top and ring-bridge sites possess a different resonance spectrum, whereas the ring-hcp and ring-fcc sites exhibit similar spectra, with very small energy shifts. A comparison of the \( n = 1 \) oscillations reveals that the ring-top site has a much higher \( \Phi \) than other sites, and the ring-bridge the lowest \( \Phi \). The absolute values for the local \( \Phi \) of graphene can be calculated by comparing the corresponding spectrum with that of Rh(111), as the \( \Phi \) of the Rh(111) surface is known to be 5.6 eV from the literature\(^{29}\).

The ring-top site is deduced to have a \( \Phi \) of 4.50 eV, while the other sites are within the range 4.25 to 4.30 eV. Notably, the \( \Phi \) of the ring-top registry is remarkably similar to the expected value for free-standing graphene (4.5 eV).\(^{31-32}\)

Figure 5.5 shows a colour-coded series of \( dZ/dV \) spectra recorded along the line indicated in the STM image. Every slice of the image corresponds to a \( dZ/dV \) spectrum collected at a given position. The continuous \( \Phi \) change across the entire supercell is calculated from the energy shift of the \( n = 1 \) Gundlach oscillation\(^{30}\), and plotted in Figure 5.6. In line with our above observations, the \( \Phi \) reaches a maximum at the centre of ring-top zones and a minimum at ring-bridge zones, with an overall variation of 220 meV. A large \( \Phi \) decrease occurs when the position moves away from the centre of ring-top, and two local \( \Phi \)
Figure 5.5: Series of $dZ/dV$ spectra (1.0 nA) recorded along the line indicated in the STM image (5 nm × 3.5 nm, 0.5 nA and 0.4 V). Note: the tip states are different when acquiring the spectra in Figures 5.4 and 5.5, which slightly shift the resonance states (especially for $n > 1$) in energy. However, the local $\Phi$ variation is extracted from the relative shift of the $n = 1$ states with the same tip state, hence the tip itself has a negligible effect on the $\Phi$ results.

Figure 5.6: (A) Work function versus position as deduced from the $n = 1$ oscillation in Figure 5.5. The red dots are the experimental data points and the blue curve is extracted from DFT calculations. (B) Atomic model for the ring-asymmetric registry of local minimum work function.
minima are observed on each side of ring-top zone. These do not correspond to the centres of the ring-fcc or the ring-hcp zones, but are offset by about 3 Å along the long diagonal of the supercell. The structures of these two sites of local $\Phi$ minima (referred to as “ring-asymmetric” sites) can be identified with the help of the ball model of graphene/Rh(111) in Figure 4.9. It is revealed in Figure 5.6B that such ring-asymmetric site has one carbon atom residing nearly on top of a rhodium atom while the other residing above a bridge site between two rhodium atoms.

We now discuss the $m$ series of resonance peaks. It is not present in the spectrum of clean Rh(111), but only in graphene/Rh(111) (Figure 5.4). This series starts in the low voltage range, and its intensity damps quickly with energy. Similar oscillations have been previously observed by Kubby et al. in the case of first-layer subsurface vacancies in Si(111)\textsuperscript{28}, and by Pivetta et al. on NaCl/Ag(100)\textsuperscript{33-34}. We hence interpret these peaks as resulting from resonance states within the region defined by two scattering planes, \textit{i.e.} the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{potential-energy-diagram.png}
\caption{Potential-energy diagram of the resonance tunnelling on graphene/Rh(111). Modified from reference\textsuperscript{28}.}
\end{figure}
vacuum barrier and the graphene/Rh(111) boundary, as illustrated in Figure 5.7. The intensity and width of such resonances are related to the lifetime of the excitation,\textsuperscript{35} that is, to the probability for tunnelling out of the well region through the two enclosing potential barriers. We see from Figures 5.4 and 5.5 that these resonances ($m = 0$ peak) are almost absent in the large region of the ring-top zone, but are quite intense in other configurations. Hence, the resonances in the ring-top configuration are necessarily shorter-lived than in other regions of the supercell. This observation suggests that the potential barrier at the graphene/Rh(111) interface is much lower for the ring-tops, which is in accordance with the weak bonding strength between graphene and Rh(111) at this location. A thorough discussion of the local electronic interactions at different registries will be presented in section 5.4.

A consequence of different resonance tunnelling at the various local registries within the graphene Moiré supercell is that the STM contrast at high voltages (> 2 V, that is, from and above the first $m = 0$ resonance encountered in Figures 5.4 and 5.5) strongly depends on the tunnelling voltage applied. The probe tip was repeatedly pulsed until it achieved a rather stable state before imaging, which is critical to guarantee a high reproducibility for the data acquired in the high bias range. The set of STM images in Figure 5.8 was collected on the same region of graphene/Rh(111) at successively increasing tunnelling biases, from 2 to 10 V. The contrast modulation as a function of voltage at different local registries is remarkable and clearly indicates pronounced electronic differences within a Moiré supercell. The unit cell highlighted in Figure 5.8 has its corners at the ring-top sites. The contrast change as a function of bias can be explained based on the $dZ/dV$ spectra presented in Figure 5.4. The main contrast change in these STM images occurs between the ring-top site and all other configurations when the bias is increased. This is due to the site dependence of the $\Phi$ within the supercell. As discussed above, a variation of the $\Phi$ will shift the field emission resonances in energy. The series of resonances for the ring-top site is rather different from those of the other sites, as shown in Figure 5.4. Hence, images acquired at biases close to the $n = 0–3$ peaks in the spectrum of ring-top will exhibit the highest tunnelling contrast on the ring-top configurations (5 V, 7 V, 8.5 V, and 10 V). Away from the ring-top resonances, the tunnelling contrast will prevail at locations corresponding to other C-Rh configurations. The tunnelling variations of the
Figure 5.8: STM images of graphene/Rh(111) obtained at high biases, from 2 to 10 V. Tunnelling current: 2 nA. Image size: 9 nm × 9 nm.

ring-fcc/hcp and ring-bridge sites are almost synchronised, with only small shifts relative to each other. Accordingly, when the bias is set to match the peaks of ring-bridge, ring-fcc, and ring-hcp, even small differences in contrast can be resolved among these configurations. This contributes to the complexity of the Moiré pattern as observed in the STM images acquired at high bias. With special reference to the $n = 1$ peak, for instance, we anticipate from Figure 5.4 that first the ring-bridge sites, followed by the ring-hollow sites (both ring-fcc and ring-hcp) and finally the ring-top sites should dominate the tunnelling contrast when the bias is increased from 6 V to 6.5 V to 7 V, respectively. This is indeed directly observed in Figure 5.8.
Chapter 5 – Surface geometry and electronic properties of graphene/Rh(111)

5.4 DFT results

To substantiate our microscopy and spectroscopy results and to obtain deeper insights into the local chemical bonding at the graphene/Rh(111) interface, extended DFT calculations were performed on a 12C/11Rh supercell. The relaxed configuration (top and side views) in Figure 5.9 shows that the carbon overlayer has a strong height modulation while the first Rh(111) layer is slightly buckled by 0.1 Å in anti-phase with the graphene corrugation.36-37 As expected, the ring-top registry lies highest, with a C-Rh distance of 3.8 Å. The ring-fcc and ring-hcp registries are located at 3.1 and 2.9 Å from the rhodium surface, respectively. The ring-bridge registry lies lowest at a distance of 2.2 Å. This is clearly different from extended DFT calculations performed on graphene/Ru(0001)15-16 and graphene/Ir(111)14. First, the lowest lying registries were reported to be ring-hcp in all cases. Although the ring-bridge registry was not specifically investigated, we understand from the literature that this configuration adopts a height slightly larger than,

![Figure 5.9: DFT relaxed structure (top and side views) of the 12C/11Rh(111) surface. The atomic configurations of the supercell corresponding to the local high-symmetry registries are highlighted with the yellow-shaded areas. The red circles and lines indicate the positions of the carbon atoms along the long diagonal of the supercell.](image-url)
The carbon overlayers on Ir(111) and Ru(0001) are generally characterised by a simple periodical height modulation with the one maximum at the ring-top site and two concaves at the ring-hollow sites. Second, we obtain from our computational results a buckling for graphene on Rh(111) of 1.6 Å, judged against 1.5 Å\textsuperscript{15} and 1.7 Å\textsuperscript{16} for Ru(0001) and 0.3 Å for Ir(111)\textsuperscript{14}. Hence, the theoretical corrugations of graphene adsorbed on Ru(0001), Rh(111) and Ir(111) are seemingly consistent with the d band model\textsuperscript{38} (detailed on page 118) in that the interaction strength follows the sequence Ru > Rh >> Ir. Despite the similar overall buckling between graphene/Rh(111) and graphene/Ru(0001), an important difference exists in the way that the graphene layer is locally deformed on the bonding registries: the ring-bridge sites are similar (lying in both cases at 2.2 Å above the surface), whereas the ring-hollow configurations differ by about 1 Å (compare the distances of about 2.2 Å on ruthenium\textsuperscript{15-16} and 2.9–3.1 Å on rhodium). This leads to two different geometries of epitaxial graphene, and indicates that the local C-TM bonding strength at the ring-hollow sites is considerably reduced on the rhodium substrate.

The experimental and theoretical height profiles for the graphene/Rh(111) system are compared in Figure 5.10. The relative contrast within the Moiré supercell (i.e. ring-top

![Figure 5.10: Typical STM line profile (in red) acquired along the main diagonal of a supercell, and height profile (in blue) of the carbon atoms along the main diagonal of the DFT computed 12C/11Rh supercell.](image)
>> ring-how > ring-bridge) observed by STM topographies is well reproduced in the theoretical results. Keeping in mind that the overall corrugation amplitude as measured by STM is necessarily dependent on the tunnelling voltage and STM tip state, such a relative agreement with our theoretical predictions is remarkable.

The electron density difference map was computed, shown in Figure 5.11, in order to examine how the local bonding varies within the graphene supercell. The upper-left panel depicts an iso-value surface (top-view) of 0.02 electrons/Å³ in the difference between the electron density of the C-Rh system and the sum of its constituents calculated at the geometry of the combined system. Blue indicates higher electron density (i.e. negative charge) on the combined system, while red shows a reduction in electron density. It is clear that the chemical bonding strength of C-Rh varies significantly across the supercell. The large zone of ring-top does not show any charge redistribution between the adsorbed graphitic overlayer and the substrate, indicative of an absence of hybridisation. However, a chemical bonding of C-Rh is evident for the other regions of the graphene supercell, with a strength following the sequence ring-fcc < ring-hcp < ring-bridge.

The lower-left panel of Figure 5.11 displays a cut through the electron density change along the main diagonal of the supercell. An accumulation of charge density at the interface between graphene and rhodium occurs at the bonding registries only. For the ring-hcp configuration (ring-fcc is similar), the chemical bonding to the rhodium substrate occurs mainly through the carbon atoms on atop sites, as a result of hybridisation between the C(π/π*) and Rh(4d) bands (or head-to-head overlap between the C(P₂) and the Rh(4dz²) orbitals, as the main component). The same conclusions were drawn for ring-hollow sites on graphene/Ru(0001) and graphene/Ir(111),¹⁴-¹⁶ as a back-donation with a net negative charge from the first-layer metal atoms to the graphene layer is found to exist as well. Even so, a comparison of our Figure 5.11A and the similar DFT data for graphene/Ru(0001) (Figure 2 of reference¹⁵ and Figure 3 of reference¹⁶) indicates that the interaction at these sites is significantly reduced on our rhodium substrate.

The electronic intermixing between the graphitic π/π* system and the metal 4d bands exhibits a markedly different behaviour at the ring-bridge sites, since various Rh(4d)
Figure 5.11: (A) Computed adsorption-induced charge density difference map for a 12C/11Rh supercell of graphene/Rh(111). Blue and red indicate an increase and a decrease, respectively, of electron density. The top panel depicts an electronic iso-surface at 0.02 electrons/Å³. The bottom panel shows a cut through the charge density along the main diagonal of the supercell, alongside two higher magnification plots highlighting the density change locally associated with the ring-bridge.
orbitals are involved in the chemical bonding with carbon. We examine this in Figure 5.12 by comparing the orbital decomposed local density of states (LDOS) for carbon and rhodium atoms representative of the various local high-symmetry configurations (ring-top, ring-hcp and ring-bridge). The Rh(d_{z^2}) and C(p_z) orbitals show no sign of hybridisation at ring-top sites. At ring-hollow sites, one of the two carbon atoms has its C(p_z) orbital strongly hybridised with Rh(d_{z^2}). This is evident from the appearance of shared density around the Fermi level (defined at 0 eV), and is in line with theoretical predictions made at ring-hcp sites for graphene/Ru(0001).16 Importantly, we note that C(p_z) at the top position hardly interacts with the two Rh(d_{xz}) and Rh(d_{yz}) orbitals, due to the absence of a hybridization in the corresponding LDOS. This is expected from the local adsorption geometry and the orbital symmetry at these sites: C(p_z) points directly to the node of Rh(d_{xz})/Rh(d_{yz}), which does not allow the formation of a chemical bonding. However, Figure 5.12 clearly indicates that the p_z orbitals of both carbon atoms in the ring-bridge configuration couple strongly to the Rh(d_{z^2}) orbital as well as to Rh(d_{xz}) and Rh(d_{yz}). This can be understood by the fact that such a phase relationship between C(p_z) and Rh(d_{xz})/Rh(d_{yz}) at ring-bridge makes possible an effective orbital overlap. A similar donation/back-donation binding occurs here, which leads to not only a strengthening of the C-Rh bonds, but also a weakening of the C-C bonds. The overall tensile stress in the graphene sheet resulting from its 12C/11Rh supercell amounts to 1% with an average C-C bond length of 1.439 Å (compared to 1.424 Å for free-standing graphene). Figure 5.11B presents the distribution of C-C bond lengths within the computed graphene supercell. The large majority of the bonds are found to retain the average length (bonds in red colour), whereas the carbon atoms in the ring-bridge zones have two (in blue colour) of their three bonds increased by a further 3%, thus becoming softened in strength. Interestingly, we can see by comparing the ball-model shown in Figure 4.9 and the bond
Figure 5.12: Orbital decomposed local density of states (LDOS) for carbon and rhodium atoms in the various local high-symmetry configurations (ring-top, ring-hcp and ring-bridge). The LDOS for the adsorbed graphene/Rh(111) system is represented by the coloured traces. The atoms, for which the LDOS is presented, are highlighted in the supercell shown on the top-right corner, alongside the $x$, $y$, and $z$ coordinate system used. The computed total DOS of free-standing graphene is appended for reference (black trace in the ring-top panel).
lengths depicted in Figure 5.11B, that the resulting uniaxial lattice stretch near ring-bridge configurations brings the two C-C bonds closer to atop positions of rhodium atoms, thereby enlarging the size of the ring-bridge zone and enhancing head-to-head overlap between the C(p_z) and Rh(d_z2) orbitals. Hence, the significantly enhanced chemical bonding of ring-bridge sites to the substrate arises as a natural consequence of the substantial C(π/π*) coupling with the Rh(d_z2), Rh(d_xz) and Rh(d_yz) orbitals, accompanied with a local weakening of the sp^2 carbon network.

5.5 Correlating RTS and DFT results

In the following we will correlate the experimental results from RTS measurements in section 5.3 and the theoretical results from DFT calculations in section 5.4, in order to obtain a comprehensive understanding of the surface electronic properties of graphene/Rh(111).

We first discuss the high-symmetry sites within the supercell. Since no electron redistribution is associated with the ring-top configurations, the local \( \Phi \) at these sites is expected to be equal to the \( \Phi \) of free-standing graphene, i.e. 4.5 eV.\(^{31-32} \) In contrast, a net negative charge is transferred to the C-Rh interface for all other configurations. Such decrease of \( \Phi \) by a net charge transfer from the substrate to adsorbate has been previously observed in surface adsorption studies\(^{39} \) and was explained to arise from a dipolar counteraction as a result of charge redistribution within the adsorbates. The charge redistribution on the carbon atoms at ring-bridge sites is indeed accompanied by a decrease in the overspill of the surface charge density into the vacuum (see the area enclosed by the dashed-line in the bottom panel of Figure 5.11A). Based on this, we can hence expect the ring-bridge configurations to exhibit the lowest \( \Phi \) and the ring-hollow sites to have an intermediate \( \Phi \).

In order to extract from our DFT data the \( \Phi \) variation across the 12C/11Rh supercell, we determined the local potential in the vacuum by choosing the plane in the middle between the rhodium slabs and subtract the Fermi energy sampled over a fine surface mesh to account for all local C-Rh registries. The computed \( \Phi \) is further smoothed using a two-dimensional Gaussian filter with a width of 0.75 nm, in order to simulate the STM...
tip convolution and to account for the inherent lateral resolution of RTS measurements as described in reference. The result is shown in Figure 5.11C, allowing for a direct comparison with our spectroscopy measurements. In line with our predictions, we observe that the $\Phi$ is highest for ring-top sites (calculated at 4.461 eV), and lowest for ring-bridge sites (calculated at 4.427 eV). A theoretical $\Phi$ modulation of 34 meV is deduced across the supercell, roughly a factor of 6 smaller than the 220 meV experimentally measured. Nonetheless, the profile of the computed $\Phi$ along the main diagonal of the supercell is in good qualitative agreement with our experimental data, as demonstrated in Figure 5.6A. In particular, the relative $\Phi$ variation at the different high-symmetry sites is remarkably reproduced with the exception of the ring-hcp configuration. The experimental identification of the ring-asymmetric sites associated with local $\Phi$ minima (or more precisely with saddles points as seen from the 2D representation in Figure 5.11C) is also confirmed. The theoretical 6-fold underestimate of the $\Phi$ modulation and the deviation at ring-hcp sites are likely to arise from the fact that three rhodium layers are not sufficient to describe the electronic structure of the bulk metal. We have not considered testing for this, due to the computationally very demanding nature of the 12C/11Rh supercell simulation. Nevertheless, the excellent qualitative agreement reached here indicates that our calculations are accurate enough to describe the qualitative variation in the surface electronic potential.

In essence, our combined microscopy, spectroscopy and theoretical data identify ring-top and ring-bridge sites as the local configurations of minimum and maximum chemical bonding to the substrate, respectively, with C-Rh bond lengths following the sequence: ring-bridge $< \text{ring-hep} \approx \text{ring-fcc} < \text{ring-top}$. Considering the qualitative dependence between the strength of the chemical interaction and the degree of geometric buckling at the graphene/TM interface, our data provide evidence that graphene/Rh(111) is corrugated at the atomic scale, in a way that the ring-top sites protrude from the surface and the ring-bridge sites lie the closest. Interestingly, our observations indicate that the tunnelling contrast acquired in the low bias regime qualitatively mirrors the topography of the graphene/Rh(111) surfaces. Since the STM contrast is a convolution of not only geometric but also electronic contributions, such an assessment is a priori ambiguous without our present investigation.
5.6 Comparison of different graphene/TM

Many of our conclusions reached for Rh(111) hold true for other TM substrates. Nevertheless, the observed trend in the local adsorption strength (ring-hollow < ring-bridge) is at odds, because the strongest local adsorption registry for graphene/TM is reported experimentally and/or theoretically in the literature to be ring-hcp for the close-packed surfaces of Ru\textsuperscript{10,15-16}, Pd\textsuperscript{40}, Pt\textsuperscript{41}, and Ir\textsuperscript{11,14,42}. In addition, the surfaces of Co(0001)\textsuperscript{43-44} and Ni(111)\textsuperscript{45-48}, both 3d metals with a lattice mismatch of about 1%, have been experimentally shown to adsorb graphene in a (1 × 1) epitaxy with the ring-hollow geometry. As previously mentioned, ring-bridge sites have escaped the attention of most studies to date. Swart et al. reported that this registry is significantly less stable on fcc-Co(111)\textsuperscript{25}. It is worth mentioning that the ring-bridge structure is favoured over ring-hcp on Ni(111) by the theoretical study of Fuentes-Cabrera et al.,\textsuperscript{49} but this conclusion is in conflict with the recent experimental findings\textsuperscript{46-48}. We now present a qualitative explanation to rationalise the differences in the bonding of graphene to the various group VIIIB TMs. With reference to studies of graphene adsorbed on 3d, 4d and 5d TM surfaces, the overall agreement between experimental and theoretical data based on DFT is rather good. For most of these studies, the d band model is invoked in first instance. This model was developed to explain trends in binding strength of adsorbed molecules on TMs\textsuperscript{38}, predicting a binding strength that (1) gradually decreases with the occupation of the d band, and (2) increases on going from the 5d to the 3d metals. However, the d band model can not give a satisfactory explanation on the trends in adsorption energy and graphene-TM bond distances. We compare for instance the binding energies obtained by DFT calculations: the averaged values over extended supercells are 40 meV per carbon atom over graphene/Ru(0001)\textsuperscript{15}, 7.8 meV/C over graphene/Rh(111) (from our DFT data), and 2 meV/C over graphene/Ir(111)\textsuperscript{14}. The d band model, however, predicts that the values for graphene/Rh(111) should be slightly lower than for graphene/Ru(0001) and significantly larger than for Ir(111). Moreover, we can deduced from the d band model that the overall physical characteristics of the graphene/Rh(111) interface should be comparable to the graphene/Ru(0001) system, with only slightly larger C-TM bond distances for the former. The C-TM distances for the bonding configurations (ring-bridge and ring-hollow) reported in the literature are about...
2.0–2.2 Å for the close-packed surfaces of both 3d and 4d TM substrates (Ni\textsuperscript{45}, Co\textsuperscript{43}, Ru\textsuperscript{36-37}, Pd\textsuperscript{50}), and 3.3-3.8 Å for 5d metals (Pt\textsuperscript{41}, Ir\textsuperscript{14}). The case of Rh(111) is hence very intriguing in the sense that the C-Rh bond follows a “d band trend” with respect to the ring-bridge configuration, whereas the ring-hollow configurations differs from what is expected from the “d band trend”.

To appropriately understand trends in binding energy of graphene on TM surfaces, we need to separate two contributing factors: electronic states (energy and symmetry) and lattice structure (type and mismatch). To a first approximation, the electronic factor can be described by the d band model.\textsuperscript{38} However, this model necessarily fails under the two following conditions: (1) the large lattice mismatch exists at the graphene/TM interface, and (2) electronic effects (exchange and correlation energies) arising from an appropriate many-electron description can not be neglected. This also explains why DFT-based calculations can yield a reliable description of the graphene/TM interface and the results are in good agreement with experimental observations, when extended supercell is adopted to account for the lattice mismatch.

In summary, we have investigated the electronic surface properties and chemical bonding of graphene/Rh(111) by means of high-resolution STM, site-specific RTS and extended DFT calculations. The observed $\Phi$ variation of about 250 meV is significant, especially considering the spatial extent over which it occurs (~ 3 nm, the size of a supercell). We have confirmed that epitaxial graphene is geometrically buckled when adsorbed on Rh(111). We furthermore identified the local C-Rh registries of maximum and minimum chemical bonding to the rhodium substrate and showed that Rh(111) is a very different substrate for graphene as compared to Ru(0001) and Ir(111).

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Chapter 6 – Magic-sized carbon clusters on Rh(111): nucleation and growth of epitaxial graphene

6.1 Introduction

The successful extraction of single layer graphene by a “top-down” approach (i.e. micromechanical cleavage of graphite) has made many fundamental studies of graphene possible in the past years. Because of the interesting electronic properties and promising applications of graphene, it is critical to find an effective “bottom-up” approach to fabricate such a 2D carbon film. The carbonisation of hydrocarbon molecules on transition metals has proven to be an effective route to graphene formation since this is a well-controlled chemical process. Nevertheless, the mechanism of this chemical approach is rather complicated: it involves two different types of reactions, namely, the C-H scission and the C-C formation. These two reactions are entangled in the CVD method, in which the reactants (i.e. hydrocarbon molecules) are continuously exposed to a hot transition metal surface to grow graphene. From a mechanistic point of view, such continuous-flow reaction is relatively difficult to investigate by conventional surface science techniques, because the precursors, the intermediate species, and the final products co-exist simultaneously during the reaction process at high temperatures.

For preparation of graphene by a typical TPG method, hydrocarbon molecules are first deposited from the gas phase onto the metal substrate, and then followed by a temperature-programmed annealing. The graphene formation process can be divided into two stages: the main dehydrogenation at relatively low temperatures (< 800 K) and the condensation of the carbidic species into graphene islands at higher temperatures (> 800 K). Since the C-H scission and the nucleation/growth of carbon network are well decoupled, the TPG method is chosen in our work to study the formation mechanism of graphene/Rh(111). In the following two parts (sections 6.1.1 and 6.1.2), we will review the literature on these two reactions involved in the graphene growth.
6.1.1 Dehydrogenation of hydrocarbons (< 800 K)

Rhodium is highly reactive for dehydrogenation reactions.\textsuperscript{6-8} Only at a very low temperature (\textit{i.e.} 100 K), ethylene is adsorbed molecularly on the Rh(111) surface. The dehydrogenation of ethylene begins when ethylene/Rh(111) is heated up to 140 K, as reported by Niemantsverdriet’s group.\textsuperscript{3} Vinylic species (-CHCH\textsubscript{2}) are formed by the initial scission of a C-H bond of ethylene. Such intermediate product further converts to stable surface species (\textit{i.e.} ethylidyne) at 190 K, described by:

\begin{align}
\text{C}_2\text{H}_4_{\text{ads}} + * & \leftrightarrow \text{CHCH}_{2,\text{ads}} + \text{H}_{\text{ads}} \tag{6.1} \\
\text{CHCH}_{2,\text{ads}} & \rightarrow \text{CCH}_{3,\text{ads}} + * \tag{6.2}
\end{align}

where * represents the rhodium atoms required to catalyse the C-H cleavage. * is freed when the C-C bond of the hydrocarbon species changes from a horizontal to a vertical geometry with respect to the rhodium surface.

Ethylidyne (≡C-CH\textsubscript{3}) is the common product of the decomposition of ethylene/acetylene on the close-packed surfaces of the VIIIB transition metals at low temperatures.\textsuperscript{6-9} A (2 × 2) superstructure is adopted by ethylidyne/Rh(111) at temperatures below 270 K. Tensor LEED measurements by Somorjai’s group show that the ethylidyne species in the (2 × 2) structure are adsorbed at the hcp hollow sites of Rh(111), and a strong adsorbate-metal bond leads to a small buckling and lateral relaxation in the rhodium surface,\textsuperscript{4} as illustrated in Figure 6.1. The (2 × 2) structure of ethylidyne/Rh(111) is observed to irreversibly transformed into c(4 × 2) at the temperatures between 270 K and 300 K, where the adsorption configuration of ethylidyne remains unchanged. The c(4 × 2) of ethylidyne/Rh(111) is then decomposed when the sample is further annealed to temperatures above 420 K.
The decomposition of ethylidyne on Rh(111) has been monitored by Thermal Desorption Spectrometry (TDS) measurements, as shown in Figure 6.2. It can be seen that the main dehydrogenation peak is located between 400 K and 450 K. However, the hydrogen desorption spectra have a long tail extending to a high temperature of about 750 K. A series of complicated chemical reactions is expected to occur in this range (400–750 K). Besides the C-H scission, the C-C bond in ethylidyne is likely broken upon heating, yielding different CHx fragments for the formation of intermediate species.
In the early 1990s, the STM technique was employed by Land et al. to follow the ethylidyne decomposition process on Pt(111).\textsuperscript{6} Figure 6.3A shows that carbonaceous particles are formed after annealing the ethylidyne/Pt(111) sample at 500 K. These different particles were found to have two different topographic heights (see Figure 6.3B) in the STM images, indicating that two different species coexist, as speculated by the authors. One is very likely to contain hydrogen in its structure, whereas the other is fully dehydrogenated. Based on this study, it is difficult to extract further information about the chemical evolution within this temperature range (\textit{i.e.} 400–800 K), because the STM topographs can hardly identify the complicated hydrocarbon intermediates.
6.1.2 Condensation into graphene (> 800 K)

The main dehydrogenation process of ethylene (or ethylidyne) on VIIIB transition metals is known to be complete at approximately 800 K.\textsuperscript{1,4-7} Carbidic clusters were commonly observed in the high temperate stage of the temperature programmed growth of graphene/TM (\textit{e.g.}, Ir(111)\textsuperscript{2}, Pt(111)\textsuperscript{9} and Ru(0001)\textsuperscript{8-9}). For instance, the STM images of the carbon clusters formed on Ir(111) at different temperatures from the work of Coraux \textit{et al.}\textsuperscript{2} are reported in Figure 6.4. It can be seen that the particle/island density on the metal terraces decreases with the annealing temperature, accompanied by the growth of well-ordered graphene islands. Smoluchowski ripening, \textit{i.e.} the reduction of island density via mobile islands coalescing upon contact,\textsuperscript{10} is proposed by the authors to be the growth mechanism of the graphene islands on Ir(111). Nevertheless, the carbidic clusters or small graphene islands, which are regarded as the building blocks for the final condensation of graphene, were not explicitly identified.

\textbf{Figure 6.3:} (A) STM image (1000 Å × 1000 Å) of the ethylidyne/Pt(111) sample annealed at 500 K for 5 seconds. (B) Distributions of heights of carbonaceous particles in the same sample. From reference\textsuperscript{6}.
Figure 6.4: STM images (2500 Å × 2500 Å, insets (A)-(C): 620 Å × 620 Å, insets (e): 400 Å × 400 Å) of graphene/Ir(111) prepared along the TPG procedure, after annealing for 20 seconds to (A) 870 K, (B) 970 K, (C) 1120 K, (D) 1320 K and (E) 1470 K. (F) Density $n$ of graphene islands as a function of the annealing temperature in the TPG. From reference 2.

Recently, photoelectron spectroscopy was used by Lacovig et al. to study the condensation stage of graphene on Ir(111). The C-1s and Ir-4f$_{7/2}$ spectra in Figure 6.5A indicate that a strong C-Ir interaction exists for in the intermediate species during the condensation process, but disappears when graphene growth is complete. This strong interaction, as the authors explained with the help of DFT calculations, is due to the close distance between the carbon atoms at the periphery of the carbidic clusters and the Ir(111) surface. Hence the carbidic clusters are assumed to possess a dome shape, as shown in Figure 6.5B.
Although the graphene condensation process has been studied by both local and non-local techniques, a direct correlation between the real-space structures and the electronic properties of the carbidic intermediates is still needed. For instance, what specific structures do the clusters adopt for the building-up of the graphene layer? This is an important link for a full understanding of the graphene growth on transition metals. In this chapter, carbon clusters were observed in the carbonisation process of ethylene on the Rh(111) surface at high temperatures. One type of carbon cluster (i.e. $7C_6$) is found to dominate the rhodium terraces when the dehydrogenation reaction is complete. The skeleton of such carbon clusters and their preferred adsorption sites on Rh(111) were resolved by high-resolution STM imaging. In order to prove that such $7C_6$ clusters are fully dehydrogenated, polyaromatic molecules (i.e. coronene) with identical carbon skeleton were deposited on Rh(111) for comparison. The electronic structures of the carbon clusters (and coronene) were revealed by $dI/dV$ spectroscopy. Moreover, the emergence of magic-sized carbon clusters on Rh(111) was investigated by a theoretical approach, whereby the total energies of the supported carbon clusters with different
dimensions were calculated. Finally, we carefully analysed the DFT-relaxed structures of 7C6 and coronene on different sites of Rh(111), and compared them with our experimental observations.

### 6.2 Experimental section

Ethylene (C2H4, 99.95%) was deposited on a clean Rh(111) surface at room temperature, resulting in 1 ML ethylidyne/Rh(111). The sample was then heated up with a rate of less than 100 K/min to different temperatures (573–973 K), and held for 30 seconds before cooling down to LHe temperature for STM measurements. Coronene molecules (C24H12, 99%), a polycyclic aromatic hydrocarbon with 7 carbon rings, were deposited by a homemade evaporator (see Figure 3.5A in Chapter 3) with the Rh(111) sample at room temperature.

During the acquisition of $dI/dV$ images of the cluster/molecule, standard lock-in techniques were utilised, whereby the feedback loop was kept active in order to maintain the tunnelling current at a constant value. The frequency of the voltage modulation is set to be higher than the bandwidth of the feedback system, hence the tip-sample distance will not react to the modulation when the $dI/dV$ signal is acquired at each pixel of the topographic images. Before collecting the $dI/dV$ image on the cluster/molecule, the STM tip was checked to ensure it has a symmetric shape and more importantly a featureless electronic structure (i.e. a smooth $dI/dV$ spectrum on the clean Rh(111) terrace).

The DFT calculations were performed (by the group of Prof. Weixue Li, Dalian, China, through collaborative arrangements) with the VASP code, with projector augmented wave potentials and the generalised gradient approximation (Perdew-Burke-Ernzerhof) for the exchange correlation functional. An energy cut-off of 400 eV was used to expand the wave functions into the plane-wave basis. The surfaces were modelled employing the repeated slab geometry composed of five metal layers in the slab and a vacuum region of about 15 Å, in which isolated carbon atoms (or carbon clusters) were adsorbed on one side of the slab. The adsorbate and the topmost two layers were relaxed during structure optimisation until the residual forces on the atoms were less than 0.02
eV/Å (or 0.05 eV/Å). For carbon atom adsorption, we used a (2 × 2) unit cell with (6 × 6 × 1) gamma centred K points for sampling of the Brillouin zone. For carbon clusters, we used (4 × 4), (6 × 6), (7 × 7) unit cells according to the cluster size and used (3 × 3), (2 × 2), (1 × 1) gamma centred K sample points, respectively. All parameters defining the numerical accuracy of the calculations were carefully tested.

The STM images were simulated by using the Tersoff-Hamann approximation. In this approximation the tunnelling current is considered to be proportional to the integrated LDOS within a given energy window that is determined by the applied bias on the sample. The positive (negative) bias indicates that empty (occupied) states are imaged, in line with what is adopted in our STM measurements.

6.3 Ethylidyne/Rh(111)

Figure 6.6 displays the STM images of the Rh(111) surface saturated with 18 L of ethylene at room temperature and followed by a flash-annealing to 423 K. A (2 × 2) superstructure is evident from the 2D Fourier transform result of the STM image. As discussed above, the ethylene molecules are dehydrogenated to form stable ethylidyne on Rh(111) at temperatures between 190 K and 420 K. Hence this (2 × 2) superstructure is ascribed to ethylidyne/Rh(111). The ethylidyne species on Rh(111) are resolved as bright triangles in the STM image with high magnification (Figure 6.6C), reflecting the molecular geometry of adsorbed ethylidyne. Overlapping the STM image with the hexagonal lattice of Rh(111) allows us to see that the ethylidyne species are located at only one type of rhodium hollow sites, in agreement with the LEED results reported by Wander et al.
Figure 6.6: STM images (A) (345 Å × 345 Å, 0.47 V, 0.10 nA), (B) (3D, 96 Å × 82 Å, -0.11 V, 0.20 nA) and (C) (30 Å × 30 Å, 0.08 V, 0.21 nA) of ethylidyne/Rh(111) formed by a saturated exposure of ethylene on Rh(111) at room temperature and flash-annealing the sample to 423 K. The inset in (A) is the 2D Fourier transform of the STM image. A Rh(111) lattice grid is overlaid on image (C).

A further flash-annealing of the ethylidyne/Rh(111) sample to 473 K leads to the formation of a rectangular c(4 × 2) superstructure, as shown in Figure 6.7. The long symmetry axis of the rectangular patches is found to have three orientations, rotated by 120° with respect to each other. This c(4 × 2) phase can also be identified in the LEED pattern in Figure 6.7C. Notably, the (2 × 2) superstructures are not completely converted to c(4 × 2) over the entire rhodium surface, as some small hexagonal domains of ethylidyne/Rh(111) can still be observed in Figure 6.7B. This might be attributed to the flash-annealing process we used.
Figure 6.7: STM images (A) (400 Å × 400 Å, 0.05 V, 1.0 nA), (B) (300 Å × 300 Å, -0.10 V, 1.0 nA) and LEED pattern (C) (electron energy: 73 eV) of ethylidyne/Rh(111) formed by saturating Rh(111) with ethylene at room temperature and flash-annealing the sample to 473 K. Some (2 × 2) and c(4 × 2) domains are highlighted by cyan and red circles, respectively. The white arrows indicate the directions of the long symmetry axis of the c(4 × 2) domains.

6.4 Condensation into graphene/Rh(111)

Annealing the ethylidyne/Rh(111) sample to 773 K in UHV results in the appearance of small clusters with sizes ranging from 1 to several nm. The STM image in Figure 6.8A shows that these clusters do not show any preferential adsorption location on the Rh(111) surface, suggesting that the dehydrogenation reaction may also occur on the rhodium terraces instead of only at the step edges. Further annealing to 973 K (Figures 6.8B-F) led to a decrease in the particle density, and an increase of the graphene coverage at the step edges of Rh(111). This was also observed in the growth of graphene on the other transition metal surfaces (i.e. Ru(0001)\(^9\) and Ir(111)\(^2\)). However, a close inspection of the intermediate products during the TPG procedure reveals the existence of two different
types of clusters. One is characterised by non-regular shapes and heights, whereas the other one (which we will later identify as 7C₆) has a minimum size (~ 1 nm) and a well-defined symmetric shape. The density of the former clusters on the Rh(111) surface decreases rapidly when the sample is annealed to 873 K. These clusters can hence be ascribed to the hydrogen-containing carbidic species as a result of incomplete dehydrogenation on Rh(111) at temperatures below 873 K. On the contrary, the 7C₆ clusters maintain roughly a constant density, until their relative population (with respect to all clusters present on the surface) starts to dominate at about 873 K (Figures 6.8D and 6.9C). Further annealing of the sample to higher temperatures leads to not only the gradual disappearance of the 7C₆ clusters, but also to the emergence of graphene islands. Most of the graphene islands are attached to the rhodium step edges, and are easily recognisable from their typical hexagonal Moiré patterns. A statistical analysis of the surface density and relative concentration of the 7C₆ clusters at different post-annealing temperatures is reported in Figure 6.8E. It can be concluded that the temperature of about 873 K signifies a starting point for the coalescence of the 7C₆ clusters, the smallest building blocks in our system, into large graphene islands.
Figure 6.8: STM images of the Rh(111) surface saturated with ethylene at room temperature followed by annealings to increasing temperatures (indicated in the images). All image sizes: $400 \text{ Å} \times 400 \text{ Å}$. 
Figure 6.9: STM images (A-C) (300 Å × 200 Å) and (D) (3D, 150 Å × 123 Å) of the Rh(111) surface saturated with ethylene at room temperature followed by annealings to increasing temperatures. (E) Temperature evolution of the surface density of $7C_6$ (in blue) and the relative concentration of $7C_6$ among all carbidic particles identified (in red). The dashed lines are guides-to-the-eye.
The graphene condensation is complete at about 973 K. A direct comparison of the samples annealed to 923 K and 973 K shows that a ripening of graphene occurs, leading to the formation of larger graphene islands with well defined boundaries at the rhodium step edges. Meanwhile the rhodium steps are also reshaped when compared to the sample annealed at lower temperatures (i.e. < 873 K). Images such as Figure 6.8F allow the estimation of the area of the Rh(111) surface covered by graphene at completion of the TPG is 18 ± 2%. We can estimate the number of carbon atoms deposited on the Rh(111) surface upon saturation with ethylene using STM images similar to Figure 6.7B. Our statistical analysis yields $6.5 \times 10^{14}$ atoms/cm$^2$ (with a Rh(111) lattice parameter of 2.69 Å). Furthermore, considering a C-C bond distance of 1.46 Å for graphene (i.e. $3.63 \times 10^{15}$ atoms/cm$^2$), we deduce that $(6.5 \pm 0.7) \times 10^{14}$ atoms/cm$^2$ are involved in our graphene islands. The good agreement between the number of carbons deposited and the number of carbons in the final graphene product confidently rules out the possibility of carbon dissolution into the bulk of the rhodium crystal.

### 6.5 Identification of 7C$_6$

The high magnification image presented in Figure 6.10 shows that the 7C$_6$ clusters are nearly perfectly hexagonal in shape. Recognising that the dehydrogenation of ethylene is complete at temperatures above 800 K$^{2,5-7,11}$, the most probable chemical structure adopted by the nano-clusters is comprised of 7 honeycomb carbon units (or equivalently 7 benzene units fused together and stripped from their protons) arranged in a hexagon, hereafter labelled 7C$_6$. This 7C$_6$, containing 24 carbon atoms, is the smallest hexagonal carbon framework after 1C$_6$ (i.e. the carbon framework of benzene). The other hexagonal carbon frameworks bigger than 7C$_6$, for example, 19C$_6$ with 54 carbon atoms, are seen to have dimensions much larger than the observed carbon clusters. Moreover, Figure 6.10B shows that all the 7 benzene units of 7C$_6$ can be clearly resolved when the probe tip is in a special high-resolution state. From the height contrast in the STM images and the measured height profiles of 7C$_6$ (Figure 6.10C), one gets the visual impression (under these tunnelling conditions) that the central carbon ring lies higher than its surrounding neighbours, suggestive of a dome-shaped configuration with a total height of about 2 Å. This observation will later be substantiated by DFT calculations.
Figure 6.10: (A) STM image (26 Å × 17 Å, 0.10 V, 0.80 nA) of 7C₆ on Rh(111). The rhodium lattice is drawn according to the atomically resolved Rh(111) background, which is visible by adjusting the image contrast. (B) 3D STM image (51 Å × 43 Å, 0.20 V, 0.40 nA) of 7C₆ on Rh(111) acquired with a special tip state, presenting a high resolution on the skeleton of 7C₆. (C) Height profiles acquired on the 7C₆ clusters in (A) and (B) along the [110] direction of Rh(111).

The 7C₆ clusters are now compared with coronene molecules, i.e. the hydrogenated analogues of 7C₆. The reason is to provide a clear experimental proof on whether the 7C₆ clusters are fully dehydrogenated. The coronene molecules were deposited on the Rh(111) surface at room temperature and imaged by STM at LHe temperature. In Figure 6.11, we put side by side topographic images of 7C₆ and coronene. Direct comparison indicates that coronene molecules are imaged slightly broader than 7C₆, irrespective of the tunnelling bias applied. This is in accordance with the fact that coronene has 12 extra peripheral protons, as compared to 7C₆.
7C_6 and coronene are observed to have different preferred adsorption sites on Rh(111). Although the carbon framework of 7C_6 has a perfect 6-fold symmetry, most of the metal-supported carbon clusters in Figures 6.11A-B and 6.11F adopt a 3-fold symmetry, which suggests that the hollow sites of Rh(111) are more preferred than other adsorption sites. Unfortunately, we have been unable to experimentally establish with good statistical significance the preferred adsorption site of 7C_6, since resolving the 7C_6 clusters while maintaining atomic resolution on Rh(111) is challenging. A careful analysis of Figures 6.10A-B reveals that these 7C_6 clusters are located on the fcc hollow sites of Rh(111), which downgrades the 6-fold symmetry of 7C_6 to the 3-fold of 7C_6/Rh(111). It is worth mentioning that the truncated hexagonal shape of 7C_6 is dependent on the bias polarity, as shown in Figures 6.11A-B. This is due to different molecular orbitals involved in the

Figure 6.11: STM images of a 7C_6 cluster acquired at (A) -1.0 V and (B) +1.0 V, respectively (15 Å × 15 Å, 0.5 nA). STM images of a coronene molecule acquired at (C) -1.0 V and (D) +1.0 V, respectively (21 Å × 15 Å, 0.1 nA). (E) Height profiles acquired on 7C_6 and coronene along the high symmetry directions (i.e. [110] and [112]) of Rh(111) and extracted from images (A) to (D). Large-scale STM images of (F) 7C_6 and (G) coronene, respectively. Image size: 100 Å × 85 Å. The molecular alignments with respect to Rh(111) are indicated by dashed lines in (G). Note: images (A) to (D) have an identical scaling in order to allow for direct topographic comparison, whereby coronene is imaged larger than 7C_6.
tunnelling, which will be discussed later. In contrast, coronene is imaged as hexagonal at positive polarity, whereas at negative polarity, it is characterised by two intense and broad lobes on two opposite sides, rendering it 2-fold symmetric. Since three different azimuthal orientations differing by 120° with respect to each other can be identified in the STM images reported in Figure 6.11G, we conclude that the coronene molecules are adsorbed on the bridge sites of Rh(111). The above results provide a first indication that the carbon cluster evolving from ethylene decomposition on Rh(111) are not comparable to coronene, although they have the same carbon skeleton.

Figures 6.12A and 6.12B show typical \( \frac{dI}{dV} \) spectra recorded on the centres of \( 7C_6 \) clusters and coronene molecules adsorbed on Rh(111), respectively. The \( 7C_6 \) spectra are characterised by a sharp peak located at -0.91 V and a broad peak at +0.76 V (easily identifiable when comparing with spectra acquired on the bare rhodium substrate) that we associate with the HOMO and LUMO states, respectively. The coronene spectrum exhibits a single broad peak near +0.6 V while neither peak nor shoulder appear at negative bias. The striking dissimilarity (originating from different electronic structures) between the spectra in Figures 6.12A and 6.12B is a second indication that \( 7C_6 \) and coronene are two different chemical entities.

At -0.91 V, corresponding to the \( 7C_6 \) HOMO resonance identified in Figure 6.12A, the cluster is imaged by constant-current STM as a slightly truncated hexagon with a height of approximately 1.5 Å (Figure 6.12C). At a positive bias of +0.76 V associated with the LUMO energy, \( 7C_6 \) is again imaged as a slightly truncated hexagon although with a rotation of 180° (Figure 6.12D). STM images of coronene molecules (Figures 6.12G), obtained at +0.6 V, corresponding to the single resonance identified in Figure 6.12B, are similar to those for \( 7C_6 \), although slightly larger and reflecting the overall shape and size of the molecule, with a reduced height of ~ 1 Å as compared to \( 7C_6 \). Note that when coronene molecules are imaged at voltages within their featureless, negative spectral region, we obtain similar images as the one discussed and presented in Figure 6.11C. In Figures 6.12E, 6.12F, and 6.12H, we present energy resolved \( \frac{dI}{dV} \) maps of \( 7C_6 \) and coronene taken at the energies of their respective resonances identified in Figures 6.12A and 6.12B. The \( \frac{dI}{dV} \) map of the highest energy resonance of the \( 7C_6 \) cluster (+0.76 V,
Figure 6.12: (A) STS spectra (in yellow) acquired on 7C₆. (B) STS spectra (in blue) acquired on coronene. STS spectra acquired on Rh(111) are in black. (C-D) Topographic STM images acquired on 7C₆ at the voltages corresponding to the HOMO and LUMO peaks identified in (A). (E) and (F) $dI/dV$ maps acquired on 7C₆ corresponding to (C) and (D), respectively. (G) Topographic image of coronene acquired at the voltage associated with the LUMO peak identified in (B). (H) $dI/dV$ map acquired on coronene corresponding to (G). The molecular orbitals look more expanded than the corresponding structural models, due to a tip convolution effect in $dI/dV$ imaging. All image sizes: 17 Å × 14 Å.
Figure 6.12F) displays three nodal structures with 120° separation, while the map of the lowest energy state at -0.91 V (Figure 6.12E) shows a network of 7 LDOS peaks located at the expected sites of 7 hexagon rings. In contrast, no intra-molecular spatial inhomogeneity in the electronic structure can be distinctively observed for coronene (Figure 6.12H). Since \( \frac{dI}{dV} \) map can reflect the real-space features of the electronic structure, our data further confirm the differences between 7C₆ and coronene in their topographic and electronic properties.

To summarise here, 7C₆ carbon clusters are produced by the dehydrogenation of ethylene on Rh(111) at high temperatures. The structure of the 7C₆ carbon cluster has been carefully examined by our local probe techniques, revealing that it is composed of 7 honeycomb ring without peripheral hydrogen atoms. However, it still remains unclear why 7C₆ is the main cluster products when the dehydrogenation process is complete. Alternatively, is 7C₆ more stable than other carbon clusters supported on Rh(111)? In order to answer this question, DFT calculations were performed to study the interactions between carbon clusters and metal substrate, and the differences between 7C₆ and coronene. We discuss these calculations in the following section.

6.6 DFT results

The carbon species can exist in the Rh(111) system in two different forms: isolated mono-dispersed carbon adatoms and 2D carbon aggregates (ranging from clusters to graphene). Isolated carbon is regarded to be the starting point for the growth of graphene prepared by the vapour deposition method.²¹-²² It will serve in our case as an important reference for discussing the theoretical stability of the carbon clusters. Due to the small size of carbon, the atoms have the possibility to diffuse into the interstitial sites of rhodium atoms below the top layer of Rh(111). We examine this by investigating subsurface carbon with coverages of 1/6 and 1/4 ML* (see the footnote below *). The preferred adsorption position for the subsurface carbon is revealed to be the octahedral site, and the corresponding adsorption energies are -7.06 eV (1/6 ML*) and -6.91 eV (1/4 ML*). For

* Fractional coverage (reference²³) is adopted in the DFT calculations in section 6.6. Hence, 1 ML* corresponds to one adsorbate (one carbon atom in our case) per one adsorption site. Relative coverage, which adopts a saturation coverage as 1 ML, is used in other sections of this thesis. As a consequence, 1 ML (in relative coverage) of graphene/Rh(111) has more carbon atoms than 1 ML* (in fractional coverage) of carbon_atom/Rh(111) by a factor of 2 × 2.69 / 2.46 = 2.19.
the isolated carbon atoms on the Rh(111) surface, we found that the preferred adsorption position is the hcp site of the rhodium atoms. The adsorption energy decreases with the carbon coverage (see Figure 6.13), suggesting an increase of repulsive interactions between carbon atoms with a smaller carbon-carbon distance. A comparison of the carbon atoms above and below the top rhodium layer with an identical coverage reveals that, the adsorption of carbon on the surface is more energetically favourable. This is in accordance with our experimental results that no carbon diffuses into the rhodium bulk at high temperatures.

Figure 6.13: The adsorption energy of mono-dispersed carbon atoms on Rh(111) plotted as a function of coverage.

We now discuss the carbon clusters and graphene supported on Rh(111). Clusters with different numbers \( n \) of honeycomb rings are relaxed on the Rh(111) surface by DFT calculations. The total energy \( E_{\text{total}} \) (per carbon atom) of the cluster is defined by the energy difference between the adsorbed cluster and the atomic carbon in the gas phase. \( E_{\text{total}} \) can be divided into two parts: the formation energy \( E_{\text{C-C}} \) (per carbon atom) of the cluster in the gas phase and the adsorption energy \( E_{\text{C-M}} \) (per carbon atom) of the cluster from the gas phase on Rh(111). Figure 6.14 shows the \( E_{\text{total}} \) (in red), \( E_{\text{C-C}} \) (in black) and \( E_{\text{C-M}} \) (in blue) plotted as a function of cluster size. The two dashed lines represent the formation energy of the isolated atomic carbon and graphene \( i.e. \) a full monolayer of carbon) on Rh(111). The x-axis represents the ratio between carbon atoms at the
periphery ($N_p$) and the total number ($N_t$), which is an important structural parameter for the carbon clusters. We can see that $|E_{C-M}|$ and $|E_{C-C}|$ have reversed trends when varying the cluster dimension. $|E_{C-M}|$ decreases with the size of the carbon cluster, which is due to the fact that (1) larger clusters have a smaller $N_p/N_t$ ratio and (2) the cluster interacts with the Rh(111) substrate mainly through the periphery atoms. Nevertheless, $|E_{C-C}|$ increases with the cluster dimension, and it reaches a maximum at the condition of graphene/Rh(111). This arises as a consequence of increasing sp$^2$-bonded carbon atoms in the larger clusters. Importantly, when comparing in Figure 6.14 the $E_{\text{total}}$ of the rhodium-supported clusters with reference to the corresponding energy of C(fcc)/Rh(111), we realize that $7C_6$ and the carbon adatoms have similar energy (their difference is within the error of calculations), and the aggregation of carbon into clusters larger in size than $7C_6$ is energetically favoured. In other words, $7C_6$ is the smallest stable carbon cluster on Rh(111). This explains very well our STM observation of the $7C_6$ clusters obtained by the

**Figure 6.14:** $E_{\text{total}}$ (in red), $E_{C-M}$ (in blue) and $E_{C-C}$ (in black) of clusters with different dimensions. $N_p/N_t$ represents the ratio of carbon atoms at the periphery ($N_p$) and the total number ($N_t$). The totally energies of C(fcc)/Rh(111) and graphene are indicated by dashed lines. A coverage of 1/9 ML$^*$ is used for C(fcc)/Rh(111), since this is comparable to the observed coverage of the carbon species (in the cluster form) on the rhodium terraces after the dehydrogenation reaction.
dehydrogenation of ethylene on Rh(111) around 873 K. Since clusters larger than 7C₆ have even lower energies, we conclude that the 7C₆ species will eventually grow into larger graphene islands at high enough temperatures. This is in a good agreement with our experimental results at temperatures higher than 873 K.

Now we focus on the structure of the 7C₆ cluster adsorbed on the Rh(111) surface. The DFT-relaxed 7C₆ on different sites of Rh(111) in Figure 6.15A are seen to have

![Figure 6.15: Structures of (A) 7C₆ and (B) coronene adsorbed at different sites of Rh(111) relaxed by DFT calculations. E(7C₆) is the energy difference between the adsorbed 7C₆ cluster and the atomic carbon in the gas phase, while E(CₙH₁₂) is the adsorption energy of coronene on Rh(111). The height of 7C₆/coronene refers to the position of the carbon atoms with respect to the rhodium surface, while the size is the distance between two furthest carbon atoms along the [110] direction.](image-url)
comparable adsorption energies (ranging from -7.30 to -7.34 eV). We experimentally observed that the 7C₆ clusters are adsorbed on the hollow sites of Rh(111), but with little statistical significance. Hence we cannot rule out that the clusters might also be adsorbed on other sites. Our calculations show that the 7C₆ cluster adopts a dome-shape structure, due to different C-Rh interactions at the centre and peripheral carbon atoms. For 7C₆ adsorbed at the fcc site of Rh(111), the local C-Rh bond length is 2.65 Å and 1.83 Å at the centre and the edge of the cluster, respectively. The width of the 7C₆ cluster, measured by the distance between two peripheral carbon atoms at opposite sides, is 7.43 Å. Coronene molecules adsorbed on Rh(111) are also computed for comparison. The adsorption energy of a coronene molecule on the bridge site of rhodium atoms is -3.76 eV, much lower than on the other sites (e.g. -2.74 eV for hcp and -2.14 eV for fcc). Hence the

**Figure 6.16:** Simulated STM images of 7C₆ and coronene adsorbed at different sites of Rh(111).
bridge site is the preferred adsorption location for coronene, in accordance with our STM results. Different from the dome-shape of 7C6/Rh(111), the coronene molecule adopts a flat geometry with a C-Rh distance of 2.15 Å. These results explain the differences between 7C6 and coronene we observed in the STM topographic images (see Figure 6.12). The width of the coronene molecule, measured by the same way as for the carbon cluster, is 7.5 Å, slightly larger than that of 7C6.

The topographic images of 7C6 and coronene are further simulated by using the Tersoff-Hamann approximation, as shown in Figure 6.16. We see that 7C6 adsorbed on the hollow sites of rhodium has a 3-fold symmetry at negative bias, while coronene has a distinct 2-fold symmetry when on the bridge site. Moreover, coronene molecules are imaged broader than 7C6. All these simulation results confirm the observed differences between 7C6 and coronene on Rh(111) by STM.

6.7 Others - larger carbon clusters

7C6 are the dominating carbon clusters in the condensation stage of graphene on Rh(111). However, other clusters with larger sizes can also be observed, although with much smaller probabilities (< 5%). For instance, the carbon clusters with a 3-fold symmetry can be found in the sample annealed to temperatures higher than 873 K. These clusters have \( m(m+1)/2 \) honeycomb rings \( (m > 5, m \) denotes the number of the honeycomb rings at the edge of the triangular cluster), hence these have much more carbon atoms than the 7C6 cluster. A larger size of the carbon clusters leads to several interesting consequences. (1) The energy gap between the HOMO and LUMO states becomes smaller, because the \( \pi \) electrons are more delocalised in a larger potential well. When the gap between the neighbouring resonance peaks is comparable to the width of the peaks (note: the \( dl/dV \) peaks are broad especially when the adsorbates interact strongly with the metal substrate\(^{20} \)), the peak overlap makes it difficult to resolve the eigenenergies in the \( dl/dV \) spectra of the carbon clusters. Interestingly, \( dl/dV \) images of the triangular clusters at negative bias always show three LDOS peaks at the corners of the triangle, as shown in Figure 6.17D. These lead to bright corners in the triangular clusters (Figures 6.17A-C) when imaged by STM with negative bias. Such a feature might be due to a scattering
Figure 6.17: STM images (A) 3D and (B) (35 Å × 34 Å, 0.5 V, 0.1 nA) of an atomically resolved triangular 28C₆ cluster formed by TPG procedure at 973 K. STM image (C) (35 Å × 33 Å, -0.88 V, 0.4 nA) and $dI/dV$ image (D) of a 28C₆ cluster, acquired simultaneously. STM images (E) (35 Å × 37 Å, -0.5 V, 0.3 nA) and (F) (35 Å × 37 Å, -1.0 V, 0.4 nA) of a triangular 36C₆ cluster. Note: images (B)-(F) have an identical scaling in order to allow for direct topographic comparison. The green grids represent hexagonal carbon skeletons.
effect within a triangular potential field at given energy states.\textsuperscript{24} (2) For the triangular clusters with larger dimensions \((N > 7)\), their STM topographs are observed to have a lower symmetry \((i.e. \ 2\text{-fold})\) at given voltages, as demonstrated in Figure 6.17F. This is very likely attributed to the fact that the size of the large cluster is comparable to the Moiré supercell of graphene/Rh(111), thus the cluster can span over different C-Rh registries within its skeleton. For example, the dark zone of the triangular cluster probably corresponds to a ring-bridge type C-Rh configuration. At this stage we only have limited knowledge about the structures of the large carbon clusters, because a low density of these clusters on Rh(111) brings difficulties to the STS measurements (note: a prerequisite of STS measurements is a symmetric and electronically-featureless STM tip. However, a long time search of the large clusters on the surface can very often modify the tip state). Nevertheless, we can envision that the carbon clusters on Rh(111) will gradually become graphene/Rh(111) when the dimension of the cluster continues to increase. A comprehensive understanding of these large TM-supported carbon clusters requires more studies in the future.

In summary, we have investigated by STM the dehydrogenation process of ethylene on Rh(111) at elevated temperatures, and observed that carbon clusters are the intermediate species for the TPG growth of epitaxial graphene. \(7C_6\) is the dominating product when the dehydrogenation process is complete at 873 K. By means of high-resolution STM, STS and a comparison with coronene, such \(7C_6\) cluster is identified to have 7 benzene rings without peripheral hydrogen atoms. Moreover, carbon clusters with different sizes adsorbed on the rhodium substrate are investigated by DFT calculations, revealing that \(7C_6\) is the smallest stable carbon cluster on Rh(111) and thus confirming our experimental observations.

References


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Monolayer graphene and carbon clusters supported on the Rh(111) surface were systematically studied by local probe techniques. Scanning tunnelling microscopy and spectroscopy (STM and STS) were combined throughout the work reported in this thesis, and have been proven very effective to reveal not only the structural characteristics but also the electronic properties of the supported carbon film/clusters.

Epitaxial graphene was grown on Rh(111) by dehydrogenation of ethylene at high temperatures. Graphene/Rh(111) exhibited a hexagonal Moiré pattern as a result of the lattice mismatch between graphene and the rhodium substrate. The structural characteristics of the graphene/Rh(111) Moiré were first investigated by STM. We observed that the local periodicity of the Moiré varies from 26.0 Å to 29.3 Å, corresponding to superstructures ranging between 12C/11Rh and 11C/10Rh (note: C represents the unit cell of graphene). By analysing the distinctive contrast variation in the STM images, we explicitly identified the local high-symmetry registries within the Moiré unit cell. Notably, the ring-bridge sites were always observed as minima in the tunnelling contrast among all local registries, regardless of the different tunnelling conditions and tip states. In order to gain a better understanding of the graphene/TM system, we presented a thorough discussion about the concepts of “commensuration” and “incommensuration” used in surface science for describing the Moiré superstructures. The graphene/Rh(111) system was concluded to have a non-simple-commensurate structure, which explained not only the variation in the local periodicity of the Moiré, but also the “apparent angular scattering” between the graphene and the metal lattices. Moreover, the boundaries and step edges of graphene/Rh(111) were carefully examined, revealing that the graphene layer adopted quantised dimensions and the rhodium substrate is accordingly reshaped in the high-coverage graphene samples.

We further investigated the electronic surface properties and chemical bonding of graphene/Rh(111) by means of site-specific resonance tunnelling spectroscopy (RTS) and extended density functional theory (DFT) calculations. Spectroscopy measurements
showed a work function modulation of 220 meV on epitaxial graphene, indicating that the chemical bonding strength varies significantly across the Moiré supercell. By combining the microscopy, spectroscopy and theoretical results, we drew the conclusion that the ring-top and ring-bridge sites are the local configurations of minimum and maximum chemical bonding to the rhodium substrate, and therefore we showed that graphene is corrugated at the atomic scale. We further discussed the electronic coupling between epitaxial graphene and the group VIIIB transition metals on the basis of the “d band model”.

The growth of graphene by pyrolytic decomposition of ethylene at elevated temperatures (following the temperature programmed growth (TPG) method) was investigated by STM. Ethylene was transformed to ethylidyne upon deposition on Rh(111) at room temperature. Further dehydrogenation of the hydrocarbons at higher temperatures resulted in the formation of carbon clusters. Importantly, we identified mono-dispersed carbon clusters, labeled 7C₆, as the dominating products on the rhodium terraces at 873 K. We proposed that these clusters serve as precursor species for the growth of graphene. High-resolution STM and STS measurements of 7C₆, combined with a comparison with adsorbed coronene molecules (also supported on Rh(111)), revealed that the 7C₆ clusters are composed of 7 honeycomb rings without peripheral hydrogen atoms. Furthermore, theoretical calculations were performed to compare the stabilities of the carbon clusters with different sizes, confirming that 7C₆ are the smallest stable carbon clusters on the Rh(111) surface. The DFT-relaxed 7C₆ structures showed a strong C-Rh bonding at the peripheral carbon atoms, hence the clusters adopt a dome-shape structure, in line with our experimental observations.

In summary, we have investigated the structural and electronic properties of graphene/Rh(111), and the growth mechanism of graphene from hydrocarbon precursors. Based on what we have achieved at this stage, further work can be undertaken towards several directions: (1) Graphene functionalisation/application. The distinctive corrugation of graphene/Rh(111) makes it an interesting 2D template to support molecules/clusters in nanotechnology: we can find out whether the ring-bridge or the ring-hollow site will be the preferred adsorption site for small adsorbates. A tuning of the band structure of
epitaxial graphene will also be important for the electronics application. This may, for instance, be realised by doping graphene with nitrogen or boron species during the synthesis. (2) Graphene reactivity. Since graphene formation represents a model system for coke formation in catalysis, this can be furthered by investigating the chemical reactivity of graphene, which is related to the coke removing reactions. An exploration into this aspect may shed light on the regeneration of the deactivated metal catalysts. (3) Other possible growth mechanisms. So far small hydrocarbon molecules were generally adopted as the starting reactants for the graphene growth. However, there are many other interesting larger aromatic molecules (such as pentacene with a linear geometry and coronene with a hexagonal geometry) that could possibly be carbonized into graphene. It is worth studying whether similar magic carbon clusters will be produced in these systems, or different kinetic processes will be discovered.
Appendix: 2D Hexagonal Moiré

A hexagonal Moiré pattern, formed by overlapping two hexagonal lattices on each other, is presented in Figure I. The two lattices have different constants, i.e. \((a_1, b_1)\) and \((a_2, b_2)\), respectively. The corresponding lattice vectors in reciprocal space are described by:

\[
|k_{a_1}| = \frac{2\pi}{\sqrt{3}/2 a_1}, \quad |k_{b_1}| = \frac{2\pi}{\sqrt{3}/2 b_1}
\]

\[
|k_{a_2}| = \frac{2\pi}{\sqrt{3}/2 a_2}, \quad |k_{b_2}| = \frac{2\pi}{\sqrt{3}/2 b_2}.
\]

Similarly, the 2D Moiré has lattice vectors \((\vec{k}_{M_a}, \vec{k}_{M_b})\) described by:

\[
|\vec{k}_{M_a}| = \frac{2\pi}{\sqrt{3}/2 M_a}, \quad |\vec{k}_{M_b}| = \frac{2\pi}{\sqrt{3}/2 M_b}
\]

where \((M_a, M_b)\) are the lattice constants of the 2D Moiré. In reciprocal space, we have

\[
\vec{k}_{M_a} = \vec{k}_{a_2} - \vec{k}_{a_1},
\]

\[
-|\vec{k}_{M_a}|^2 = |\vec{k}_{a_1}|^2 + |\vec{k}_{a_2}|^2 - 2 |\vec{k}_{a_1}| \cdot |\vec{k}_{a_2}| \cdot \cos(\phi_{a_1, a_2})
\]

\[
\rightarrow \quad M_a = \left( \frac{2\pi}{\sqrt{3}/2 a_1} \right)^2 + \left( \frac{2\pi}{\sqrt{3}/2 a_2} \right)^2 - 2 \frac{2\pi}{\sqrt{3}/2 a_1} \cdot \frac{2\pi}{\sqrt{3}/2 a_2} \cdot \cos(\phi_{a_1, a_2}) \quad (I.1)
\]

where \(\phi_{a_1, a_2}\) is the angle between lattice vectors \(a_1\) and \(a_2\). Similarly we have:

\[
\rightarrow M_b = \left( \frac{1}{b_1} \right)^2 + \left( \frac{1}{b_2} \right)^2 - \frac{2}{a_1 a_2} \cdot \cos(\phi_{b_1, b_2}) \quad (I.2)
\]

where \(\phi_{b_1, b_2}\) is the angle between lattice vectors \(b_1\) and \(b_2\). It can be seen that equations (I.1) and (I.2) are similar to equation (4.2), which means that the 2D Moiré pattern can be decomposed into two independent 1D Moiré patterns when performing structural analysis.
Figure I: Schematics of a 2D Moiré pattern formed by superimposing of two hexagonal lattices.
List of publications

1. Coupling epitaxy, chemical bonding and work function at the local scale in transition-metal supported graphene
   

2. Size-selective carbon nano-clusters as precursors to the growth of epitaxial graphene
   
   Wang, B.; Ma, X. F.; Caffio M.; Schaub, R.; Li, W.X. Accepted by *Nano Letters*.

3. Structure of epitaxial graphene on Rh(111)
   