Hydrogenation of graphene on Iridium(111) by vibrationally excited molecules

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Abstract

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Introduction

It's not rocket science.

Figure 1.1: det er nok at skrive filnavnet, for main.tex kigger efter figurer i /figures/

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Graphene

2.1 Graphene

Graphene is a two dimensional honeycomb lattice of carbon atoms. Each carbon atom is sp^2 hybridized where one s orbital and two p orbitals form three planar bonds with a separation angle of 120°. The distance between the individual carbon atoms is 1.42 Å. Due to the flexibility of the sp^2 bonds in the z direction, many other structures can be formed by a sheet of graphene, such as fullerenes, carbon nanotubes, and graphite. The graphene unit cell consists of only two lattice points, and the lattice vectors can be written as the following:

$$a_1 = \frac{a}{2}(3, -\sqrt{3}) \; a_2 = \frac{a}{2}(3, \sqrt{3})$$

2.2 Graphene on Ir

As a monolayer of graphene is synthesized on top of a metal surface the underlying metal and the graphene monolayer rarely has identical lattice parameters. This causes a mismatch between the two layers and these will be rotated at an angle compared to each other. A moiré superstructure appears when this surface is examined by STM, because certain areas has carbon directly above iridium, and certain areas has carbon and iridum perfectly out of phase. Below, figure 2.1 shows the the graphene-iridium moiré unit cell.
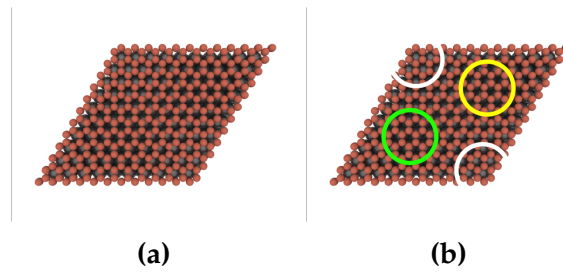
(a)   **(b)**

Figure 2.1: Graphical interpretation of the Gr/Ir moire unit cell. [1]

2.3 Hydrogenation of graphene using vibrationally excited deuterium

2.4 Hydrogenation of graphene using atomic deuterium

3

Techniques

3.1   Scanning Tunneling Microscopy - STM

The main technique used in this study is STM, and more specifically the Aarhus STM. The working principle of the STM is the tunneling transmittivity which depends exponentially on the distance between a sharp tip and the sample. A bias is applied between the sample and the tip, and at relatively large distances the barrier that the electrons perceive is too high, and no tunneling occurs. As the distance between the sample and the tip is reduced the probability of an electron tunneling through the vacuum barrier increases until a point where tunneling happens, and the current can be measured. The tunneling current is reduced by about a factor of 10 for every ångstrøm. [2] This ensures that the STM is a very precise technique and hence essential for surface scientists. In order to achieve the tunneling current it is necessary that the tip as well as the sample is conducting.

In order to create an image, the surface of the sample is scanned with the tip, which is moved by piezo-elements. The tunneling current is dependant on distance between tip and sample as well as the local density of states (LDOS). A map of the LDOS is therefore obtained when the tip is scanned across the surface of the sample. This is used to indirectly create an image of the surface.

3.2 Temperature Programmed Desorption - TPD

3.3 Low Energy Electron Diffraction - LEED

3.4 Raman Spectroscopy

4

Experimental Setup

4.1 The Coal Chamber

The experiments is carried out under UHV (ultra high vacuum) conditions. This is crucial because contaminants easily can absorb to the surface which ruins the quality of the gathered data. During this project the vacuum chamber named 'The Coal Chamber' is used which is one of many vacuum chambers in the SDL lab.

The equipment mounted on The Coal Chamber, which is used in this study, is described in the following section along with the experimental approach. The sample is introduced to the coal chamber from a loadlock where the sample is attached to a transfer arm. Transfer of the sample from the loadlock to the main chamber takes place as the pressure in the loadlock is reduced sufficiently by a turbo pump. In the main chamber a manipulator is apparent in the center from where the sample can be transferred to the STM by a wobble stick. A filament lies behind the sample in the manipulator, which is used during anneals.

4.1.1 Turbo pump

In order to achieve proper UHV conditions a turbo pump is needed in addition to the roughing pump. The turbo pump is directly connected to the vacuum chamber and consists of a series of rotor blades. Each of these adds momentum to the remaining gas molecules that collide with the blades and hence removes these from

the chamber. In order to function properly these rotor blades spins up to 80.000 RPM. [**?**]

4.1.2   H2 cracker - Vibrationally excited molecules

Vibrationally excited molecules are produced using a H_2 cracker.

4.2   STM

4.3   TPD

A mass spec is connected to the UHV chamber, and this was used to investigate the desorption of deuterium from the sample surface. The sample was positioned in the manipulator as the experiments were carried out. From here the nozzle of the mass spec was brought within millimeters of the sample. The temperature was logged together with the amount of deuterium detected by the mass spec. The mass spec was set to count masses of 4 amu, in order to exclude other molecules than deuterium. This setup was made with the computer program 'MASsoft' by Hiden Analytical.

A Eurotherm 2704 controller was used to control the current going to the filament in the manipulator, in order to manage the temperature of the sample. The controller was programmed to ramp the sample temperature from 300K to 900K at a rate of 1K per second. At maximum temperature the eurotherm was set to rest for 30s, and then slowly decrease the temperature to a final temperature of 300K. This cycle was performed each time a TPD measurement was carried out. During this procedure most of the deuterium on the surface should be desorped from the sample.

The temperature of the sample was measured on the backside by a thermocouple, and hence the feedback was not an actual measure of the surface temperature. An optical pyrometer was therefore used to measure the actual temperature of the surface alongside with the logged temperature by MASsoft, in order to calibrate the system. Since the sample is Iridium , the emissivity of the pyrometer was set to 23%.The acquired data is shown in figure 4.1, where the temperature of the surface versus the thermocouple is plotted. The
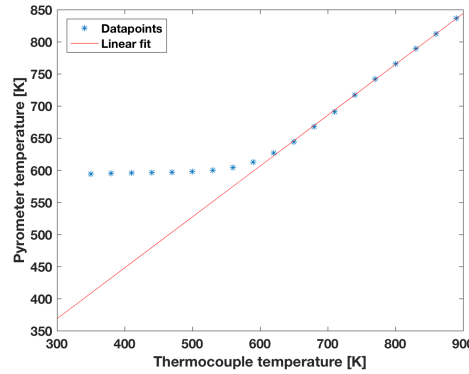
Figure 4.1: Calibration of the temperature during the TPD measurements. The temperature of the surface measured by an optical pyrometer is plotted against the thermocouple temperature.

calibration factors obtained from the fit is the following:

$$T_{surface} = T_{TC} * 0.7921 + 131.2$$

In figure 4.2a the data obtained from a typical TPD measurement is shown. Since the desorption of deuterium from the surface is investigated, a mass of 4 amu is monitored along with the temperature. It is seen that the temperature follows the linear trend except for the extremities of the temperature interval where some fluctuations start to happen. Since the temperature is controlled and logged with the Eurotherm controller, it is possible to plot the counts of deuterium against the temperature. These plots are presented in chapter 5.
A triple gaussian function was fitted to the datapoints around the peak, in order to determine the temperature belonging to the peak. The peak value was estimated by visual observation, and the datapoints within ±60°C are included in the fit. The temperature at the maximum of the fit was determined, and these values are presented in chapter 5 as the peak temperatures. An example of the fit to the peak values is shown in figure 4.2b. From this figure it is seen that the temperature at which the maximum counts is observed, not necessarily corresponds to the correct peak temperature. The green circle in figure 4.2b shows the found peak from which the temperature was gathered.
In order to compare the individual peaks, the background was subtracted from every datapoint. The sample was positioned stationary in front of the nozzle for a period of time before the measurements

were carried out. These datapoints were used to calculate a mean background count, which was subtracted.

(a)

(b)

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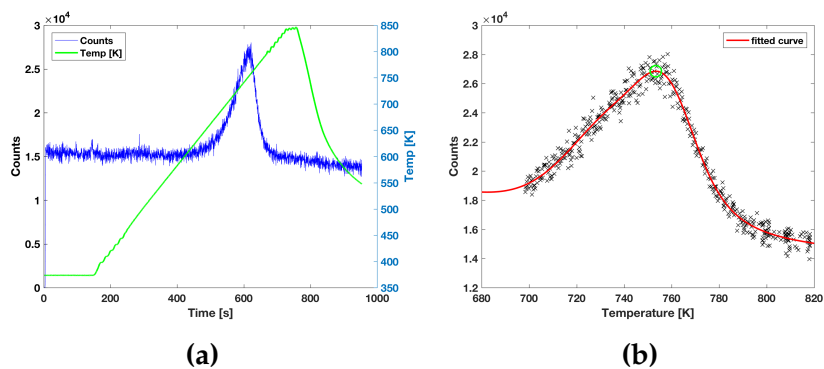
Results

5.1 Graphene on Ir

The quality of the graphene was checked each time D_2 was dosed on the sample, in order to ensure that the amount of defects was at a minimum. STM pictures of pure graphene on Ir(111) is shown in this section. On figure 5.1 pictures of graphene on Ir in different sizes is shown. Figure 5.1a shows a large image of a graphene monolayer covering the Ir surface. Although the quality of the image is of low quality, the moire pattern is perceived. Also several step edges from the underlying Ir surface is seen. Several line scans has been performed on these edges, which show that the height difference is 2Å ±0.4Å. This value is consistent with the value of 0.22nm found in the litterature. [3]

On figure 5.1b a high resolution image of Gr/Ir is seen. The moire pattern is very prominent in this figure, and the spacing between the individual sites in the moire unit cell can be determined from a line scan. A line scan was drawn on figure 5.1b and two points were positioned in the corners of the moire unit cell in order to obtain the moire periodicity. The morié periodicity is 25.2 ± 0.4Å according to the litterature. [4] This agrees with the measured length of 25.24 Å from the line scan. Typical defects on of the graphene monolayer is seen as well in this figure. Also the hexagonal pattern of graphene is sensed because of the atomic resolution. On figure 5.1c the individual carbon atoms are even more clear.
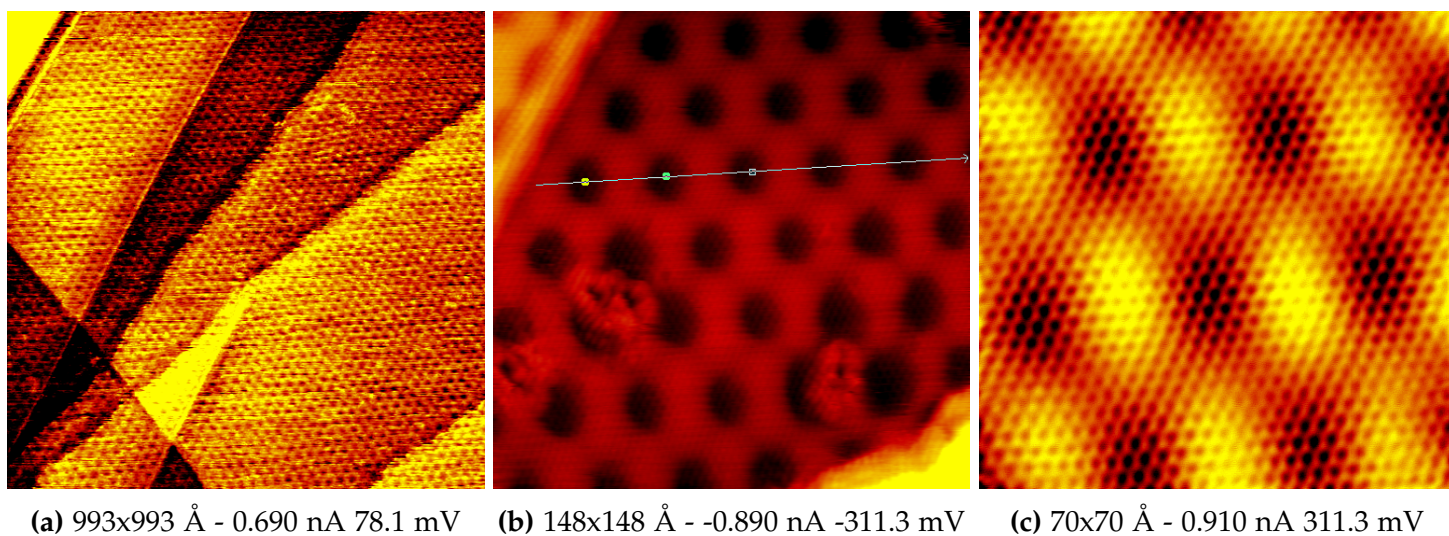
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(a) 993x993 Å - 0.690 nA 78.1 mV **(b)** 148x148 Å - -0.890 nA -311.3 mV **(c)** 70x70 Å - 0.910 nA 311.3 mV

Figure 5.1

5.2   D2 on graphene

Dosing at temperatures of, 1340C, 1540C and 1740C were performed in order to determine the threshold temperature of the hydrogenation of graphene.

Full coverage D2 on graphene
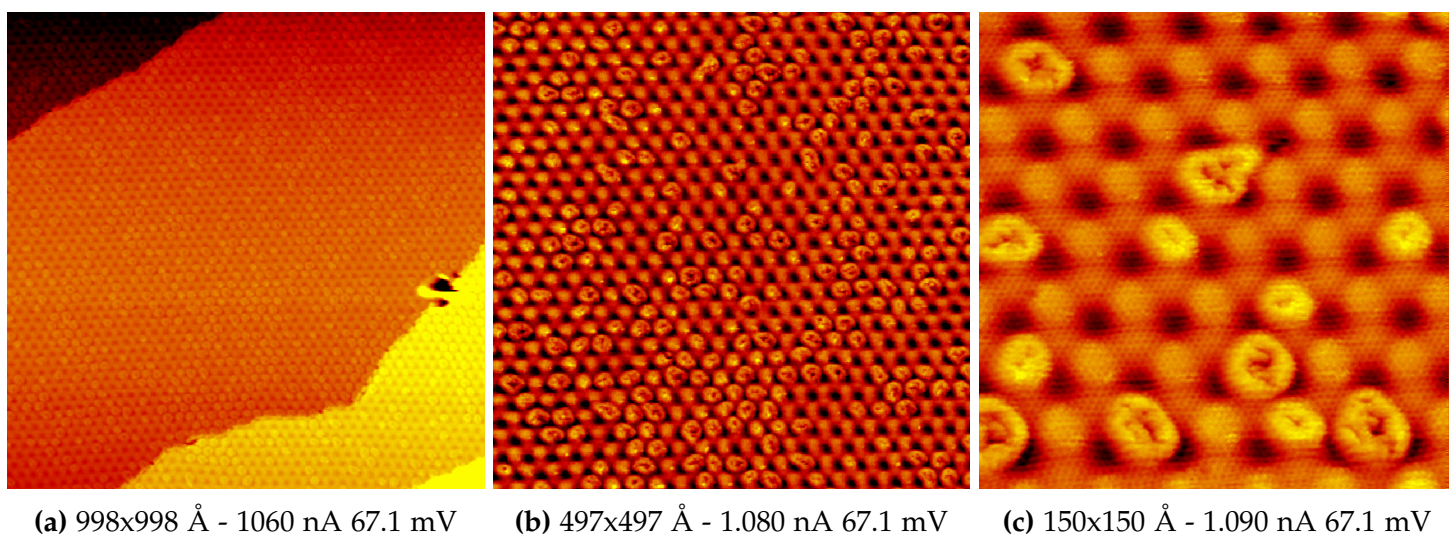
1740 C doser ...

(a) 998x998 Å - 1060 nA 67.1 mV **(b)** 497x497 Å - 1.080 nA 67.1 mV **(c)** 150x150 Å - 1.090 nA 67.1 mV

Figure 5.2

1593 C doser ...

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(a) 488x488 Å - 0.900 nA 190.4 mV   **(b)** 180x180Å - 1.020 nA 190.4 mV   **(c)** 97x97 Å - 1020nA, 190.4mV
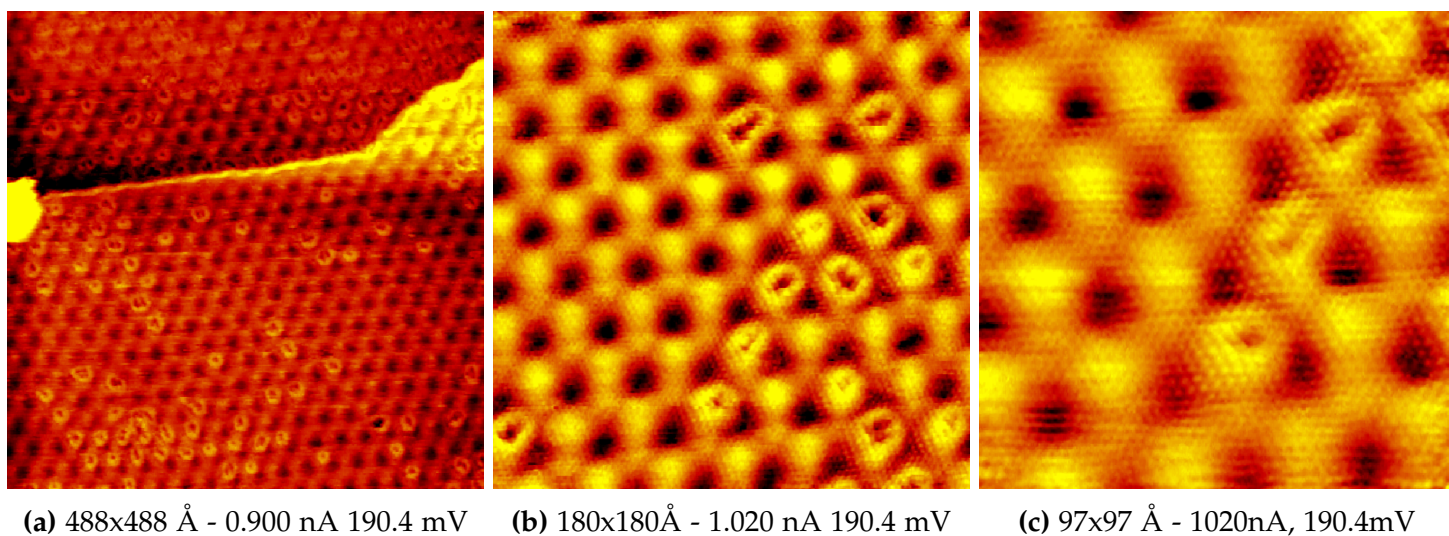
Figure 5.3

5.3 TPD measurements - Atomic and molecular D2

In figure 5.4 below, the data from the TPD is gathered in two different figures. TPD measurements were made for both the vibrationally excited molecules and atoms. Figure 5.4a shows the data aquired for the D2 dose and figure 5.4b shows the data for the dose with hot atoms.
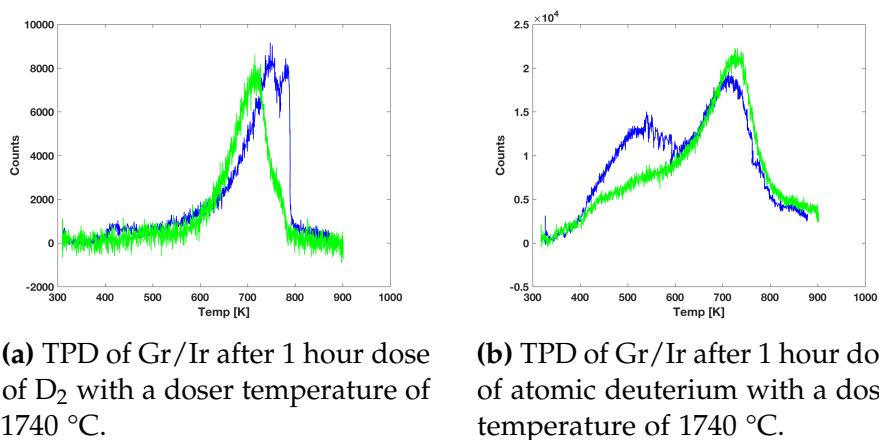

(a) TPD of Gr/Ir after 1 hour dose of D_2 with a doser temperature of 1740 °C.

(b) TPD of Gr/Ir after 1 hour dose of atomic deuterium with a doser temperature of 1740 °C.

Figure 5.4

Figure 5.5

5.4 Bilayered graphene on Ir

5.5 LEED of bilayered sample

(a) LEED without flashing. 145eV

(b) LEED after low temperature flash of the sample. 145eV

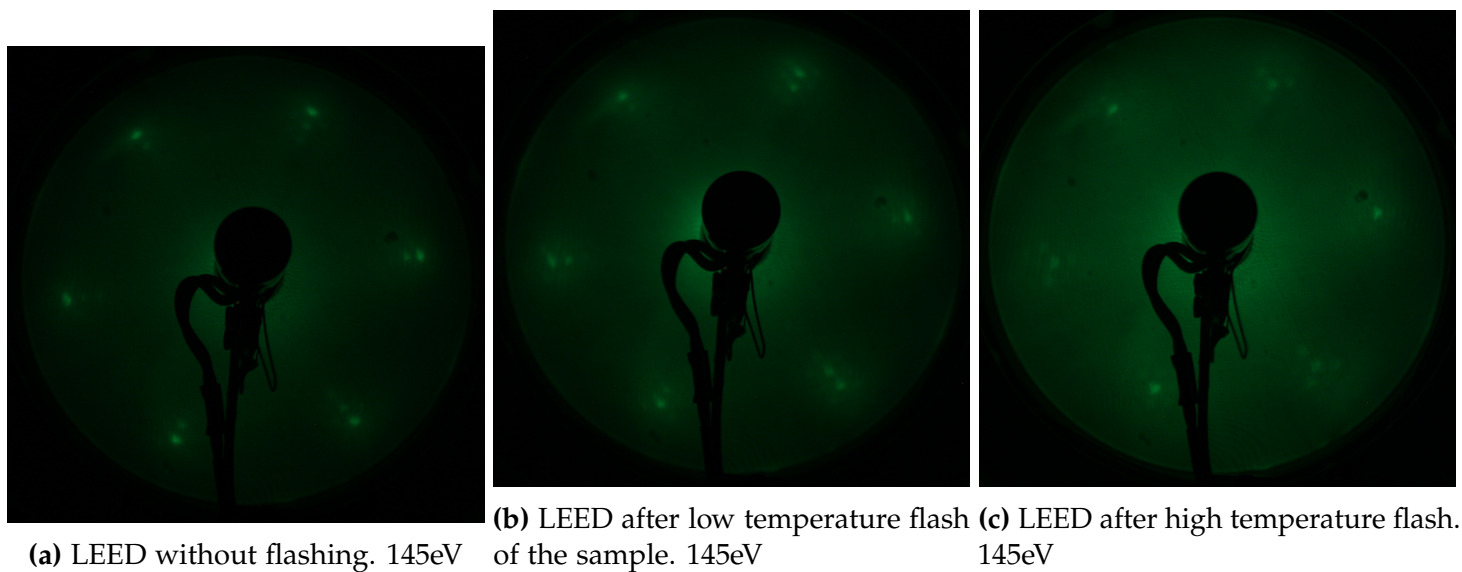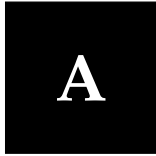**(c)** LEED after high temperature flash. 145eV

Figure 5.6

6

Conclusion and future perspectives

A

Additional figures

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[4] Alpha T N'Diaye, Johann Coraux, Tim N Plasa, Carsten Busse, and Thomas Michely. Structure of epitaxial graphene on ir(111). *New Journal of Physics*, 10(4):043033, 2008.