

HYDROGENATION OF GRAPHENE
ON IRIDIUM(111) BY
VIBRATIONALLY EXCITED
MOLECULES



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Abstract

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1

Introduction

It's not rocket science.



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

2

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 \AA . 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:

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

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 iridium perfectly out of phase. Below, figure 2.1 shows the the graphene-iridium moiré unit cell.

2.4. Hydrogenation of graphene using atomic deuterium

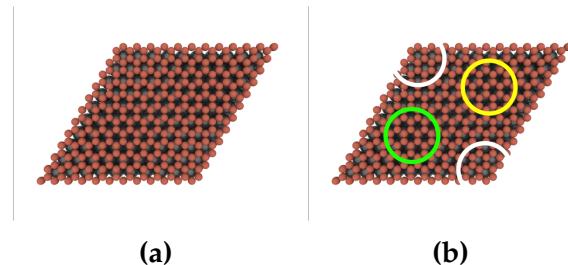


Figure 2.1: Graphical interpretation of the Gr/Ir moire unit cell. [1]

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.

3.4. Raman Spectroscopy

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

4.3. TPD

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 H₂ cracker.

4.2 STM

write things about linescans, calibration and FFT/noise removal.

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 'MASSsoft' 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 desorbed from the sample.

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

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

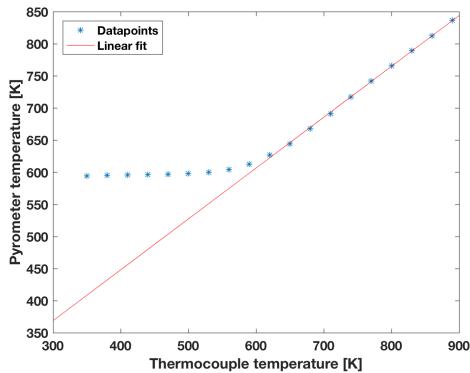


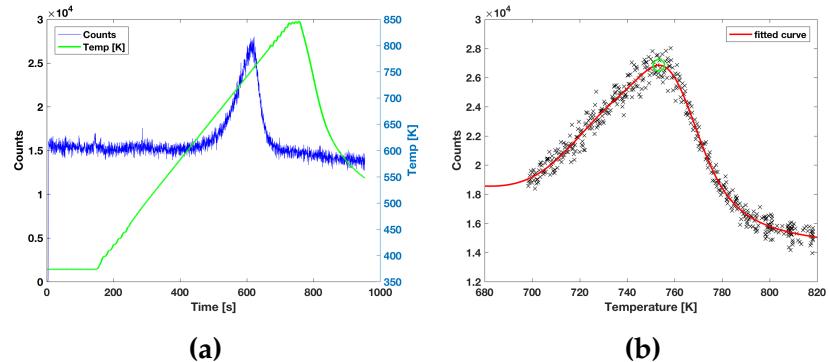
Figure 4.1: Calibration of the temperature during the TPD measurements. The temperature of the surface measured by an optical pyrometer is plotted against the thermocouple temperature.

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 $\pm 60^\circ\text{C}$ 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.

4.3. TPD



5

Results

In the following sections, the data from the dose of vibrationally excited molecules are presented. It was desireable to determine the threshold temperature of the hydrogenation of graphene, and hence the temperature of the doser was changed in order to shift the distribution of vibrationally excited states. Therefore the data includes dosages at temperatures of, 1343°C, 1543°C and 1745°C. A dose at 1300°C were performed as well, however the STM broke, and no pictures are therefore included.

5.1 Graphene on Ir

The quality of the graphene was checked each time D₂ 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

5.2. D2 on graphene

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 $25.2 \pm 0.4\text{\AA}$ according to the litterature. [4] This agrees with the measured length of 25.24\AA 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.

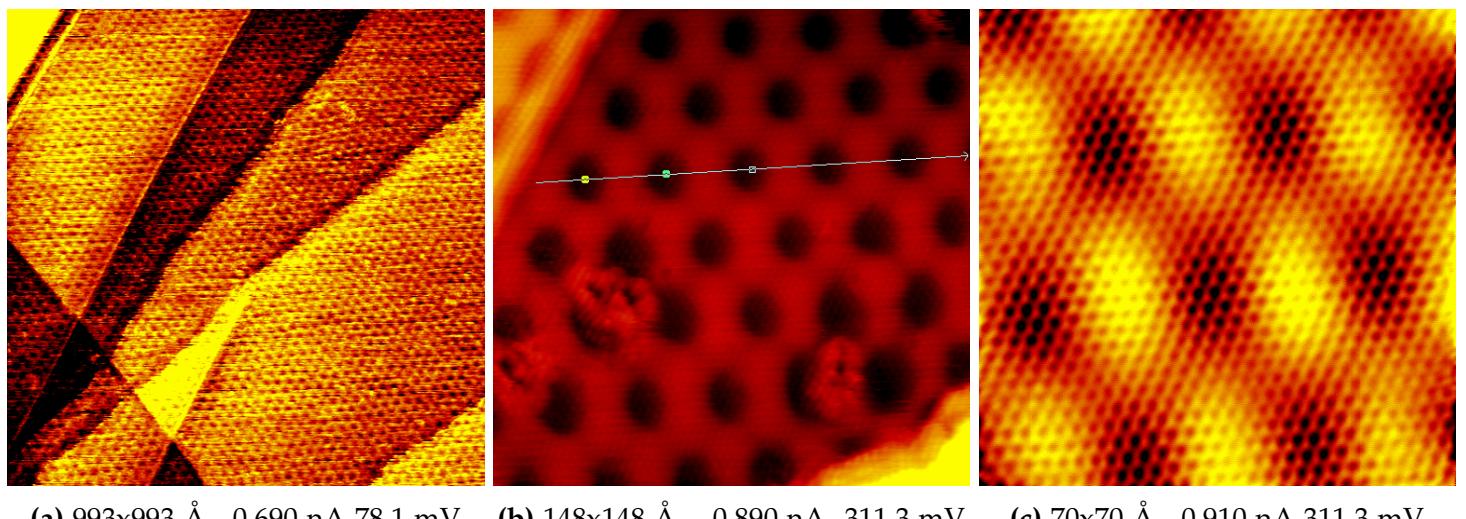


Figure 5.1

5.2 D2 on graphene

5.2.1 Full hydrogen coverage

In order to compare the results from dosing molecular hydrogen STM pictures were taken of a fully hydrogenated surface. On figure 5.2 images of different scales can be seen. The surface was hydrogenated by filling the chamber with hydrogen at a pressure of $1.02 \cdot 10^{-5}\text{mbar}$ and leaving the ion gauge on for 12 hours. As seen on figure 5.2a the sample is not just locally hydrogenated. A line scan was performed on the sample in order to check the periodicity of the hydrogenation. The line scan is seen on figure 5.2c and the distance between the two points is measured to 24.2\AA . This value is very close to the periodicity of the moiré unit cell, which is expected.

As seen on figure 5.2b, the most common pattern, of the hydrogenated surface, is ring shaped structures with a bright rim and a darker center. By comparing figure 5.2b with figure 5.1b it is obvious that the adsorption of hydrogen on the surface changes the LDOS. It is noticeable that the defects on figure 5.1b looks like the ring shaped structures seen on figure 5.2, and hence these defect might be the caused by adsorbed hydrogen. Furthermore some areas of the saturated surface seem to melt together in a bigger structure, seen as the bone- and three point star shaped structures on figure 5.2b.

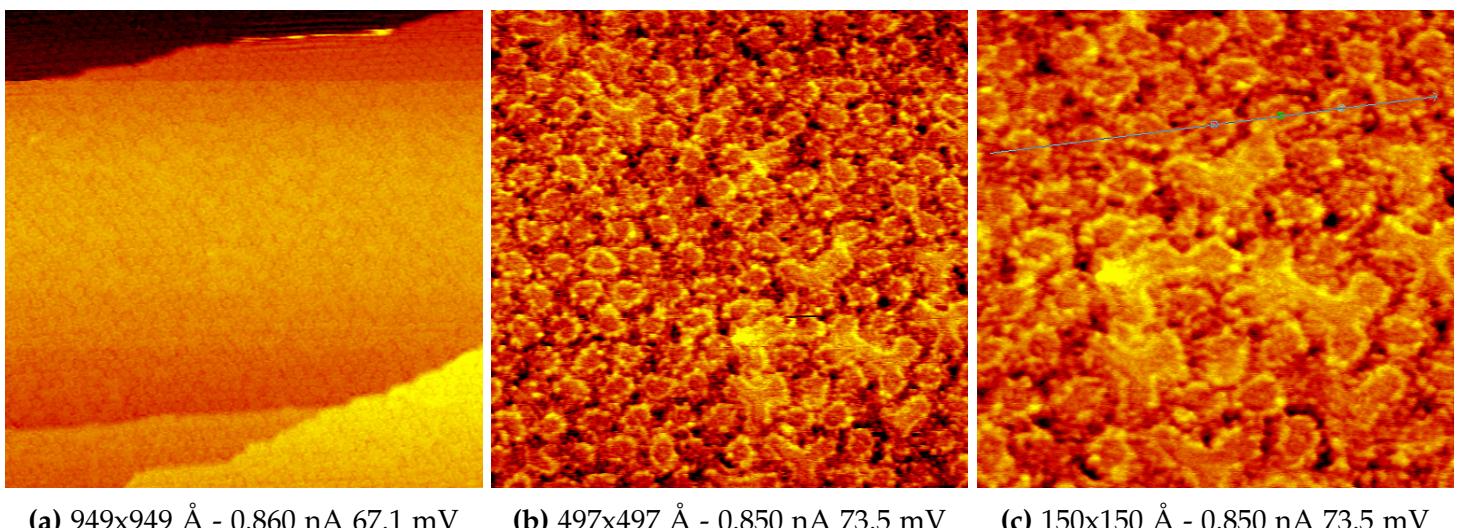


Figure 5.2: Fully hydrogenated Gr/Ir surface.

5.2.2 1745°C dose

This dose happened at a pirani pressure of $6.8 \cdot 10^{-2}$ mbar, and with the doser at a temperature of 1745°C. The dosage time was 20 min. The graphene was checked before the dose in order to ensure that no abnormal amount of defects was present. Three images at different scales are shown in figure 5.3. These pictures were taken right after the dose had ended, and the pressure dropped sufficiently. As seen on figure 5.3a, the surface is far from saturated, compared to figure 5.2a. It is also worth noting that none of the hydrogenated sites melt together to form bigger structures, which indicates that this phenomenon happens after the surface has been saturated.

Individual hydrogen atoms are not distinguishable from the STM images, and therefore the coverage is estimated as a percentage of

5.2. D2 on graphene

the number of hydrogenated sites, compared to the total number of unit cells. Figures 5.3b and 5.3c were used to calculate an estimate of the saturation of the surface. The coverage on figure 5.3b was calculated to 41% and the coverage on figure 5.3c was calculated to 29%. This means that about one third of the surface is covered with hydrogen after a dosage of excited molecules for 20 min, at a chamber pressure of $5 \cdot 10^{-5}$ mbar.

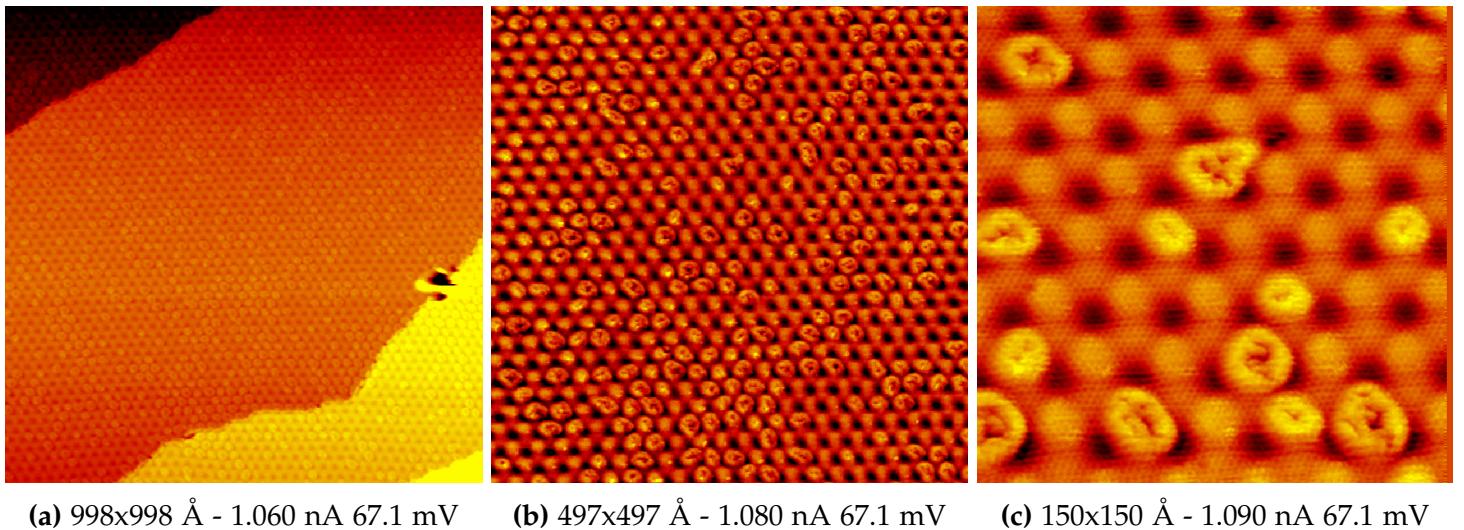


Figure 5.3: Hydrogenated Gr/Ir surface after dose of H₂ at a doser temperature of 1745°C.

5.2.3 1593°C dose

This dose happened at a pirani pressure of $6.8 \cdot 10^{-2}$ mbar and a doser temperature of 1593°C. Again the dose had a duration of 20 min. The pictures from this dose are shown in figure 5.4. The resemblance between the pictures shown in figure 5.3 and 5.4 is quite high. Again the ring shaped structures are seen, and the shape of these are very similar to the ones observed earlier. Figures 5.4a and 5.4b were used to calculate the coverage of hydrogenation, with values of 32% and 25% respectively. These values are however very position dependant, and therefore they do not necessarily reflect the accurate coverage. It is however pretty obvious that some hydrogen has adsorbed to the surface.

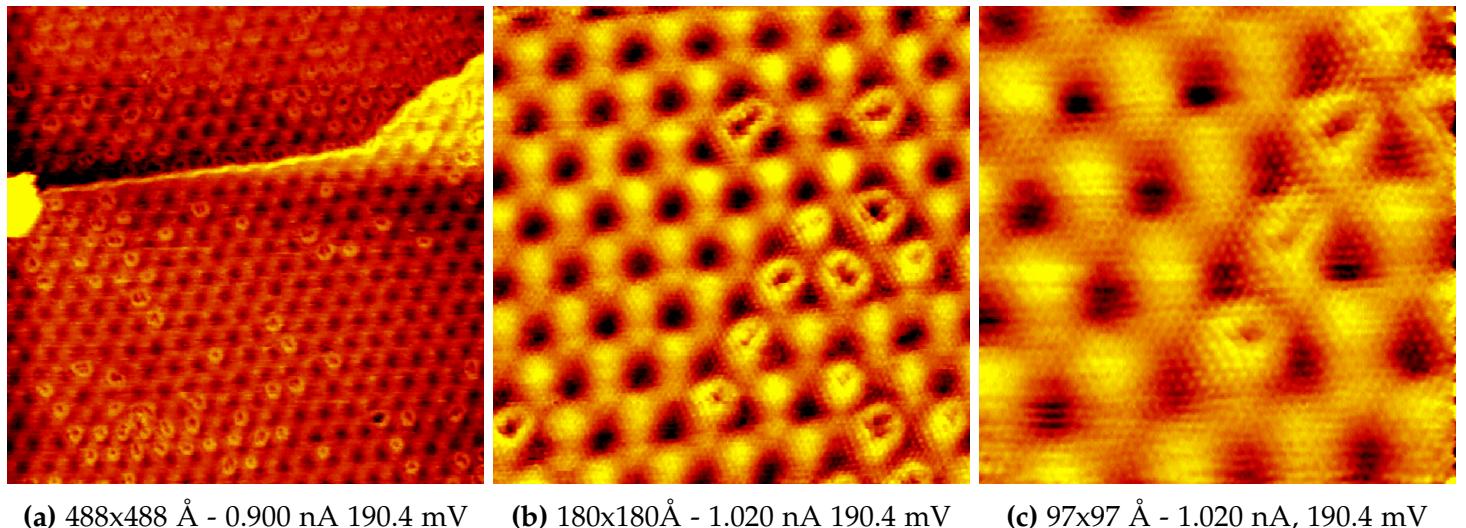


Figure 5.4: Hydrogenated Gr/Ir surface after dose of H₂ at a doser temperature of 1593°C.

5.2.4 1343°C dose

The pirani pressure was measured to $6.8 \cdot 10^{-2}$ mbar, and the doser had a temperature of 1343°C. Hydrogen was dosed for 20 min as earlier. As seen on figure 5.8 several high quality pictures of the sample was taken. On figure 5.8a it would seem like some hydrogen is adsorbed due to the several ring shaped structures. As a smaller image is taken such as the one in figure 5.8b the defects looks somewhat different from those seen earlier on figures 5.4b and 5.3c. The ring shaped structures are much smaller in diameter on figure 5.8b, even though the scanning parameters are close to each other.

A high resolution image is seen on figure 5.8c, where the hexagonal graphene is highly visivble. On this picture it is clear that the graphene is defected, although it is unclear whether this is due to the presence of hydrogen. It is also seen that the shape of the sites in the moiré unit cell looks different than earlier although both pictures are from the same scan session. This is due to a tip effect, where the LDOS of the tip probably has changed, which has a influence on the tunneling current. This feature might happen if the tip picks up an atom from the surface, or if the physical dimensions of the tip changes after a tip treatment.

It should be noted that the graphene had defects before the dose was initiated. The abundance of these defects was indistinguishable, compared between before and after dosage. Therefore it is not possi-

5.3. TPD measurements - Atomic and molecular D2

ble to conclude whether the threshold temperature of the hydrogen adsorption from excited molecules lies at 1340°C. It is however very likely that no hydrogen is adsorbed. In order to investigate the threshold temperature further, it would be rational to conduct TPD measurements of the sample after hydrogen dosage at 1343 °C.

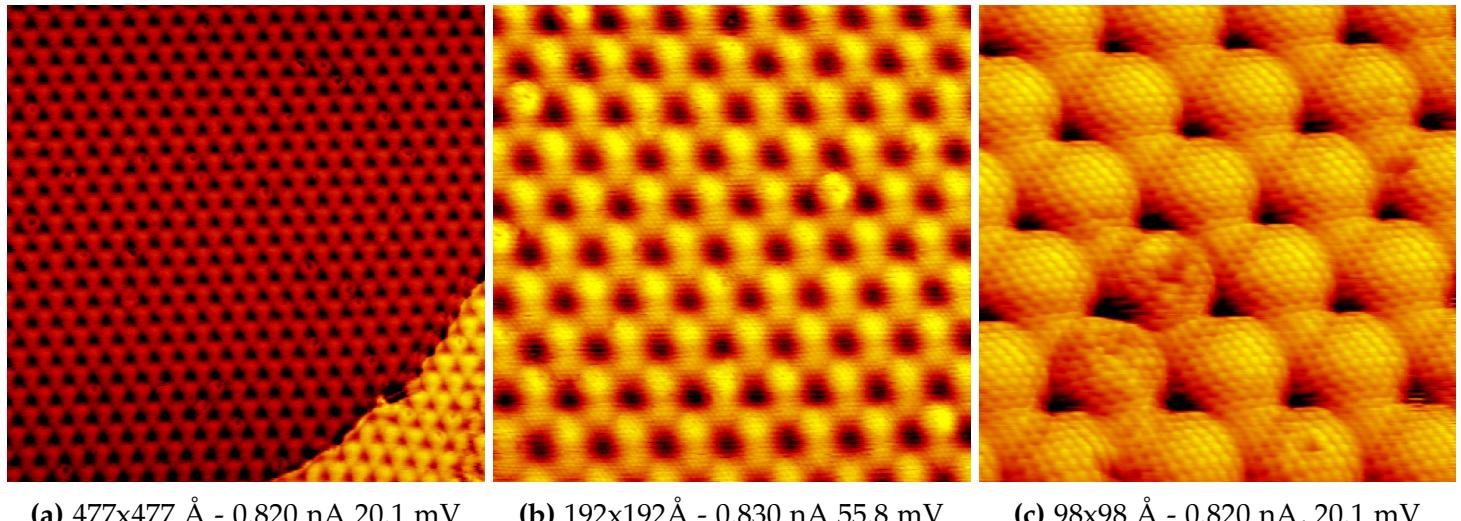


Figure 5.5: Hydrogenated Gr/Ir surface after dose of H₂ at a doser temperature of 1340°C.

5.3 TPD measurements - Atomic and molecular D2

In figure 5.6 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 5.6a shows the data acquired for the D2 dose and figure 5.6b shows the data for the dose with hot atoms. After dosage of excited molecules a single peak is observed. On figure 5.6a this peak is seen from two different datasets. It is worth noting that the peaks are shifted regarding to each other. The reason for this might be the fact that the sample was had different thermocouples, which has a big influence on the measured temperature. For the second dataset, corresponding to the blue graph, a quite big peak is seen after the main peak, at a temperature of about 800K. This is due to a temperature spike caused by the Eurotherm temperature controller. As shown in figure 4.2a it is shown that a linear ramp of the temperature is desired. However the

5.3. TPD measurements - Atomic and molecular D2

Sample #	Gr/Ir-#1	Gr/Ir-#2	Gr/Ir-#3	Gr/Ir-#4	Gr/Ir-#5	Gr/Ir-#6	mean
Peak T [K]	724.8	698.4	694.0	709.1	739.1	753.4	719.8

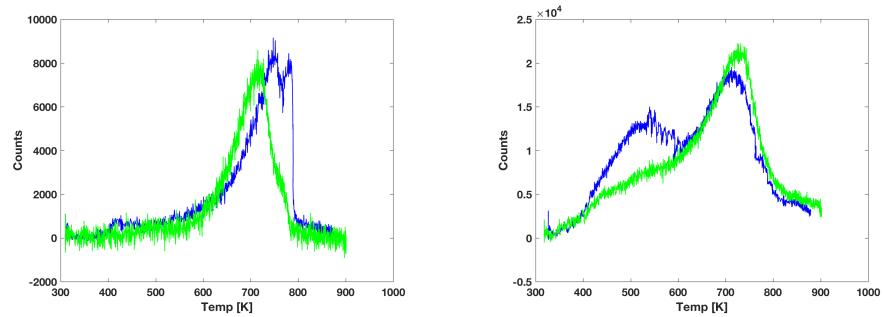
calibration of the Eurotherm during this experiment was poor, which results in noticeable fluctuations in the desorption of hydrogen. This implies that either the thermocouple adapts at a poor rate or that the desorption of hydrogen is sensitive to large changes in temperature. This phenomenon is also observed on figure 5.6b, on the blue graph. This dataset was gathered during the same chamber and sample conditions as the blue graph in figure 5.6a. Therefore the calibration of the Eurotherm was poor as well, which is seen after the small peak at about 500K in figure 5.6b. Here several small bumps are seen due to the non-constant change in temperature.

The temperature at the peak was found by the procedure described in chapter 4. The single peak in figure 5.6a must correspond to the hydrogen adsorbed on the HCP and FCC sites in the moiré unit cell. This statement is supported by the preceding STM pictures that show no sign of hydrogen dimers in the ATOP sites. The temperature of this peak was found for 6 datasets in all, and the values of these are shown in the table below, along with the mean value.

Another peak appears when observing the Gr/Ir sample after it has been dosed with hot atoms as seen on figure 5.6b. The green graph was initially observed, and from this it is obvious that more hydrogen desorbs from the surface at lower temperature, compared to the green graph on figure 5.6a. After a second try however, an actual peak was observed. The temperature of this peak was found by the same procedures as earlier, and the value was found to be 550.4K. This suggests that a different type of Gr-H bond is present. The most plausible explanation is the presence of hydrogen dimers on the ATOP site of the moiré unit cell. The fact that no hydrogen adsorbs as dimers, when excited molecules are dosed, is supported heavily by the fact that this peak around 550K is completely absent from all the data obtained from the molecular dosage seen in figures 5.6a and 5.7.

As a further study of the adsorption of hydrogen on Gr/Ir, bilayers were grown on the sample by annealing in ethylene for a long period of time. STM pictures of these bilayers are shown in the following section. TPD measurements were however conducted on the sample

5.3. TPD measurements - Atomic and molecular D2



(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 5.6

before and after the long anneal. vibrationally excited hydrogen molecules were dosed for an hour in order to saturate the surface. On figure 5.7 the red graph corresponds to the sample before the long anneal and the green graph corresponds to the sample after bilayers supposedly were grown. The background count of hydrogen was subtracted from both datasets and the same calibration is used to correct the temperature. It is seen that bilayers reduce the amount of hydrogen on the surface by a significant amount. This suggests that hydrogen is not adsorbed on the bilayered graphene. This theory is supported by the STM pictures below.

It should be noted that only two datasets were gathered from this experiment. The peak intensity from the TPD measurements tends to vary slightly and hence the amount of bilayers grown on the sample might not be perfectly related to the drop in peak intensity.

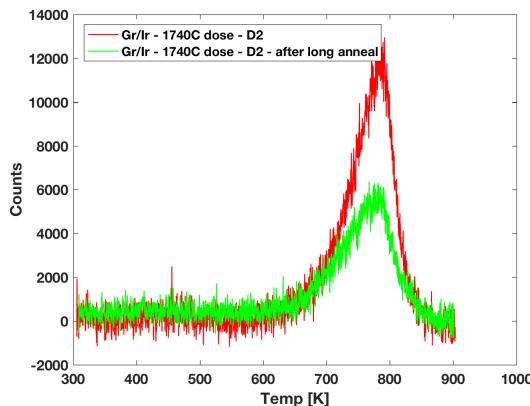


Figure 5.7

5.4 Bilayered graphene on Ir

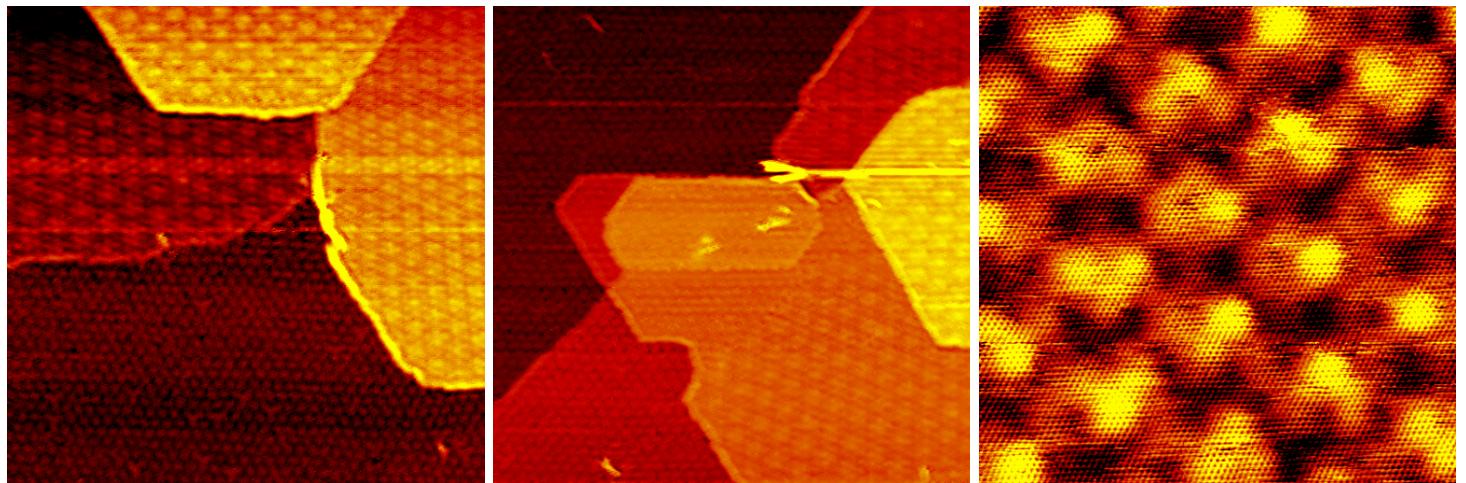


Figure 5.8: Patches of bilayered graphene on Ir after a long hydrogen dosage.

5.5 LEED of bilayered sample

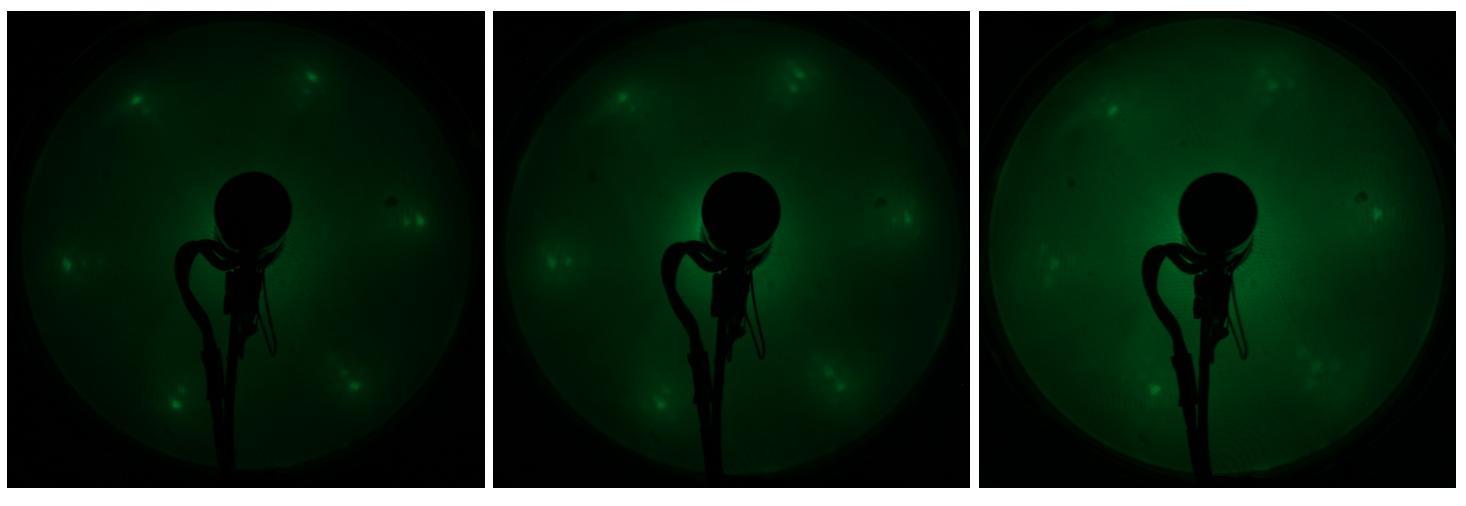


Figure 5.9

6

Conclusion and future perspectives

6.1 conclusion and future perspectives

A

Additional figures

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