

Grade: 1,3

Protocol for the experiment

**2D materials –**

**Preparation and optical characterization**

November 30, 2021

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# 1 Introduction

The detection and research of 2D materials has led to astonishing findings in recent years. Researchers discovered that the single-layer lattices have special physiochemical properties due to the precise arrangement of the atoms and their unique electronic structure. Furthermore, it was found that the electronic and optical properties of the materials can be influenced by introducing functionalisation in the form of molecules on the surface. For this reason, 2D materials are considered to play an important role in the future development of electronic devices such as catalytically active metal complexes, light-gathering antennas and molecular photo switches, and it is even assumed that the materials will replace silicon in electronic devices [1].

In this experiment, the optical properties of the 2D materials graphene and MoS<sub>2</sub> were investigated and monolayers of the two materials were determined. For this purpose, both materials were first prepared with the scotch-tape method in order to subsequently detect possible monolayers under an optical microscope. Recorded images of these are used to analyse their contrast at reflection and transmittance and thus determine the number of layers of a given flake, taking literature values into account [2].

## 2 Technical background

### 2.1 2D materials

#### 2.1.1 Graphene

The material graphene, discovered in 2004, is a monatomic layer of graphite in which the carbon atoms are arranged in a honeycomb lattice. Normally, the two-dimensional graphene layers, which are bound to each other with von van-der-Waals forces, are present in a bulk graphite. Using the scotch-tape method, the researchers succeeded in creating individual graphene layers by removing them individually from the bulk with the help of an adhesive tape [2]. Graphene is of great interest because of its special thermal, electronic and optical properties due to the hexagonal arrangement, the  $\pi$ -electrons present in the structure and the high crystal quality of the lattice. The free charge carriers in the lattice are the reason for the very high thermal conductivity and charge carrier mobility. In addition to these properties, the material is characterised by its high strength and ductility

[3] [4]. It is assumed that currently graphene is the material with the highest thermal and electrical conductivity and the greatest strength [5].

### **2.1.2 MoS<sub>2</sub>**

MoS<sub>2</sub> (molybdenum disulphide) is a transition metal dichalcogenide. The monolayers of this group are characterized by their multilayer structure consisting of a transition metal and a chalcogen atom [2]. MoS<sub>2</sub> is ordered in a three-layer prismatic structure and is composed of a molybdenum atom surrounded by two sulphur atoms in a hexagonal lattice. Due to the multilayer structure, MoS<sub>2</sub> is a semiconductor and also has catalytic properties [6] [7].

## **2.2 Optical microscopy**

The basic setup of a light microscope consists of a light source and two lenses, one in the objective and one in the eyepiece. The sample to be analysed is placed between the light source and the objective. When light rays pass through the sample and reach the lens in the objective, they are refracted. This creates a magnified image of the sample. The light rays are then refracted again by the lens in the eyepiece and focused in the intermediate image plane [8].

The resolution of a light microscope, which is the smallest distance at which two image points can be distinguished, depends on three factors. It is proportional to the wavelength of the light used and inversely proportional to the aperture angle of the objective and to the refractive index of the medium between the sample and the objective. Since the visible wavelength range of a human being is 400 to 700 nm, the resolution is thus limited [9].

## **3 Execution**

### **3.1 Sample preparation**

For the experiment, the two 2D materials graphene and MoS<sub>2</sub> were prepared in the same way by using mechanical exfoliation. In doing this, a bulk crystal of the material was placed on an adhesive tab and the tape was folded and opened several times to form small crystals. If there were enough small crystals, these were then applied to a wafer cleaned with isopropanol. The wafer has two layers: a Si (silicon) and a 90 nm thick SiO<sub>2</sub> (silicon dioxide) layer [2]. For easier application to the wafer, the hotplate could alternatively be used, whereby the heat resulted in better adhesion of the flakes to the wafer. The wafer was then placed under the microscope to examine the flakes and look for monolayers of the material. The microscope was set in reflection mode, where the

light came from above and reflected light from the sample could be recorded. If a possible monolayer was found during the examination on the basis of the light grey tone, it was examined at objective magnifications 5, 10, 20, 40 and 50 and pictures were taken. For the subsequent investigation of the flake at transmittance, a gold grid was placed on it using a manipulator for the correct placement and isopropanol was added so that adhesive forces occurred between the monolayer and the grid. The wafer with the grid was dried on the hotplate for 10 minutes. After the drying process, KOH was applied to the sample and grid, which dissolved the SiO<sub>2</sub> layer of the wafer and thus removed the grid and sample from the wafer. The grid was then placed in water and isopropanol for 30 seconds each to remove KOH residues, as these can influence the transmission of light by crystallising out. It was examined under the microscope in transmittance mode, in which the light is radiated from below. Here, too, different objective magnifications of 5, 10, 20, 40 and 50 were selected and images of the monolayer were taken.

### 3.2 Explanation of theoretical contrast

In order to determine whether a thin flake is a monolayer or a multilayer, its contrast is determined through means of the intensities in the presence and absence of the flake and the result is compared with theoretically calculated contrast values. The contrast of graphene and MoS<sub>2</sub> at reflection depends on the wavelength of the radiated light, as well as the thickness of the sample layer and the SiO<sub>2</sub> layer. These factors are also taken into account when calculating the theoretical contrast values. If they are known, the intensity of the flake can first be calculated according to formula 1:

$$I(n_1) = \left| \frac{r_1 e^{i(\varphi_1 + \varphi_2)} + r_2 e^{-i(\varphi_1 - \varphi_2)} + r_3 e^{-i(\varphi_1 + \varphi_2)} + r_1 r_2 r_3 e^{i(\varphi_1 - \varphi_2)}}{e^{i(\varphi_1 + \varphi_2)} + r_1 r_2 e^{-i(\varphi_1 - \varphi_2)} + r_1 r_3 e^{-i(\varphi_1 + \varphi_2)} + r_2 r_3 e^{i(\varphi_1 - \varphi_2)}} \right|^2 \quad (1)$$

with:

$$r_1 = \frac{n_0 - n_1}{n_0 + n_1}$$

$$r_2 = \frac{n_1 - n_2}{n_1 + n_2}$$

$$r_3 = \frac{n_2 - n_3}{n_2 + n_3}$$

Here  $n_0$  is the refractive index of the air,  $n_1$  the refractive index of the sample and  $n_2, n_3$  are the refractive indices of the  $\text{SiO}_2$  and the Si layer. The phase shift of the different layers  $\varphi_i = 2\pi n_i d_i / \lambda$  can be calculated by means of the wavelength of the illuminated light  $\lambda$ , the respective layer thickness  $d_i$  and the respective refractive index  $n_i$ . Using the calculated intensities of the wafer with flake  $I(n_1)$  and the wafer without flake  $I(n_1 = 1)$ , the contrast is calculated as shown in formula 2.

$$C = \frac{I(n_1 = 1) - I(n_1)}{I(n_1 = 1)} \quad (2)$$

If the calculation is carried out with different wavelengths and different  $\text{SiO}_2$  layer thicknesses, the resulting contrasts of graphene and MoS2 on reflection can be plotted in diagrams (see figure 1 and figure 2) [3] [6]. The theoretical contrast values of the diagrams are used in the determination of monolayers in chapter 5.

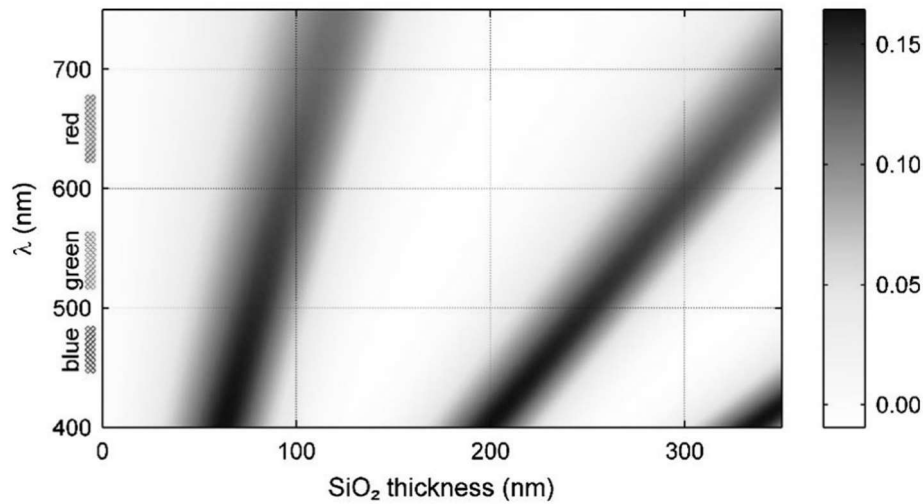


Figure 1: Theoretical contrast of graphene at reflection as a function of the  $\text{SiO}_2$  layer thickness and the wavelength of the radiated light [3]

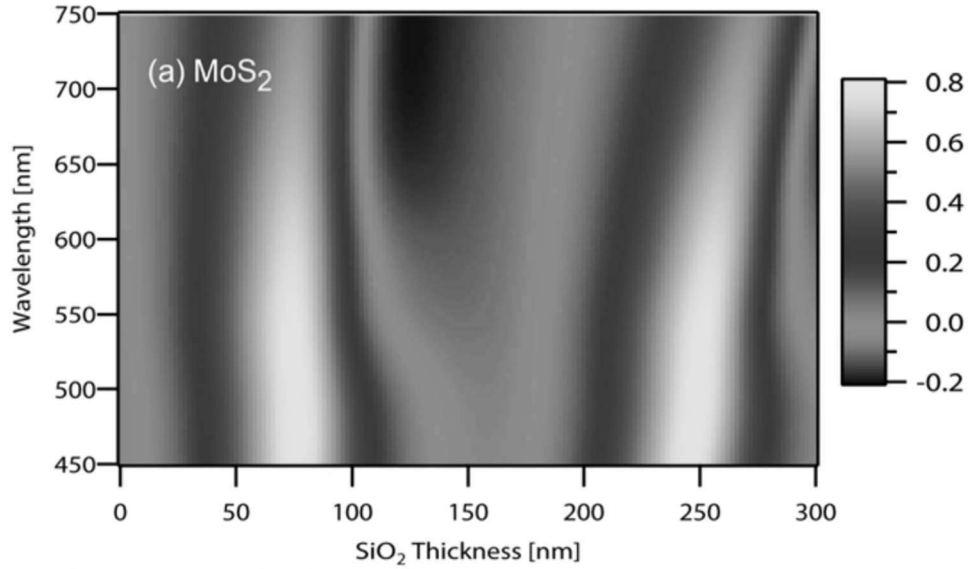


Figure 2: Theoretical contrast of MoS<sub>2</sub> at reflection as a function of the SiO<sub>2</sub> layer thickness and the wavelength of the radiated light [6]

In contradistinction to the contrasts of flakes at reflection, there are other dependencies on the ambient conditions for graphene and MoS<sub>2</sub> at transmission. The contrast of a monolayer of graphene at transmission is constant at 2.3 %, since this is independent of the wavelength of the illuminated light, the temperature and the SiO<sub>2</sub> layer thickness [2].

The contrast of MoS<sub>2</sub> at absorption, on the other hand, is not only dependent on the wavelength and the SiO<sub>2</sub> layer thickness, but also on the ambient temperature (see figure 3) [10].

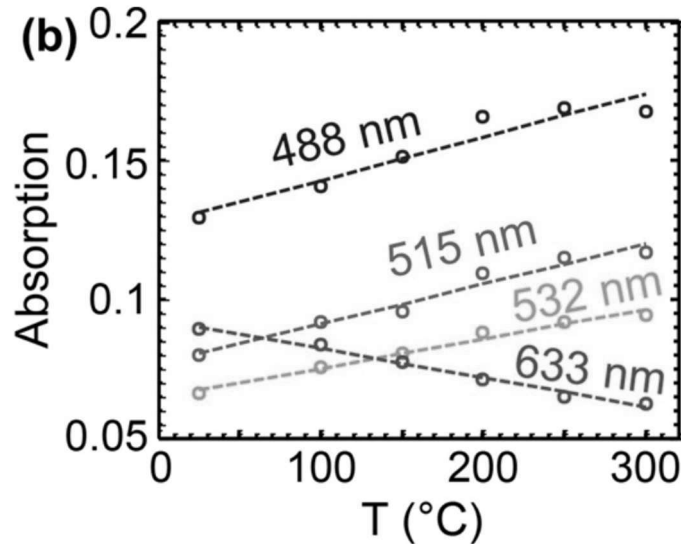


Figure 3: Theoretical contrast of MoS<sub>2</sub> at transmittance as a function of SiO<sub>2</sub> layer thickness, wavelength of radiated light and ambient temperature [10]

## 4 Results

During the experiment, four possible graphene monolayers, as well as one MoS<sub>2</sub> monolayer, were found and images were taken of them. The data sets of two graphene samples and of the MoS<sub>2</sub> flake were evaluated using Fiji [11]. For the evaluation, each image was divided into the red, green and blue parts of the visible light and a "Plot Profile" and histogram were created from the green image, with which the average grey tone of the respective flake and that of the background (Ref.) were determined. In the following, the results of the individual flakes are described in more detail.

Figure 4 shows the thin flake of Graphene sample 1, which was recorded in reflection mode. From the histogram and the "Plot Profile", a mean value of 174 was obtained for the grey tone of the background and a value of 162 for the grey tone of the flake. The contrast was calculated from the values using formula 2, which was 6.9 %.

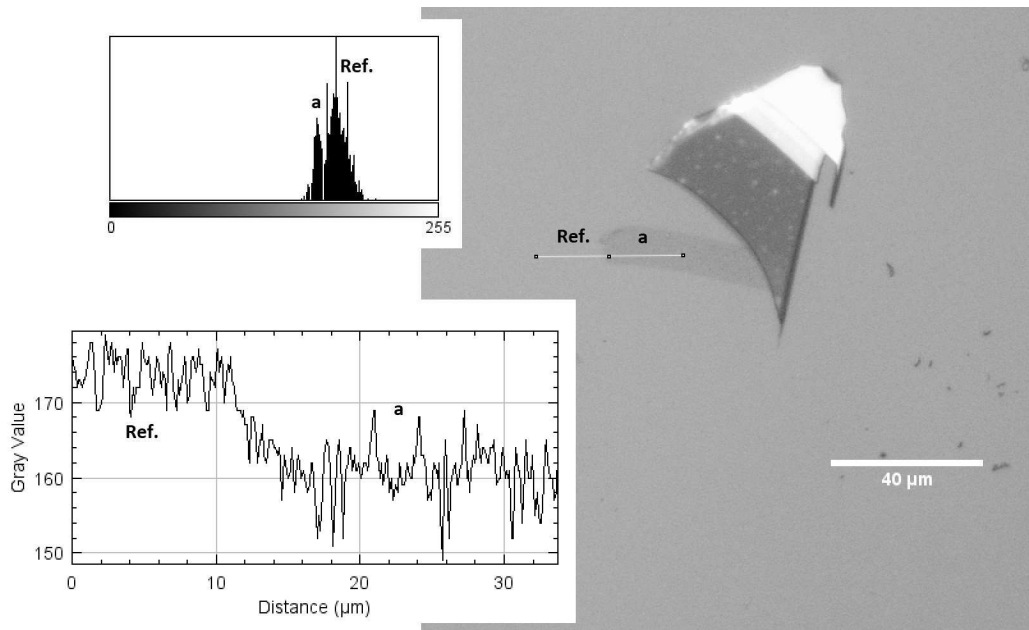


Figure 4: Graphene sample 1 illuminated with green light at reflection and 50x magnification, histogram and plot profiles of the flake shown on the left

No evaluation of the contrast at transmittance was carried out from this flake, as the flake was damaged in the course of the experiment and therefore no evaluable transmittance image could be recorded.

The second thin graphene flake found is shown in figure 5. This was taken in the reflection mode of the microscope. It can be seen that there are two thin layers of graphene, the contrast of each of

which was evaluated individually. From the "Plot Profile", the mean grey value of 162 was determined for the thinner layer, as well as the grey value of 154 for the thicker graphene layer. It was difficult to read the individual values from the histogram, as only a Gaussian curve was recognisable, which only had one peak. The average grey value of the background was 174. According to formula 2, a contrast of 6.9 % was calculated from the grey values for the thinner layer and 11.49 % for the thicker layer.

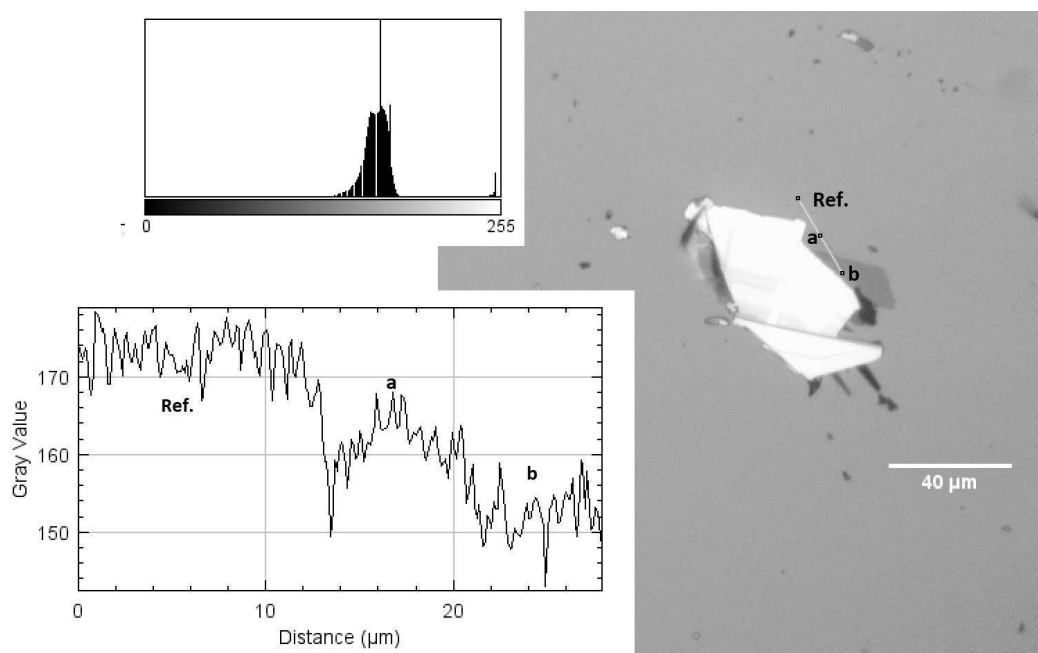


Figure 5: Graphene sample 2 illuminated with green light at reflection and 50x magnification, histogram and plot profiles of the flake shown on the left

The contrast of images taken in transmittance mode was also determined for Graphene sample 2 (see figure 6). Since the histogram only showed a Gaussian curve in which no different significant peaks could be seen, the "Plot Profile" was again used to read the values. In this case, a mean grey value of 195 was determined for the thin layer of graphs and a grey value of 188 for the thicker graphene layer. The reference value of the background was about 200. This resulted in a contrast of the absorption of 2.5 % for the thin and 6 % for the thicker graphene layer.

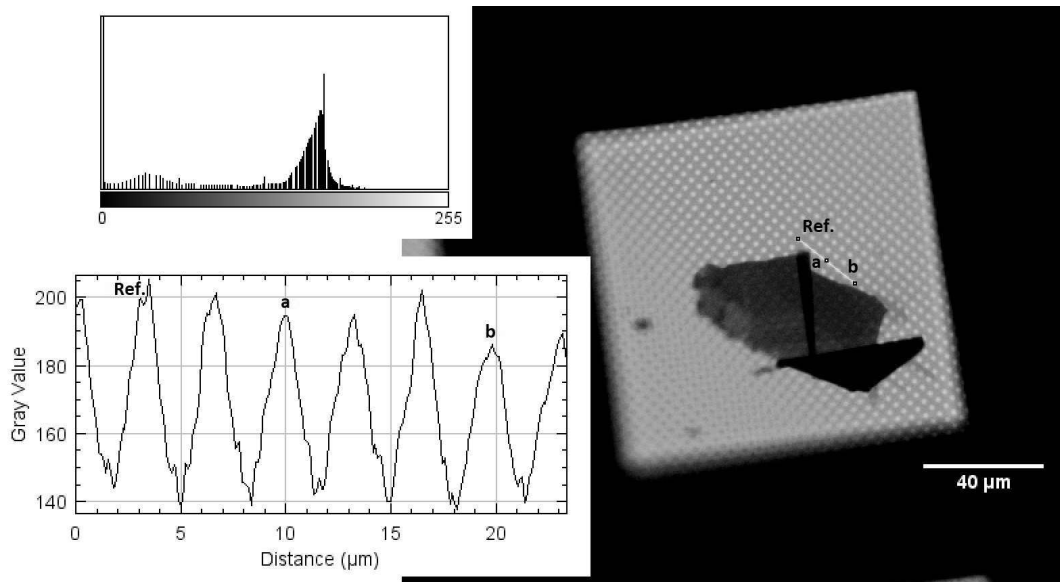


Figure 6: Graphene sample 2 illuminated with green light at transmittance and 50x magnification, histogram and plot profiles of the flake shown on the left

Figure 7 shows the image of the flake of MoS<sub>2</sub> in reflection mode of the microscope. From the histogram and "Plot Profile", a mean grey value of 123 could be determined for the flake, as well as a value of 152 for the background. According to formula 2, this resulted in a contrast of 23.58 %.

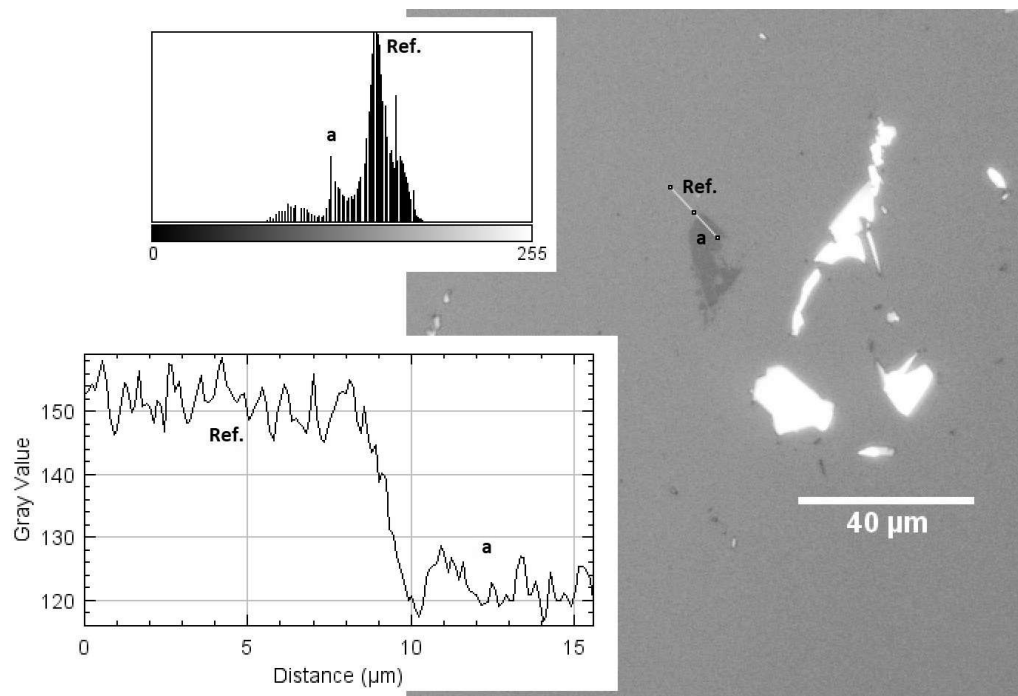


Figure 7: MO<sub>2</sub> sample illuminated with green light at reflection and 50x magnification, histogram and plot profiles of the flake shown on the left

The MoS<sub>2</sub> flake was also examined in transmittance mode of the microscope and the absorption values were analysed (Figure 8). There were difficulties in identifying the flake in the lattice during the microscope examinations, so a picture was finally taken of a flake that was assumed to be the MoS<sub>2</sub> flake based on the grey tone. However, unlike the flake recorded in reflection mode, it had a different shape and two layers of different thickness. A mean grey value of 170 was determined for the thinner of the two layers, and a grey value of 158 for the thicker one. The grey value of the background was 190, giving a transmission contrast of 10.53 % for the thinner layer and 16.84 % for the thicker layer.

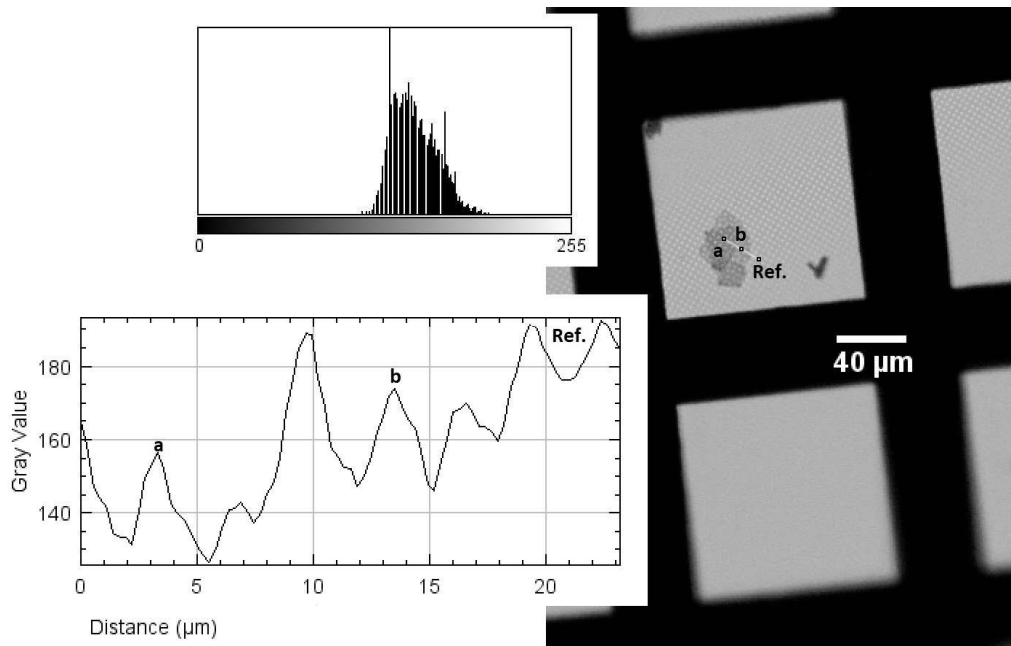


Figure 8: MoS<sub>2</sub> sample illuminated with green light at transmission and 50x magnification, histogram and plot profiles of the flake shown on the left

## 5 Discussion

The calculated contrast values of the different flakes at transmission and reflection from chapter 4 were compared with the literature values from chapter 3 to determine the layer thickness of the individual flakes. It is assumed that the SiO<sub>2</sub> layer has a thickness of 90 nm, the wavelength range is in the green range of 500 -600 nm and that the images were taken at a room temperature of about 20 °C.

The values of the contrast at reflection of the first graphene flake, as well as the thinner layer of the second graphene flake, corresponded to about 6.9 %. This is approximately in agreement with

the literature value of 6 % -12 % from the diagram of contrast values of graphene at reflection, which suggests that the flakes in question are a monolayer of graphene. The thicker layer of the flake of graphene sample 2 showed a contrast of 11.49 %, which is approximately twice as high, so that it is probably a bilayer of graphene.

The contrasts of 2.5 % for the thinner and 6 % for the thicker layer of graphene sample 2 in transmission mode confirm the assumption that the former is a monolayer and the latter a bilayer, since the theoretical value for a monolayer is 2.3 % and thus the contrast of the thinner layer corresponds to that of a monolayer, that of the thicker layer to twice that.

In the case of the MoS<sub>2</sub> flake, the thickness of the layer cannot be determined precisely from the contrast at reflection, as the diagram of literature values shows strong fluctuations in the contrast values for a monolayer in the range of green light and a SiO<sub>2</sub> layer of 90 nm. The literature values range from about 30 % to 60 %. The contrast of the flake is 23.58 %, which is lower than the literature value, indicating that it is not MoS<sub>2</sub>. However, since the SiO<sub>2</sub> layer of the wafer is unevenly thick, this inaccuracy can be the cause of the low contrast value. The flake may be a monolayer, as the literature values are only 10 % - 40 % for a SiO<sub>2</sub> layer thickness of 95 nm – 100 nm. The MoS<sub>2</sub> flake recorded in transmission has two-layer thicknesses, whereby the thinner layer with a contrast of 10.53 % and the thicker layer of 16.84 % is above the literature values for a monolayer of about 6 %. It is possible that the thinner layer is a bilayer, as the contrast value is about twice the theoretical value, and the thicker layer is a trilayer, as the contrast is about three times higher. This is in contradistinction to the fact that on reflection the flake had the contrast of a monolayer. Since the shape of the flake found in transmission mode is also very different from that of the flake in reflection mode, there is a suspicion that it is an impurity.

The inaccuracies in the determination of the layer thicknesses of the individual flakes are due to errors that happened during the execution and evaluation. During the evaluation, errors in the creation and reading of the histograms and the "Plot Profiles" led to inaccuracies. On one hand, an area of the image to be examined was defined manually for their creation, which possibly resulted in areas being included in the diagrams that did not correctly reflect the intensity values of the flake or the background. On the other hand, the values in the histogram and "Plot Profiles" were subject to a high degree of scattering, which meant that they were only read approximately.

The same applies to the diagram with the theoretical literature values, as there was a wide range of contrast values in the broad wavelength range of green light. Another error is that the values were rounded when calculating the contrast, which resulted in rounding errors. In addition to the errors in the calculation and evaluation, inaccuracies also occurred during the experiment. It was

found that the incidence of light from the microscope was not homogeneous, resulting in poorly illuminated areas of the specimen, which ultimately falsified the grey values of the flakes and the background. Another source of error was that the  $\text{SiO}_2$  layer of the wafer was not uniformly 90 nm everywhere, which led to a change in the intensity of different areas and thus to a change in contrast. Especially with the  $\text{MoS}_2$  flake, this can lead to inaccuracies in the determination of the layer thickness, as the literature values vary greatly with the smallest changes in the layer thickness. Finally, it should be mentioned that, as the work was not carried out in a clean room, impurities were present on the sample and these can influence the contrast of the background or the flake or were even mistaken for a thin flake.

## 6 Conclusion

In summary, it can be said that the experiment was carried out successfully and a statement about the thickness of the different flakes could be made by means of the evaluation. The two possible monolayers of graphene found were confirmed as such during the evaluation, whereby a bilayer was also found next to the monolayer in the second sample. The  $\text{MoS}_2$  flake could also be a monolayer due to the low contrast, although this could not be clearly confirmed due to inaccuracies and the fluctuating values of the diagram with the literature values.

In order to be able to make more precise statements about the contrast and the layer thicknesses of the flakes, a microscope with a homogeneous incidence of light would be advantageous, so that all areas would be evenly illuminated. Homogeneous illumination and a uniform  $\text{SiO}_2$  layer on the wafer would result in a more accurate result of the grey values of the flakes and ultimately a more correct calculation of the contrast. It would also make sense to work with monochromatic light, so that when determining the layer thickness, the wavelength range would be limited and thus the reading of the literature values could take place in a more restricted range. A measurement of the room temperature would in turn make it easier to read the literature values of  $\text{MoS}_2$  at transmittance, as this was only roughly estimated at 20 °C during the evaluation and is not a precisely measured value. Finally, it would be optimal to work in a clean room so that dirt particles on the sample, which can influence the contrast, are avoided. With these changes, the measurements could be made reproducible and more precise statements about layer thickness and contrast could be made.

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