

2D Materials

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I hereby declare that my elaboration was made independently and is not a copy (even partially) of an existing protocol.
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1 Introduction

The aim of this experiment was to prepare graphene and molybdenum disulfide (MoS_2) mono- and few-layer structures by the famous scotch tape method. The obtained structures were analysed and evaluated by using an optical microscope. By additionally applying the image software FIJI it was possible to characterize the observed structures by their interference contrast and optical absorption.

1.1 2D Materials

2D materials are characterized by their thickness of a single unit cell or even a single atomic layer that is built up by a periodically ordered arrangement of atoms [1]. Due to their specific crystal lattice structures, these materials have electrical properties that vary from insulating [2] to superconducting behaviour [3], dependent on the specific material.

1.1.1 Graphene

Several 2D materials are known, however the most popular one is graphene. It was first observed practically in 2004, and it therefore represents the initial existing 2D material [4]. Graphene consists of an atomic layer of carbon atoms that are bound in hexagonal lattice structures [4]. The distance between the atoms in the lattice is $1.42 \text{ \AA}$ [4]. Due to its 2D crystal lattice structure, the material provides huge potential for several applications [5]. Its high crystal quality leads to extraordinary electrical and optical properties, for example low electrical resistance [1] that might be used e.g. in transistors [4]. The structure of graphene makes it an extremely hard but also stretchable material, that is additionally able to carry a high electrical current density [6].

1.1.2 Molybdenum disulfide

Other famous 2D materials are transition metal-dichalcogenides with the common formula MX_2 [6]. However, monolayers of this group of 2D materials consist of actually three layers of atoms that build one unit together [3]. The layer in the middle (consisting of transition metal atoms) is sandwiched between a layer of X atoms (consisting of chalcogen atoms) on each side [3]. Belonging to this group, MoS_2 has other electrical properties than graphene as MoS_2 is semiconducting [3].

1.1.3 Preparation of 2D Materials

Generally, 2D materials are prepared by the technique of mechanical exfoliation using adhesive tape [5]. This technique was used when preparing the first monolayer of graphene in 2004 and is used as the most effective method until today [4]. By using this technique, weak van der Waals forces, that hold the layers of the bulk structure together, are broken up due to adhesion [1]. This leads to splitting off more and more layers when being applied repetitively [1]. The micromechanical cleavage out of small pieces of the origin material leads to a potential generation [1] of microscopic flakes of the desired material that, at the best, include mono- and few-layer structures [3]. These flakes can easily be placed on a silicon oxide/silicon substrate (Si wafer) to enable further investigation and characterization of the structures with an optical microscope [3].

1.2 Optical Microscopy

Optical microscopy enables to visualize the amount of single layers of thin flakes that were prepared by mechanical exfoliation before, and thus can be used for differentiating between mono- and several few-layer structures that were put on a Si wafer [1]. This is necessary because by using mechanical exfoliation, several flakes with multiple layers that vary in their

thickness were produced and have to be characterized [1]. The discrimination of the different layers by their thickness is made by measuring the relative contrast between the Si wafer and the respective layer structure.

1.2.1 Contrast Measurement

The contrast measurement is based on the refractive index n that is material dependent and therefore varies for different media [1]. At an interface between two media with different refractive indices, light can be reflected in a certain way due to light refraction, depending on the refractive index. Incident light comes from the air ($n_0=1$) onto a trilayer structure that consists of the monolayer of the specimen (e.g. graphene), the SiO_2 and the Si layer [1]. The SiO_2 and the Si layer both have a certain known thickness (d_2 and d_3) and their refractive indices n_2 and n_3 are dependent on the wavelength λ of the light [1]. The specimen has the known thickness d_1 and its refractive index n_1 is independent of λ [1]. The reflected light intensity I is caused by the interference of the reflected photons [1]:

$$I(n_1) = \left| (r_1 e^{i(\Phi_1+\Phi_2)} + r_2 e^{-i(\Phi_1-\Phi_2)} + r_3 e^{-i(\Phi_1+\Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1-\Phi_2)}) / (e^{i(\Phi_1+\Phi_2)} + r_1 r_2 e^{-i(\Phi_1-\Phi_2)} + r_1 r_3 e^{-i(\Phi_1+\Phi_2)} + r_2 r_3 e^{i(\Phi_1-\Phi_2)}) \right|^2 \quad (1)$$

The values r_i are the relative indices of refraction and can be written as [1]:

$$r_i = \frac{n_{i-1} - n_i}{n_{i-1} + n_i} \quad (2)$$

The phase shifts Φ_i are caused by direction changes in the optical path [1]:

$$\phi_i = \frac{2\pi n_i d_i}{\lambda} \quad (3)$$

The contrast between the mono- and few-layer structures and the Si wafer, that is taken as background in the measurement, can be calculated by the following equation [1]:

$$C = \frac{I(n=1) - I(n \neq 1)}{I(n=1)} \quad (4)$$

$I(n = 1)$ is the intensity of reflected light in the absence of the respective specimen (thus the background) and $I(n \neq 1)$ in the presence of the respective specimen [1]. In this experiment the light intensities I are measured.

1.2.2 Color Plots

The calculated contrast that is based on measured light intensity values can be compared to a color plot that shows the expected contrast for a monolayer of the respective specimen. So, it can be deduced whether the observed structure is a mono- or few-layer structure, thus if the measured contrast matches with the expected one from the color plot or if the measured contrast is multiple times the expected one and therefore matches with a structure of more than one layer in thickness). The color plots in figure 1 depict the theoretical contrast of graphene and MoS_2 monolayers, depending on the wavelength of the light that is used for analysis, as well as on the thickness of the Si wafer on which the graphene or MoS_2 is attached to. The values in this color plot (figure 1) are calculated theoretically by equation 4 using the calculated light intensities according to equation 1. A calculation of the theoretical contrast can be seen in section 1.2.3 as example. The scale on the right gives the expected value for the contrast of a monolayer of graphene or MoS_2 .

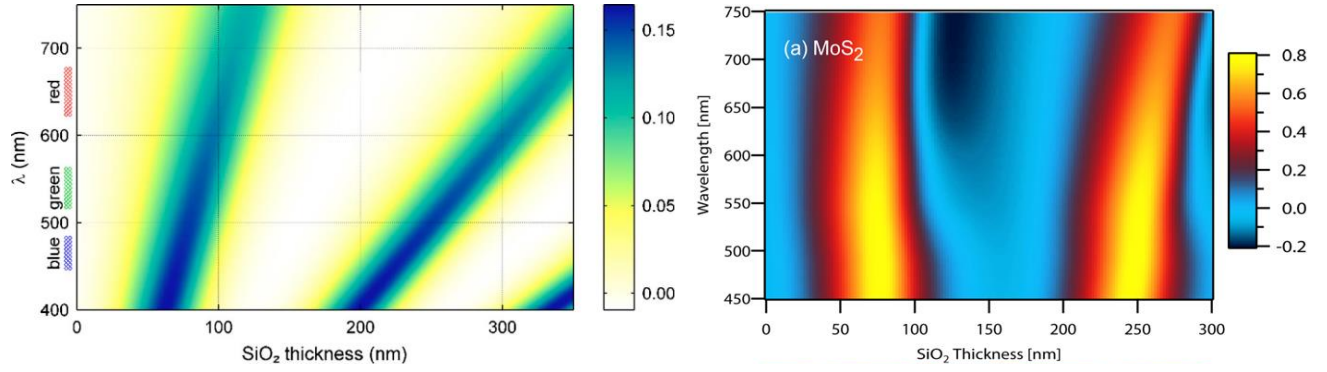


Figure 1: Color plot of the theoretical contrast of graphene (left) and MoS₂ (right) monolayers as a function of wavelength and Si wafer thickness [1, 3]

1.2.3 Example Calculation of Theoretical Contrast for 400 nm of Wavelength

In the following the theoretical contrast for graphene ($d_1 = 0.34$ nm) on a 90 nm Si wafer is calculated when using a wavelength of 400 nm [1]. Further parameters of measurement are given in the following [1].

Equation 1 for $n_1 \neq 1$: $I(n_1) = 0.2761$

With: $n_1 = 2.6 - 1.3i$, $n_2 = 1.47$, $n_3 = 5.6 - 0.4i$

$$r_1 = -0.51 + 0.18i, r_2 = 0.34 - 0.21i, r_3 = -0.59 + 0.02i$$

$$\Phi_1 = 0.01 - 0.01i, \Phi_2 = 2.08$$

Equation 1 for $n_1 = 1$: $I(n_1) = 0.3034$

With: $n_1 = 1$, $n_2 = 1.47$, $n_3 = 5.6 - 0.4i$

$$r_1 = 0, r_2 = -0.19, r_3 = -0.59 + 0.02i$$

$$\Phi_1 = 0, \Phi_2 = 2.08$$

Theoretical contrast according to equation 4:

$$C = \frac{I(n=1) - I(n \neq 1)}{I(n=1)} = \frac{0.3034 - 0.2761}{0.3034} = 0.0899 = 8.9 \%$$

This theoretically calculated contrast of 8.9 % for a graphene monolayer on a Si wafer with 90 nm of thickness can also be seen in the color plot (figure 1, left) for a wavelength of 400 nm.

1.2.4 Absorption Measurement

The absorption (1-T) of mono- and few-layer structures can be measured by the contrast of the transmitted light intensity T of the different structures. The absorption for graphene can be calculated by the following equation [7]:

$$(1 - T) = \frac{\pi e^2}{\hbar c} = \alpha \pi = 2.3 \% \quad (5)$$

with $\alpha \approx 1/137$ as fine structure constant [7].

Due to its specific electronic properties, graphene is known to always absorb 2.3 % of incident white light [7]. The light absorption of graphene is therefore only dependent on the fine structure constant α and not influenced by the wavelength of the transmitted light or other factors [7].

In contrast to graphene, the absorption of free-standing MoS₂ is dependent on the wavelength of the incident light, as well as on the temperature [8]. This dependency is depicted in figure 2.

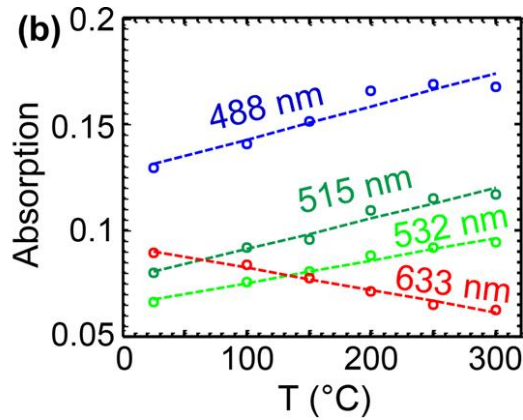


Figure 2: Absorption for different wavelengths of free-standing MoS₂ in dependence of the temperature [8]

Assuming that the free standing MoS₂ is heated up to about 60 °C due to the light of the optical microscope, in this experiment a theoretical value for the absorption of free-standing MoS₂ of 9.0 % is taken, using green light with a wavelength of 515 nm [8].

2 Materials and Methods

Monolayers of graphene were prepared by the common mechanical exfoliation technique. Therefore, an adhesive tape was attached onto graphite, and peeled off afterwards. After that, the side with the thin graphite layer on the tape was stuck to another free area of the tape and peeled off again. This procedure was repeated for another three or four times, to decrease the thickness of graphene. At the end monolayers and few-layers of graphene remained on the tape. Between these steps, the tape was slightly heated up with water vapor. Then, the resulting thin graphene layers were transferred onto the surface of a Si wafer with a thickness of 90 nm by attaching the adhesive tape with graphene onto them. The Si wafer was cleaned with isopropanol and dried with pressurized nitrogen right before.

To increase the attachment of the flake on the Si wafer, the wafer with the flake on it was heated for a few seconds on a heating plate, until some flakes were attached to the wafer and so, the tape could be removed. The Si wafer with the flakes on it was then investigated with an optical microscope for mono- and few-layer graphene by measuring the optical contrast.

In a further evaluation step, the absorption of a free-standing graphene flake of interest was measured. It was therefore transferred onto a TEM grid (Transmission Electron Microscope grid). This “Quantifoil” grid, consisting of a surface with one side of gold and one side of carbon was brought on top of the Si wafer with the graphene layers on it. By using KOH and water the SiO₂ layer dissolved and so, the flake of interest was attached to the grid. The grid with the attached flake of interest was then put for about 20 s into isopropanol for accelerated drying. By using a tweezer, the flake on the grid could then be investigated under the optical microscope with just air as background.

The same preparation steps and experiments were conducted with MoS₂ afterwards.

Images of the flakes were taken by an optical microscope. For the determination of the contrast, the light intensities were measured applying the reflected light method. For the determination of the absorption, the light intensities should be measured using the transmitted light method, however for determining the absorption of graphene, the reflected light method was used accidentally.

All images that were taken during the investigation of the samples with the optical microscope were evaluated with the FIJI software afterwards. For evaluation, the green color channel was used. The respective light intensities, measuring the background and the different layers of the flakes, were determined as gray values. These gray values were taken as light intensities for calculating the contrast and the absorption by equation 4.

3 Results and Discussion

3.1 Contrast Measurement

3.1.1 Contrast of Graphene on Si Wafer

Figure 3 shows a graphene flake on a Si wafer that was prepared by mechanical exfoliation. The image was taken by observing the flake under an optical microscope with the magnification of 50x. The numbers 1, 2a, 2b and 3 show the areas that look different in their contrast when observing the flake under the optical microscope. Area 3 represents the background (the Si wafer), whereas 1, 2a and 2b represent different areas of the graphene flake that vary in their thickness and are therefore further investigated.

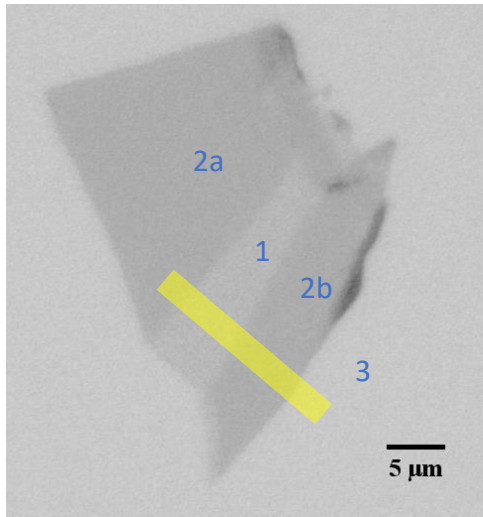


Figure 3: Graphene flake on Si wafer

Along the yellow bar, the profile plot of gray values, that can be seen in figure 4, was registered. The upper left end of the bar represents the distance of 0 μm in the profile plot. The measured gray values are plotted against the distance in μm from the start.

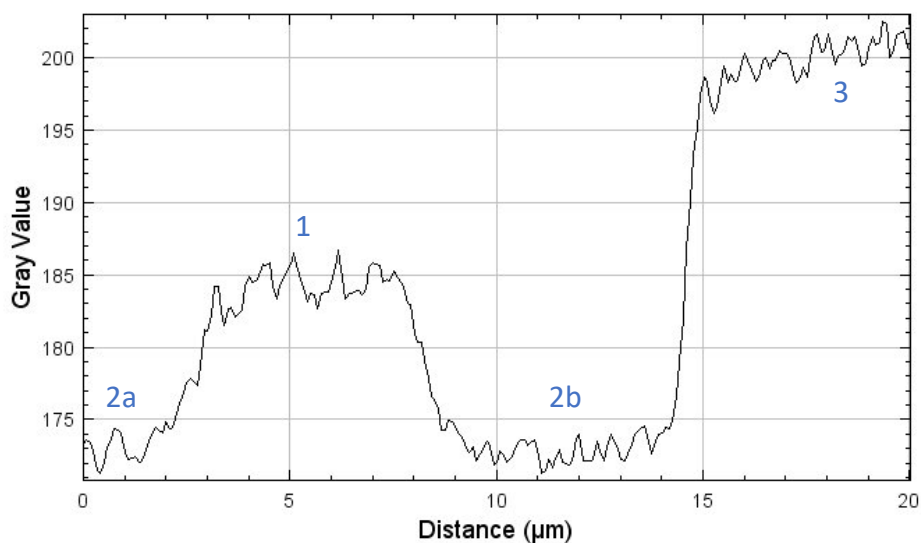


Figure 4: Gray value profile plot of graphene flake, starting point with a distance 0 μm is in the upper left end of the yellow bar in figure 3

Table 1 shows the observations that can be drawn from the gray value profile plot of the graphene flake. The contrast based on the measured gray values was calculated according to equation 4. In the following it is calculated as example for the contrast of area 1:

$$C = \frac{I(n = 1) - I(n \neq 1)}{I(n = 1)} = \frac{200.4 - 182.9}{200.4} = 0.087 = 8.7 \%$$

Table 1: Data of gray value profile plot and evaluation for graphene flake

Area	Distance in Profile Plot [μm]	Average Gray Value [1]	Contrast [%]	Assumed Number of Layers [1]
2a	0.0-2.5	173.6	13.4	2
1	3.0-8.0	182.9	8.7	1
2b	9.0-14.0	173.1	13.6	2
3	15.0-20.0	200.4	0	Background

In literature (see figure 1) the theoretical contrast of a graphene monolayer on a 90 nm Si wafer is given as about 12 % when using green light [1]. In this experiment the most bright area (area 1) has a resulting contrast of 8.7 %. So, this contrast is less than the expected one due to literature. However, area 1 can be assumed as a monolayer. There are several reasons, that the measured contrast differs from the theoretical one. First, according to Blake et al., in theory the contrast is often overestimated due to deviations from the normal light incidence [1]. This might be due to high numerical aperture (NA) and a different extinction coefficient of graphene compared to graphite [1]. Furthermore, dependent on the exact wavelength of the green light, the contrast can also change slightly.

The areas 2a and 2b almost have the same contrast. Therefore, it can be expected that these two areas have the same number of layers. Their contrast is about 1.6 times the contrast of the identified monolayer in area 1. So, it can be assumed that 2a and 2b are bilayers of graphene. Reasons that the measured contrast of the bilayers is not 2.0 times the contrast of the monolayer might be due to an inhomogeneous thickness of the Si wafer, or a slight change in the light intensity density. Here, minimal variations can already make a significant difference in the resulting contrast as it can be deduced e.g. from the color plot (figure 1).

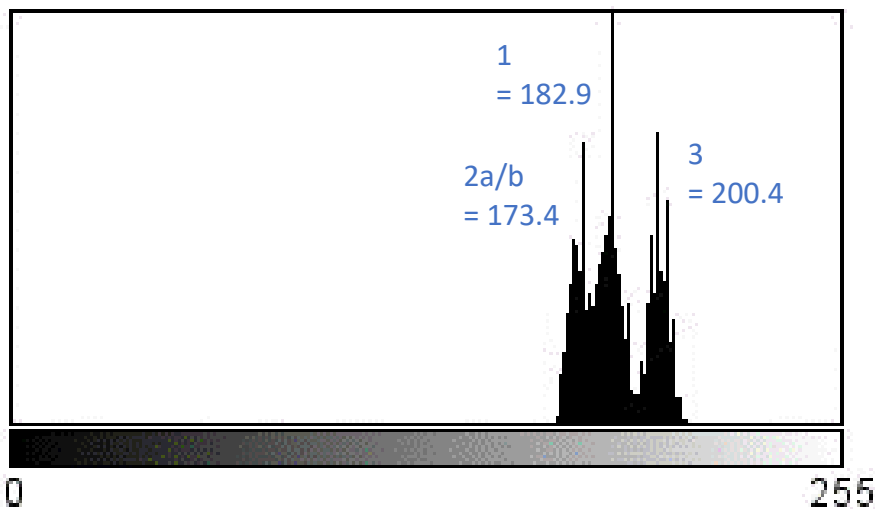


Figure 5: Histogram of gray values of graphene flake

The histogram in figure 5 shows three peaks what confirms the background at a gray value of about 200, as well as that there are two areas on the flake that slightly vary in their thickness.

3.1.2 Contrast of MoS₂ on Si Wafer

Figure 6 shows a MoS₂ flake on a Si wafer that was prepared by mechanical exfoliation. The image was taken by investigating the flake under an optical microscope with the magnitude of 50x. The numbers 1a, 1b, 2, 3 and 4 show the areas that look different in their contrast when observing the MoS₂ flake under the optical microscope. Area 2 represents the background, whereas the numbers 1a, 1b and 3 represent different areas of the flake, that obviously show different contrasts. Along the yellow bar the profile plot of gray values of MoS₂ was recorded, that can be seen in figure 7. The upper left end of the yellow bar represents the distance of 0 μm . Area 4 seems to be a defect in the material and can therefore be neglected for the evaluation. Due to the reason that area 3 consists of too many layers of MoS₂, it disturbs the measurement of the flake and is therefore also not further evaluated.

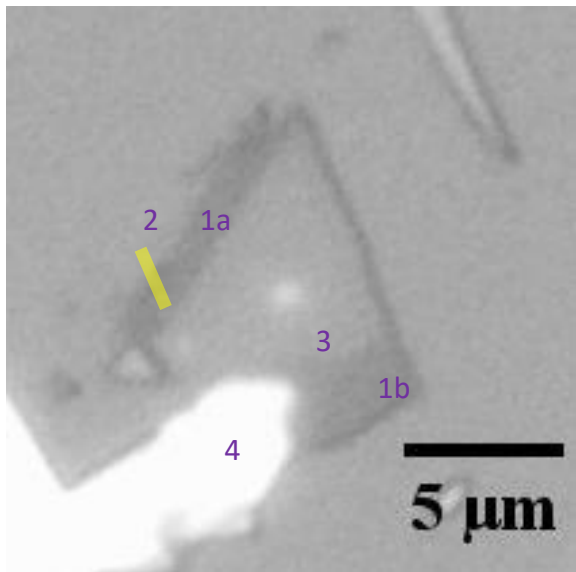


Figure 6: MoS₂ flake on Si wafer

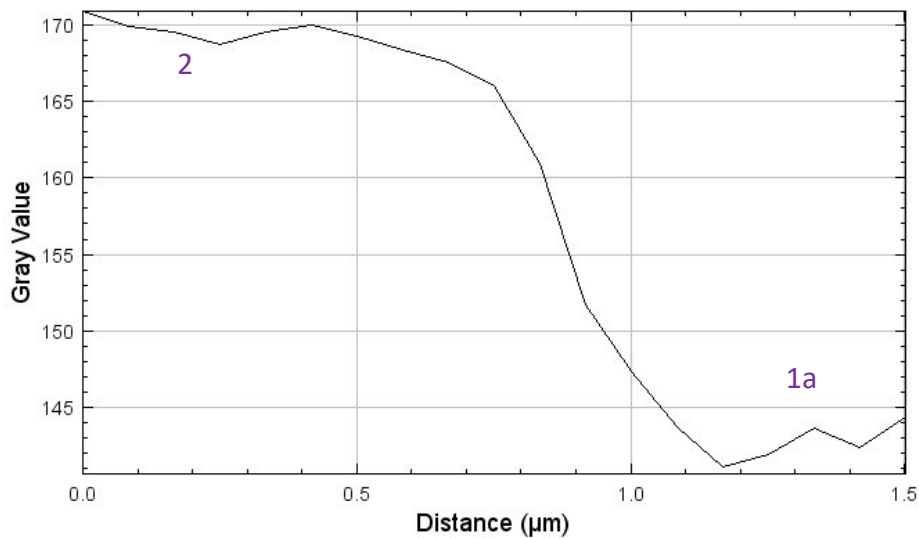


Figure 7: Gray value profile plot of MoS₂, starting point with a distance 0 μm is in the upper left end of the yellow bar in figure 6

Table 2 shows the observations that can be drawn from the profile plot of gray values of the MoS₂ flake for the areas 1a and 2. The gray value of area 1b was determined with the histogram (figure 8, right). The contrast values are calculated from the measurement data as before.

Table 2: Data of gray value profile plot and evaluation for MoS₂ flake

Area	Distance in Line Profile [μm]	Average Gray Value [1]	Contrast [%]	Assumed Number of Layers [1]
2	0.0-0.6	168.7	0	Background
1a	1.1-1.5	143.0	15.2	1
1b	-	145.1	14.0	1

In literature (see figure 1) the theoretical contrast of a MoS₂ monolayer on a 90 nm Si wafer is given as about 40 % when using green light [3]. In this experiment the areas 1a and 1b were the only ones that could be measured additionally to the background. They show a contrast of 15.2 % and 14.0 % respectively. So, this contrast is much less than the expected one. As it can be seen in the color plot in figure 1, the contrast ranges between 0 % and 80 % for a thickness of the Si wafer between 85 nm and 105 nm. Therefore, slight variations in the thickness of the Si wafer seem to result in significantly different contrast values. For a wafer thickness of e.g. 100 nm the resulting contrast from this experiment would coincide well with the theoretical value. So it can be assumed that due to their low contrast the areas 1a and 1b represent monolayers of MoS₂. The slight deviation in the contrast between areas 1a and 1b can be explained by differences in the light intensity during the measurement.

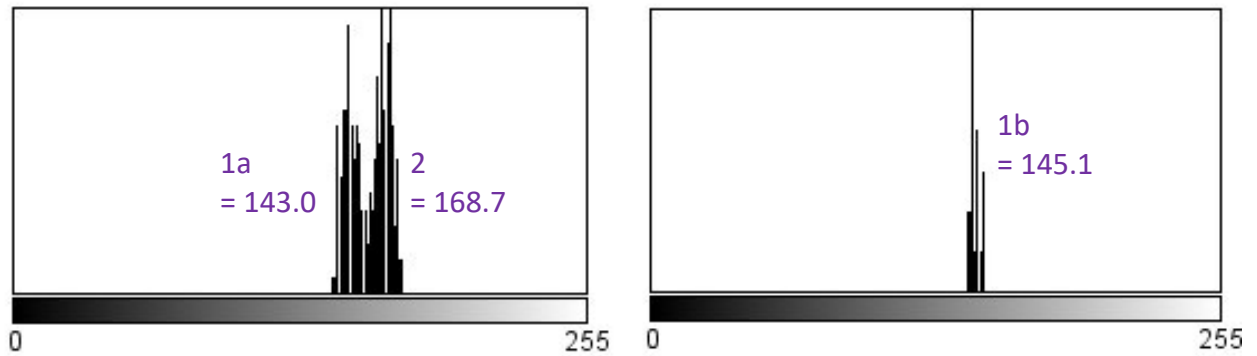


Figure 8: Histograms of gray values of MoS₂ flake (areas 1a and 1b show monolayers and area 2 shows the background)

The histograms in figure 8 show the peaks of the respective areas of the MoS₂ flake and the background.

3.2 Absorption Measurement

3.2.1 Absorption of Free-Standing Graphene

Figure 9 shows on the left the graphene flake after it has been transferred on the TEM grid. The marked holes in the grid that represent the areas 1, 2a and 3 are assumed to be the respective areas that were found for the graphene flake on the Si wafer, that can be seen on the right for comparison. It can be seen that the shape of the graphene flake slightly changed during its transfer, especially at the lower right side, it seems like the flake has accidentally folded up.

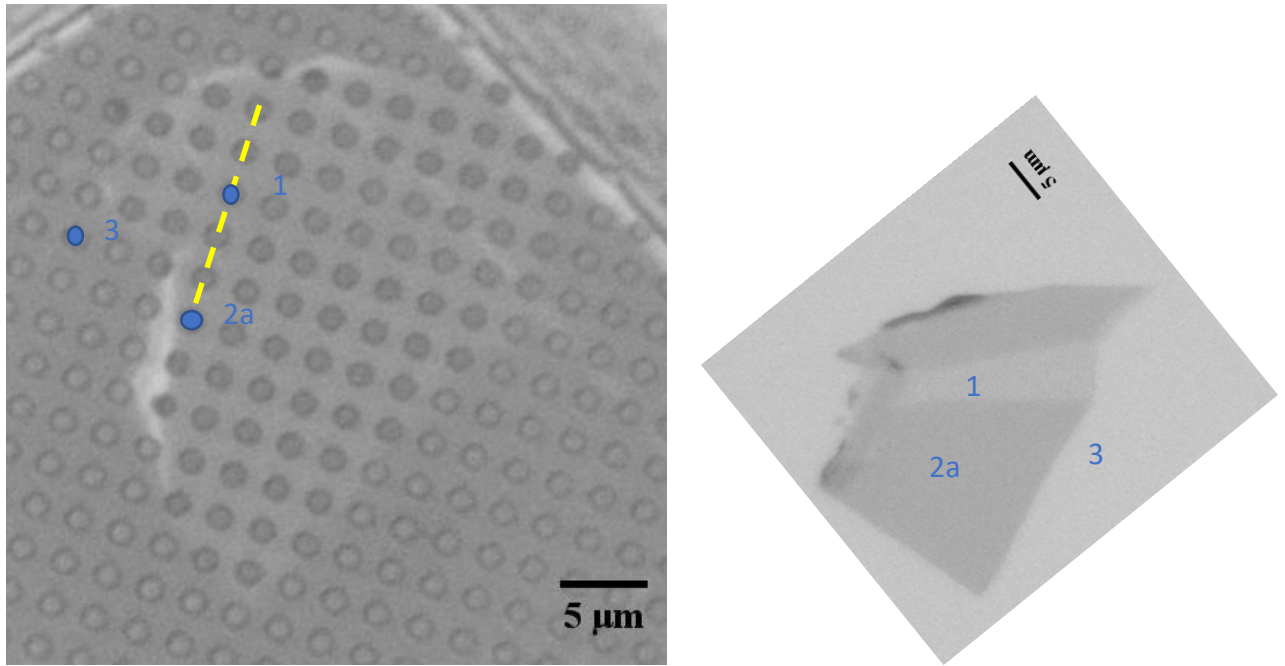


Figure 9: Graphene flake after transfer on TEM grid (left), graphene flake on Si wafer (right)

Table 3 shows the analysed data from the graphene flake, that is on the TEM grid. The average gray values were determined by measuring the average gray value of a certain hole in the grid, where it was assumed that there is the respective layer, that could be detected when measuring the graphene flake on the Si wafer.

Table 3: Data of gray value profile plot and evaluation for graphene flake on TEM grid

Area	Average Gray Value [1]	Absorption [%]	Assumed Number of Layers [1]
1	139.9	2.8	1
2a	136.1	5.4	2
3	143.9	0	Background

The literature value for the absorption of a free-standing graphene monolayer is given as 2.3 % [7]. Therefore, the measured absorption of 2.8 % for area 1 indicates that the monolayer is still present there. Area 2a seems to be still a bilayer because the measured absorption of 5.4 % is about 1.9 times the measured absorption of the monolayer. Slight deviations from the literature value might be because of minor changes in the light intensity profile across the flake. It can also be concluded that the absorption of mono- and bilayers of the flake can also be observed by reflected light method instead of transmitted light method, like it was accidentally done in this experiment. Furthermore, the deviations of the resulting absorption values from theory may be due to the accidental measurement with the reflected light method.

The profile plot of gray values of the free-standing graphene flake (figure 10) shows slight differences of the respective gray values in each of the holes. The high peaks that are between 150 and 155 do not belong to the measurement, they just show the contrast of the grid and can therefore be neglected. The distance of 0 μm represents the upper end of the yellow bar that can be seen in figure 9.

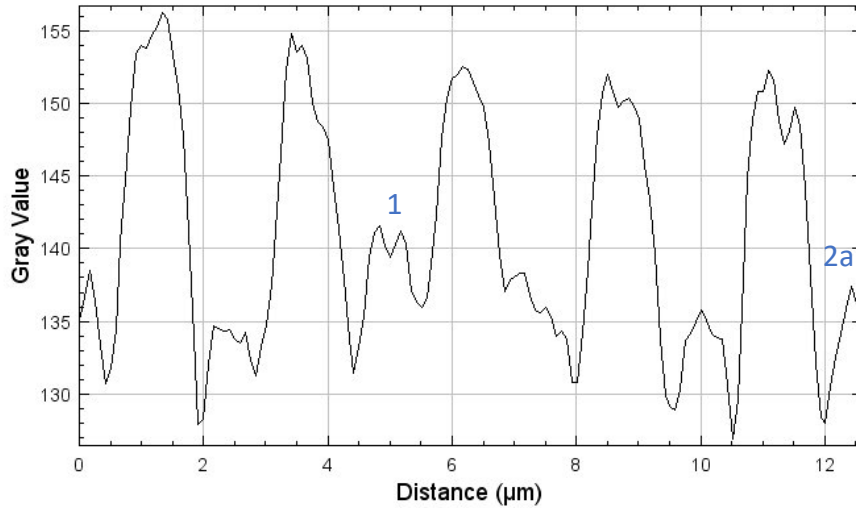


Figure 10: Gray value profile plot of graphene flake on TEM grid using reflected light method, starting point with a distance 0 μm is in the upper end of the yellow line in figure 9

3.2.2 Absorption of Free-Standing MoS_2

Figure 11 shows, on the left, the MoS_2 flake that has been transferred on the TEM grid. Compared to the MoS_2 flake that was observed on the Si wafer (figure 11, right) it can definitely be seen that the original shape of the flake does not exist anymore. This indicates that the transfer of the MoS_2 flake from the Si wafer to the TEM grid was not successful. It was impossible to attach the complete flake to the grid. A possible reason for that might be that the TEM grid, that was used for the experiment, is better suitable for the transfer of graphene than of MoS_2 . It cannot be even proven that the observed structures on figure 11 (left) belong to the initial MoS_2 flake. Nevertheless, the absorption of the background (area 2) and the observed structure (area 1) were measured by transmitted light method. The dark structure on the right seems to be an artefact that appeared during the transmission.

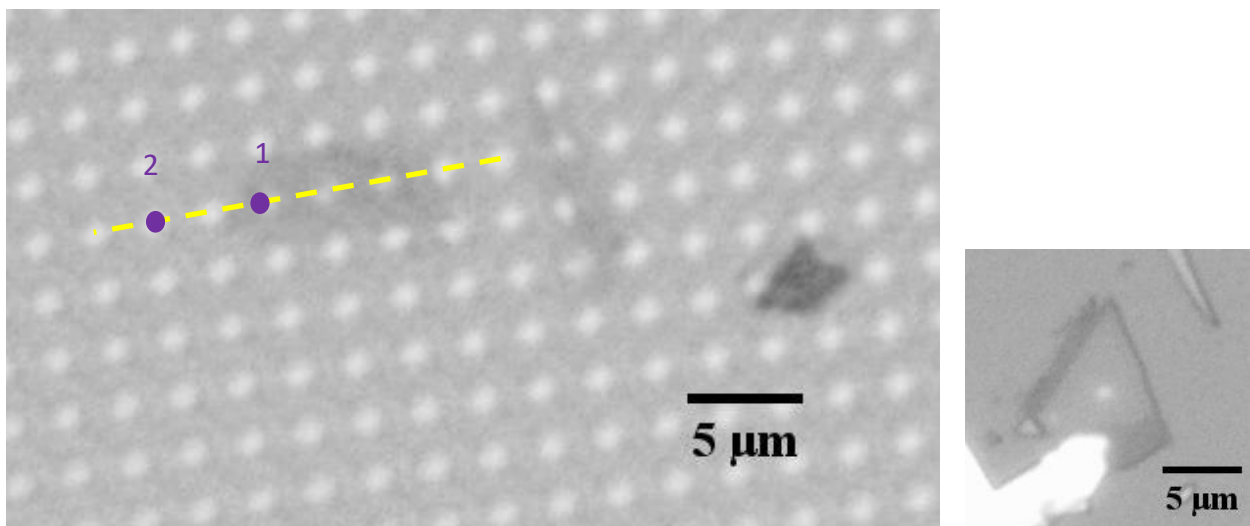


Figure 11: MoS_2 flake after transfer on TEM grid (left), MoS_2 flake on Si wafer (right)

Table 4 shows the analysed data from the MoS_2 flake, that is on the TEM grid. The average gray values were also determined by measuring the average gray value of a certain hole in the grid (positions 1 and 2).

Table 4: Data of gray value profile plot and evaluation for MoS₂ flake on TEM grid

Area	Average Gray Value [1]	Absorption [%]	Assumed Number of Layers [1]
1	198.3	9.9	1
2	220.1	0	Background

The literature value for the absorption of a free-standing monolayer of MoS₂ is given as approximately 9.0 %, depending on the exact temperature and wavelength of light [8]. So, due to the minimal deviation of the measured absorption and the value given in literature, it may be possible that the observed structure indeed represents a monolayer of MoS₂. However, this cannot definitely be said. The observed structure can also be a completely different artefact.

The profile plot of gray values of the free-standing MoS₂ flake (figure 12) shows that the structure that can be seen in figure 11 has the same absorption over all the three holes that are in the grid (the three peaks around 200 in the middle). The starting point of 0 μm is at the left end of the yellow line in figure 11.

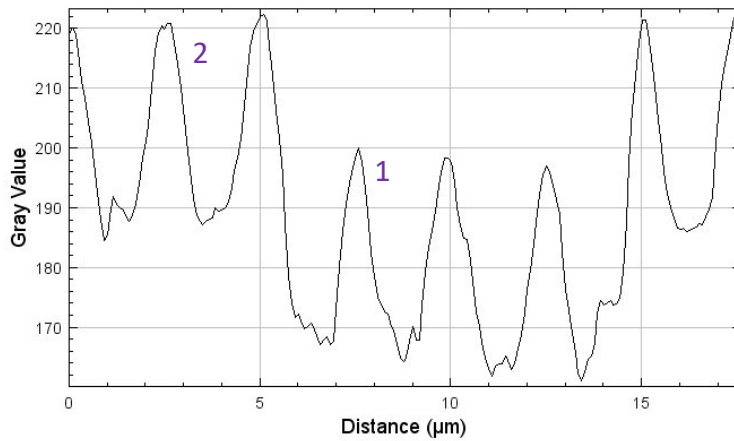


Figure 12: Gray value profile plot of MoS₂ flake on TEM grid using transmitted light method, starting point with a distance 0 μm is in the left end of the yellow line in figure 11

4 Conclusion

Since the technique of mechanical exfoliation for preparing graphene out of graphite has been discovered less than 20 years ago, it is now widely used for producing several 2D materials. These 2D materials show special electrical properties ranging from insulators to superconducting. Furthermore, they partly have an outstanding mechanical stability.

In this experiment mono- and few-layers of graphene and MoS₂ were prepared by this technique. The evaluation of the layers under an optical microscope and the subsequent analysis of the images, that were taken from the structures of interest, proved that mechanical exfoliation is a suitable method for preparing 2D materials. Results for optical contrast and absorption were calculated based on gray values that were captured from reflexion and transmission light measurements. The contrast of structures of 2D materials on 90 nm Si wafers on the one hand and the absorption of free-standing 2D structures via a TEM grid on the other hand revealed, that the results in the present experiment were much better, and thus closer to the values given literature when investigating graphene compared to MoS₂. The results for MoS₂ were deviating more strongly from the literature values what indicates that the present experiment was not working as successful for MoS₂ as for graphene.

5 Literature

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