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1 Introduction

Lately the research and applications of 2D materials gained increasing relevance. 2D materials in general describe flat, ultrathin structures which only consist of one single layer of atoms or molecules [1]. Crystalline materials can be generally described by their grid structure. The smallest repeating unit in this grid is called unit cell [1]. Especially the material properties of some 2D materials, as graphene, are raising great interest in scientists. But also the high variety of 2D materials regarding their optical, mechanical and chemical properties caused by the multiple different compositions, make it possible to make use of such materials in a wide range of applications as semiconductors, tissue engineering or biomedical technologies [1]. Hereby, the different properties from 2D materials compared to their 3D-structure result of the missing interactions between the different layers that do not exist in 2D materials. Another reason is the different surface-bulk ration that is very high in 2D materials. Furthermore, geometrical effects influence the material properties [2]. In general, the diversity and amount of applications of 2D materials are considered to grow further, because some of the mechanisms are yet to be understood and lately there have been multiple discoveries in the field of super capacitors, batteries and photo detectors [3].

In the following protocol, the theoretical background of the topic of 2D materials and some methods will be covered. Furthermore, the experiment where graphene and MoS₂ were investigated will be evaluated. In the experiment, graphene and MoS₂ monolayers were studied, after preparing these with the scotch-tape method. After optical microscopy of the monolayers, the reflection and transmission contrasts were calculated based on the pictures taken and then compared to theoretical values.

2 Theoretical background

2.1 Graphene

The most investigated and popular example for 2D materials is graphene. It is a monolayer of graphite and was also one of the first examples of 2D materials to be investigated [2]. To generate a monolayer out of graphite, multiple methods were discovered and used over the last decades, including the scotch-tape method, which will be later described in detail. Most of the investigations and applications regarding graphene focus on its unique electronic properties. It is a semiconductor and because of its fine structure it can react to small changes in electric fields, which can be used for highly sensitive electric detectors and more [2]. Furthermore, the high density of free charge carriers in the honeycomb lattice of graphene leads to a high thermal conductivity [4]. Another important property of graphene is the high mechanical robustness [5]. It can be quantified by Young's modulus which is around 2.4 TPa [6] and by that much higher than around 30 GPa, which is a typical value for metals as carbon steel or nickel steel [5].

The third characteristic regarding graphene is the special optical behavior. Because of the special electron structure of graphene, the transmittance of graphene is defined by the fine structure constant of the grid which only refers to electromagnetic interactions between the charged molecules [7] [8].

2.2 MoS₂

MoS₂ (Molybdenum disulfide) belongs to the group of dichalcogenides. The basic formula for materials of this group is MX₂, where M is a transition metal as molybdenum (Mb), tungsten (W) or titanium (Ti) and X is selenium (Se), sulfur (S) or tellurium (Te). Because of these different possible compositions, dichalcogenides differ in their properties and overall structure. For example, depending on the composition the dichalcogenide can be either a semi-conductor, a superconductor or something in between [9]. MoS₂ which is used in this practical work, has semiconductor properties, combined with great electrochemical and fluorescence attributes [10]. Because of these properties, an application for MoS₂ are optical and electrical biosensors [10].

2.3 Optical Microscopy

Optical microscopy is one of the most common methods, to view an object which is magnified through lenses [11]. It is also the oldest microscopy technique, but still very popular because of the simplicity of the process, which makes it very cheap and also time-efficient. An optical microscope typically consists of a light source, to illuminate the object of interest. Hereby the light source is either placed above or under the sample. Thus the light is either transmitted or reflected by the sample. The magnification of the object occurs because of the optical system, which consists of multiple lenses. The magnification is here distributed to the ocular and the objective. The ocular lens or eyepiece usually has magnification values of 5-20x. The ocular lens of the microscope that was used in this experiment had a magnification of 10x. The objective, which is placed above the sample, first magnifies the object, typically by 10-100x. Together with the ocular lens, the total magnification is achieved [12]. The general principle is very simple. The object is either surpassed by the light of the light source or reflects it. The rays are then manipulated by the optical system of the microscope and then focused behind the ocular lens. The resolution of the microscope is limited by the wavelength of the used light, the refractive medium and the aperture angle of the respective lenses. [12]

3 Methods

3.1 Sample preparation of different 2D materials

In the practical work, the two different materials MoS₂ and graphene and their respective monolayers were first prepared and then examined. Mechanical exfoliation was used to produce single layers out of their natural structure. For mechanical exfoliation, the material must consist of multiple layers, which are held together by Van-der-Waals forces. Since MoS₂ and graphene contain multiple layers this method was chosen to be the best for this experiment. Hereby the different crystals are placed on adhesive tape. After removing the crystal, parts of the crystal stick to the tape. Since these layers are still too thick, the tape is folded several times to achieve thinner layers after each folding procedure. After folding several times the layers are thinned out enough and the tape is placed on the wafer which consists of a Si-layer and a SiO₂-layer of 90nm thickness. To improve the efficiency of the transfer of the flakes on the tape to the wafer, the whole structure was heated on a hotplate. After cooling down, the wafer with the flakes was then studied under the optical microscope. The sample was first looked at in reflection mode, which means that the light source which illuminated the sample was on the same side as the objective system. In this mode, thin flakes that possibly consisted of one single layer or a bilayer were located on the sample and pictures were taken with the different magnifications of the microscope. The magnification of the objectives were 5x, 10x, 20x, 40x and 50x. Subsequently, the same flakes were observed in transmission mode. For that, a gold grid was placed on top of the respective flake by using a piezo micro-manipulator. After that, the flakes were flooded up by isopropanol which led to the flake sticking to the grid because of adhesive forces. Isopropanol evaporates quickly, but to assure the complete evaporation and drying of the grid, it was placed on the hotplate for 10 minutes. To remove the flake from the Si-wafer, potassium hydroxide (KOH) was poured on top of the sample which resulted in the dissolution of the SiO₂ layer. To wash away the leftovers of KOH in the grid which could influence the contrast values, it was placed in each water and isopropanol for 30 seconds. Afterwards the transmission mode, with the light source under the sample was used and the flakes were again recorded for the different magnifications [13].

3.2 Theoretical contrast

Because of the use of mechanical exfoliation, the thickness of the respective flakes is uncertain. To gain knowledge about the thickness, the contrasts of the flake in the reflection and transmission mode of the microscope can be measured. The values are then compared to literature values and by that, the number of layers can be determined.

The reflection coefficient which determines how much of the incident light is reflected only depends on the refractive indices of the two respective media. It is given by equation 1.

$$r = \frac{n_0 - n_1}{n_0 + n_1} \quad (1)$$

Another important value is the contrast. For reflection, it is defined as the relative intensity of the reflection in presence ($n \neq 1$) and absence ($n = 1$) of the sample. For this

practical work, this corresponds to the reflection intensity through a flake ($n \neq 1$) or a space without the flake ($n=1$). The contrast is then given by equation 2.

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

The reflective contrast in this experiment depends on the wavelength of the radiated light and the thickness of the SiO₂ and the Si layer because of interference and reflection at these layers. Hereby a phase shift of the light wave takes part at every transition to a new medium. For the three layers in this experiment the refractive indices are n_1 for the flake, n_2 for the SiO₂ layer and n_3 for the Si-layer. Furthermore also the refractive index of the surrounding layer n_0 is also important, since the first shift of a medium is between air and the flake in this experiment. The observed intensity is therefore given by equation 3 which calculates the interference phenomena at the different interfaces between each layer.

$$I(n_1) = \left| \frac{r_1 e^{i(\Phi_1 + \Phi_2)} + r_2 e^{-i(\Phi_1 - \Phi_2)} + r_3 e^{-i(\Phi_1 + \Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1 - \Phi_2)}}{e^{i(\Phi_1 + \Phi_2)} + r_1 r_2 e^{-i(\Phi_1 - \Phi_2)} r_1 + r_3 e^{-i(\Phi_1 + \Phi_2)} + r_2 r_3 e^{i(\Phi_1 - \Phi_2)}} \right|^2 \quad (3)$$

Here Φ is the phaseshift and defined by $\Phi_i = 2\pi n_i d_i \lambda$. d_i is the thickness of the respective layer. The reflection coefficients are given by formula 4.

$$r_n = \frac{n_{n-1} - n_n}{n_{n-1} + n_n} \quad (4)$$

To determine the thickness of a specific flake, literature values can be used. In figure 1, the theoretical contrast of graphene at reflection is shown, which changes based on the wavelength of the incoming light and the SiO₂-layer thickness. If a contrast of a graphene flake is measured, one can determine whether it is a monolayer or if it is a multilayer flake. Figure 2 shows the same theoretical reflection contrast values for MoS₂ on a SiO₂-layer.

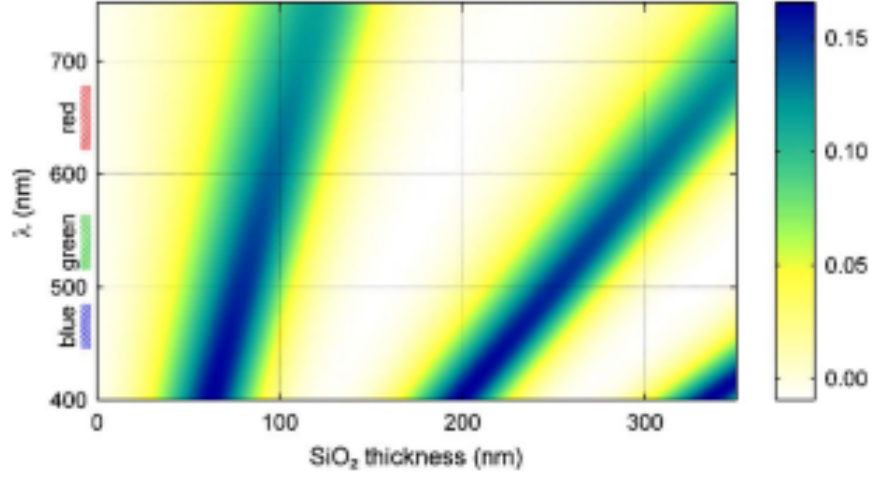


Figure 1: Contrast of graphene at reflection dependent on the thickness of the SiO_2 -layer and the wavelength of the light [14]

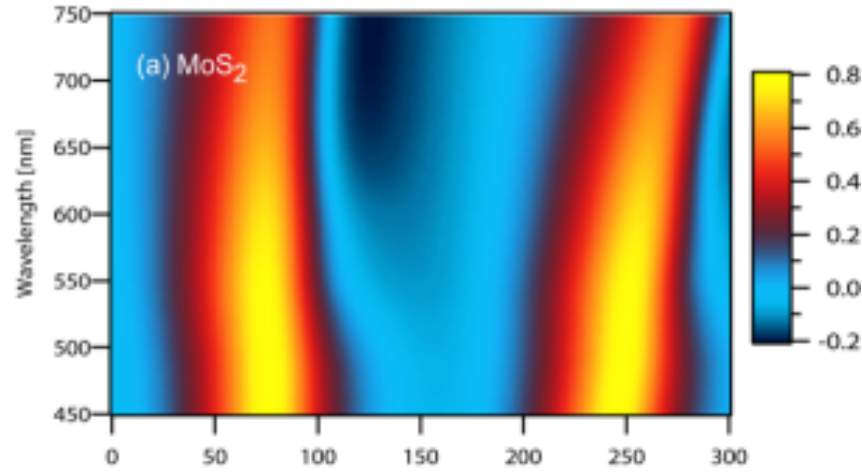


Figure 2: The contrast of MoS_2 at reflection dependent on the thickness of the SiO_2 -layer and the wavelength of the light [9]

The other mode of microscopy technique addressed in this protocol is the contrast at transmission. For monolayer graphene, the contrast at absorption is always 2.3%. That means that it is independent of the wavelength of the radiation source and the surrounding temperature. The absorption contrast for MoS_2 values can be looked up in literature and is shown in figure 3. As shown, it is dependent on the temperature and wavelength of the light source.

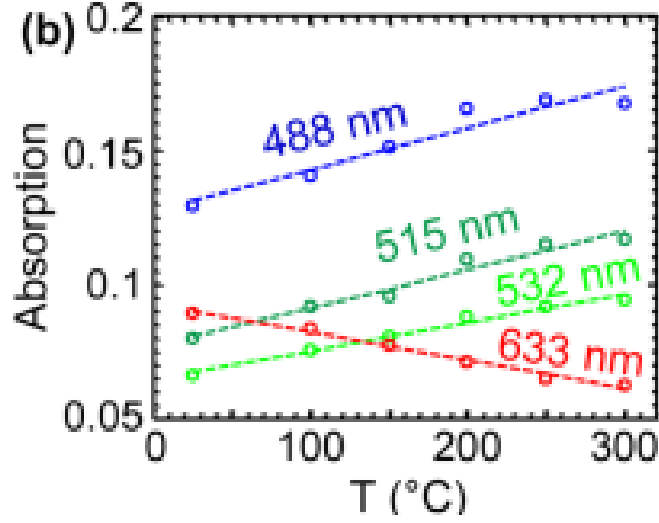


Figure 3: The contrast of MoS₂ at transmission dependent on the temperature and the wavelength of the light [15]

4 Results and Analysis

The pictures of the flake were investigated by using the Fiji ImageJ software. The channels were split into green, red and blue to get clearer results regarding the contrast values. For the following pictures, only the green channel of each picture was used. For each flake investigated a plot profile and histogram of the grey values over a certain distance was plotted. The first graphene flake showed a thin layer that was investigated and can be seen in reflection mode figure X. The contrast was calculated as shown in formula 2. With a background grey value of 192 and a grey value of 177 for the flake, a contrast of 7.8% was calculated. The flake could not be transferred onto the gold grid, which made an investigation at reflection impossible.

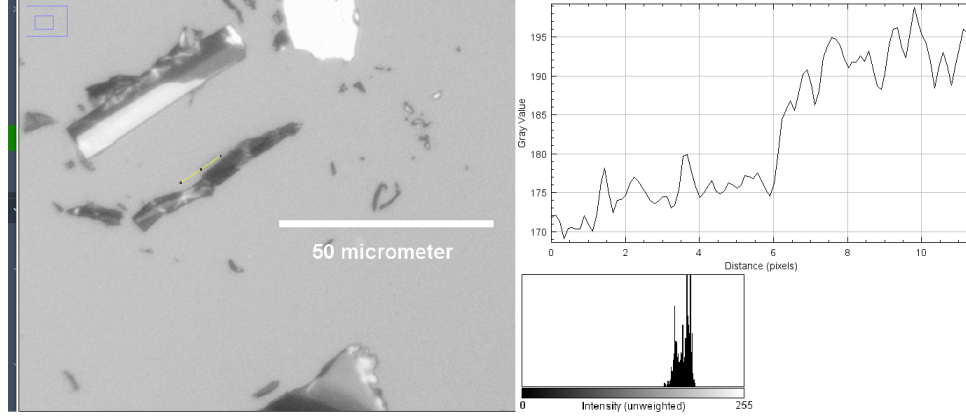


Figure 4: The first graphene flake in reflection mode with the respective plot profile and histogram of the yellow line in the microscopic image

The second flake observed, was thicker but still investigated to get an idea of the number of layers. It can be seen in figure 5 with the respective plot profile and histogram. The background grey value of 196 and grey value of 150 of the flake resulted in a contrast value of 23%. After successfully transferring it onto the gold grid, the flake was also investigated

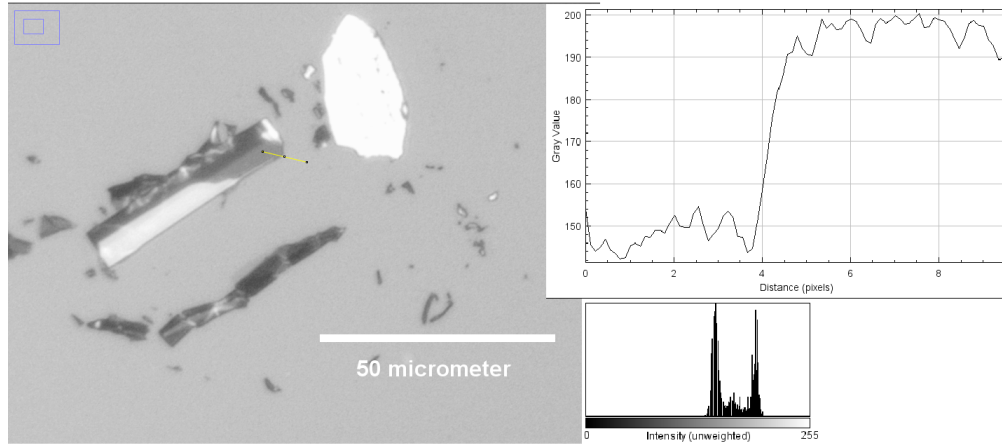


Figure 5: The second graphene flake in reflection mode with the respective plot profile and histogram of the yellow line in the microscopic image

in transmission mode. Figure 6 shows the flake under the microscope with the plot profile and the histogram. The background grey value was 150 with the grey value of 115 for the flake. Resulting of that, a contrast of 23% could be calculated.

For the MoS_2 flake, the same procedure was done. Figure 7 shows the reflection of the flake under the microscope under 50x magnification. The mean grey value of the background was determined to be 178, while the flake had an average grey value of 158.

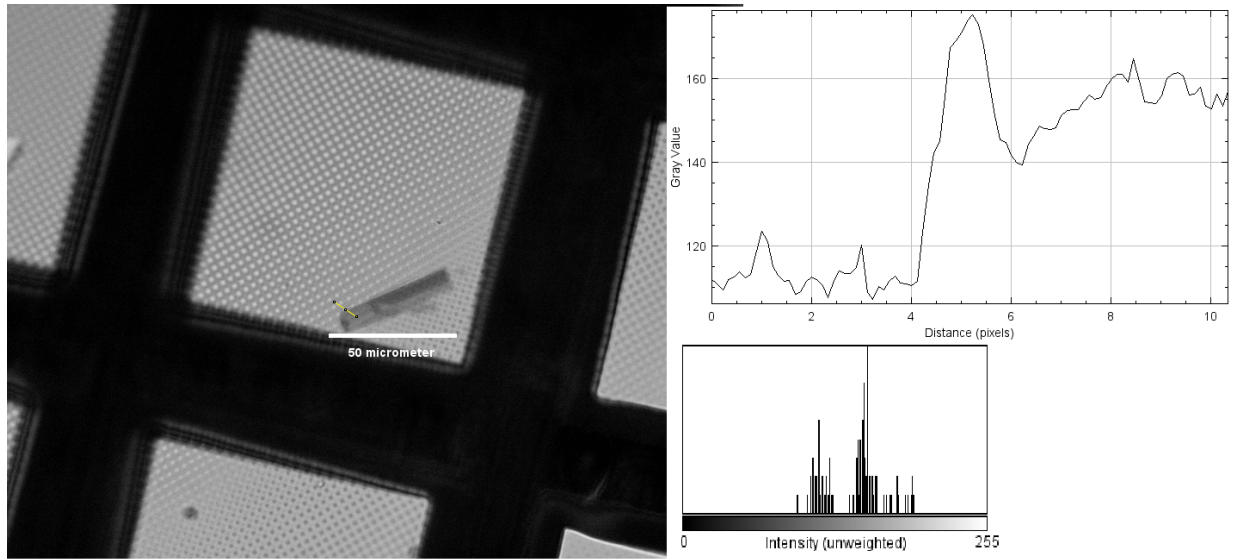


Figure 6: The second graphene flake in transmission mode with the respective plot profile and histogram of the yellow line in the microscopic image

With formula 2 a contrast value of 11.2% can be calculated.

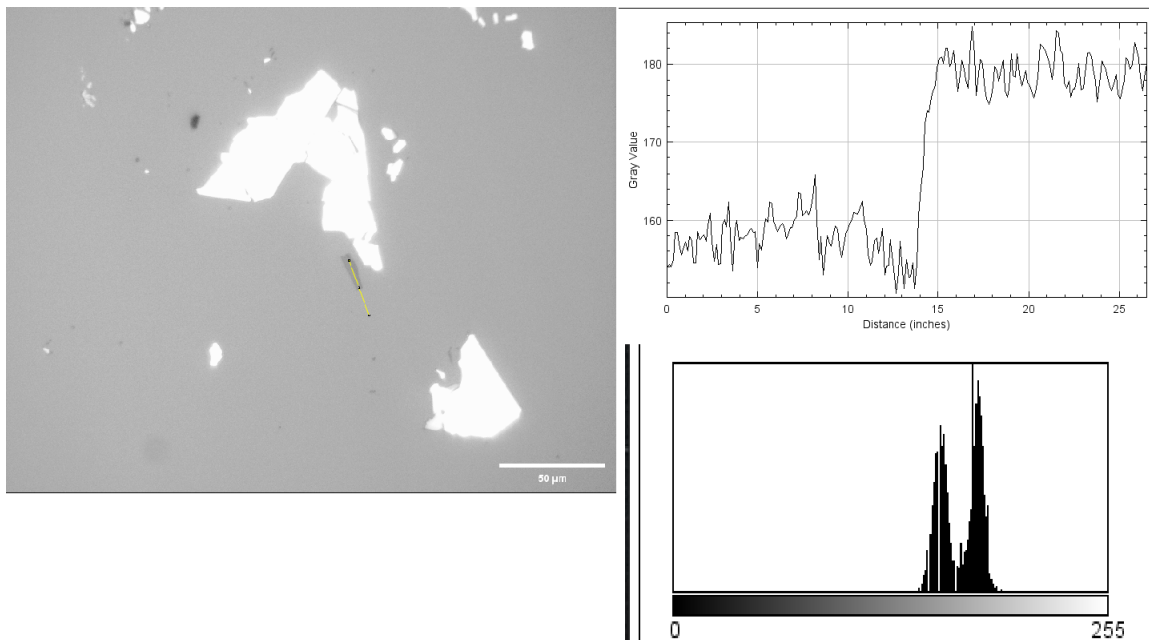


Figure 7: The MoS₂ flake in reflection mode with the respective plot profile and histogram of the yellow line in the microscopic image

The same flake was then investigated in the transmission mode of the microscope which is shown in figure 8. Here the mean grey value of the background was 190 and 172 for the flake. This results in a transmission contrast value of 9.4% for the MoS₂ flake.

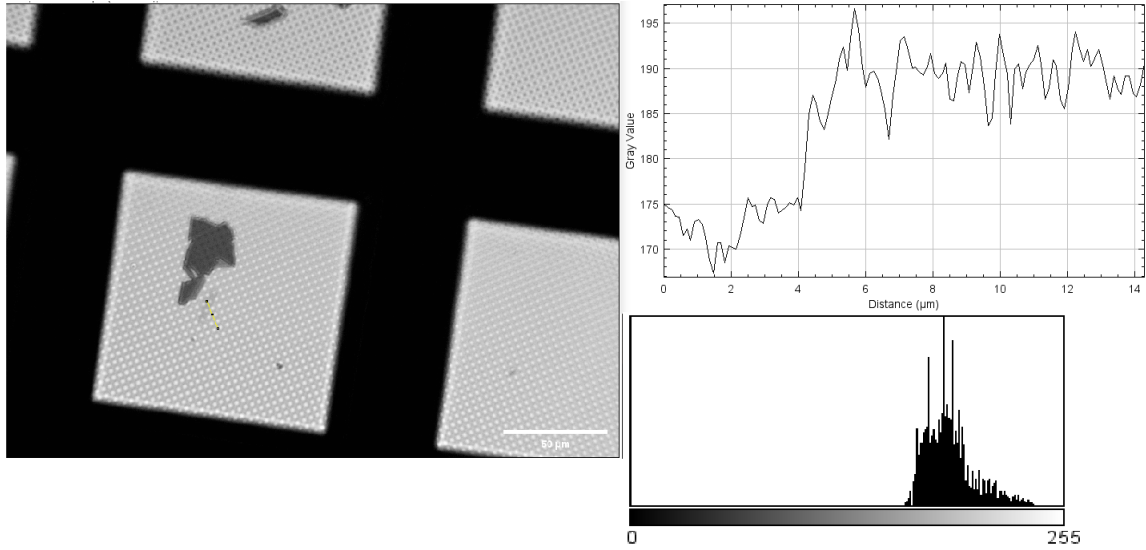


Figure 8: The MoS₂ flake in transmission mode with the respective plot profile and histogram of the yellow line in the microscopic image

5 Discussion

In this section, the different experimental contrast values of the respective flakes are compared with literature values to determine the layer thickness. Hereby the thickness of the SiO_2 layer was assumed to have a thickness of 90 nm, the wavelength of green light to be 500-550 nm and a room temperature of 20°C. With these parameters, the theoretical values for a monolayer of the graphene or MoS_2 flake could be read out of figures 1,2 and 3.

The first graphene flake investigated (figure 4) had a contrast value of 7.8%. Figure 1 shows a theoretic value of 7-15% for the given parameters, which suggests, that in the case of the first flake a monolayer can be suspected. The range of the theoretical contrast is so big, because the parameters could only be taken from the manufacturer and not precisely measured and controlled.

The second graphene flake (figures 5 and 6) showed different contrast values. For the reflection contrast, a value of 23% was calculated. According to the theoretical contrast values, this suggests the flake either to be a bi- or a trilayer. To confirm that, the absorption values can be taken into account. Since the absorption for graphene is always the same at 2.3% and after transfer onto the gold grid, the SiO_2 layer was not present anymore, the error sources were minimized. The experimental contrast value of 23% here denies the presumption that the flake is a bi- or trilayer.

The observed MoS_2 flake showed an experimental contrast at reflection of 11.2%. In figure 2 the theoretical contrast of a MoS_2 monolayer for the respective parameters is 20-50% which is a wide range. However, the contrast of the investigated MoS_2 flake is not located in this range. As mentioned earlier, multiple error sources make it still possible, that the flake was a monolayer. Especially the SiO_2 can be considered to be an error factor because at the SiO_2 layer thickness of 90nm, already a few nanometers deviation of the layer thickness can lead to various contrast values. For example, the respective contrast at absorption for a SiO_2 layer thickness of 105nm is around 10-25% which would make a presumption of a monolayer possible.

To get more information about the number of layers, the absorption values can be taken into account. The experimental value here was calculated to be 9.4%. Figure 3 suggests the theoretical absorption to be around 6-8% for a given temperature of 20°C and a wavelength of 500-550 nm. Since this is only a small deviation from the experimental value, the MoS_2 might have been a monolayer.

The deviations of the literature and the experimental values in this experiment have multiple reasons. Possible inaccuracies could be induced by the SiO_2 layer thickness, which was not measured specifically. Furthermore, the temperature in the room where the experiment was conducted was not precisely measured and also changed over the time of the experiment. Since the experiment did not take place in a clean room, impurities might have changed the outcome of the experiment. Another inaccuracy results of the light source that illuminated the sample while using the microscope. Since it was polychromatic, the comparison with literature values was complicated and inaccurate. Furthermore, the sample was not illuminated homogeneously over the whole area, which also could have led to inaccuracies. By using grey values that were located as close as possible, this error was minimized but can not be excluded completely. Another error source that should be mentioned is, that the software was used and evaluated by the laboratory workers themselves. This also leads to

inaccuracies that influence the contrast values of the experiment. Also, the transfer method that was used to position the flake onto the gold grid, could be replaced by a method, which is more effective and less prone to errors but to achieve that, further research has to be conducted.

6 Conclusion

In conclusion, the practical values calculated in this experiment add up to the theoretical values taken from literature. The first graphene flake that was investigated was most likely a monolayer, although this could not be verified by observing the flake in transmission mode. The second graphene flake turned out to be a multilayer flake, where the number of layers could not be precisely determined because of deviating contrast values for reflection and transmission. The MoS_2 flake also possibly was a mono- or a bilayer, although literature values have a very high range due to inaccurate parameters in this experiment. Nevertheless, the fundamental procedures behind the monolayer production techniques and ways to estimate the number of layers were practically applied, which led to a deeper understanding of 2D materials.

To improve the experiment, it could be conducted in a clean room. This would lead to minimized possible impurities of the sample and a constant temperature, which is necessary to get accurate results in comparison to the theoretical values. Furthermore, it could not be assured, that the thickness of the SiO_2 layer was precisely and homogeneous 90nm. This error could be eliminated by determining the layer thickness prior to the experiment. Another optimization of the experiment would be the use of a monochromatic light source which would also lead to more accurate practical values and easier comparison to literature values. However, these optimizations are not possible in this practical work, because the experiment would require much more time and effort.

References

- [1] P. Avouris, T. F. Heinz, and T. Low. *2D Materials*. Cambridge University Press, 2017.
- [2] Rubén Mas-Ballesté, Cristina Gómez-Navarro, Julio Gómez-Herrero, and Félix Zamora. 2d materials: to graphene and beyond. *Nanoscale*, 3(1):20–30, 2011.
- [3] Nicholas R. Glavin, Rahul Rao, Vikas Varshney, Elisabeth Bianco, Amey Apte, Ajit Roy, Emilie Ringe, and Pulickel M. Ajayan. Emerging applications of elemental 2d materials. *Advanced materials (Deerfield Beach, Fla.)*, 32(7):e1904302, 2020.
- [4] Gao Yang, Lihua Li, Wing Bun Lee, and Man Cheung Ng. Structure of graphene and its disorders: a review. *Science and technology of advanced materials*, 19(1):613–648, 2018.
- [5] Caterina Soldano, Ather Mahmood, and Erik Dujardin. Production, properties and potential of graphene. *Carbon*, 48(8):2127–2150, 2010.
- [6] Jae-Ung Lee, Duhee Yoon, and Hyeonsik Cheong. Estimation of young’s modulus of graphene by raman spectroscopy. *Nano letters*, 12(9):4444–4448, 2012.
- [7] Qiang Li, Jun Lu, Prince Gupta, and Min Qiu. Engineering optical absorption in graphene and other 2d materials: Advances and applications. *Advanced Optical Materials*, 7(20):1900595, 2019.
- [8] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim. Fine structure constant defines visual transparency of graphene. *Science (New York, N.Y.)*, 320(5881):1308, 2008.
- [9] M. M. Benameur, B. Radisavljevic, J. S. Héron, S. Sahoo, H. Berger, and A. Kis. Visibility of dichalcogenide nanolayers. *Nanotechnology*, 22(12):125706, 2011.
- [10] Shaswat Barua, Hemant Sankar Dutta, Satyabrata Gogoi, Rashmita Devi, and Raju Khan. Nanostructured mos 2 -based advanced biosensors: A review. *ACS Applied Nano Materials*, 1(1):2–25, 2018.
- [11] Michael W Davidson and Mortimer Abramowitz. Optical microscopy. *Encyclopedia of imaging science and technology*, 2(1106-1141):120, 2002.
- [12] Jerome Mertz. *Introduction to optical microscopy*. Cambridge University Press, Cambridge, United Kingdom, second edition edition, 2019.
- [13] Jannik Meyer. 2d materials - preparation and optical characterization.
- [14] P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim. Making graphene visible. *Applied Physics Letters*, 91(6):063124, Aug 2007.

- [15] Eilam Yalon, O. Burak Aslan, Kirby Smithe, Connor McClellan, Saurabh Suryavanshi, Feng Xiong, Aditya Sood, Christopher Neumann, Xiaoqing Xu, Kenneth Goodson, Tony Heinz, and Eric Pop. Temperature dependent thermal boundary conductance of monolayer mos2 by raman thermometry. *ACS applied materials interfaces*, 9, 10 2017.