Exercise 2: Optical reflectance measurements

Location: MED 2 117 (Photonics TP Lab)

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1. Summary

In this exercise you will carry out basic optical characterization of the transferred MoS_2 produced in exercise 1 either by you, your colleagues or the assistants. The goal is to confirm that the material that has been transferred has the correct optical reflectance spectrum, corresponding to MoS_2.

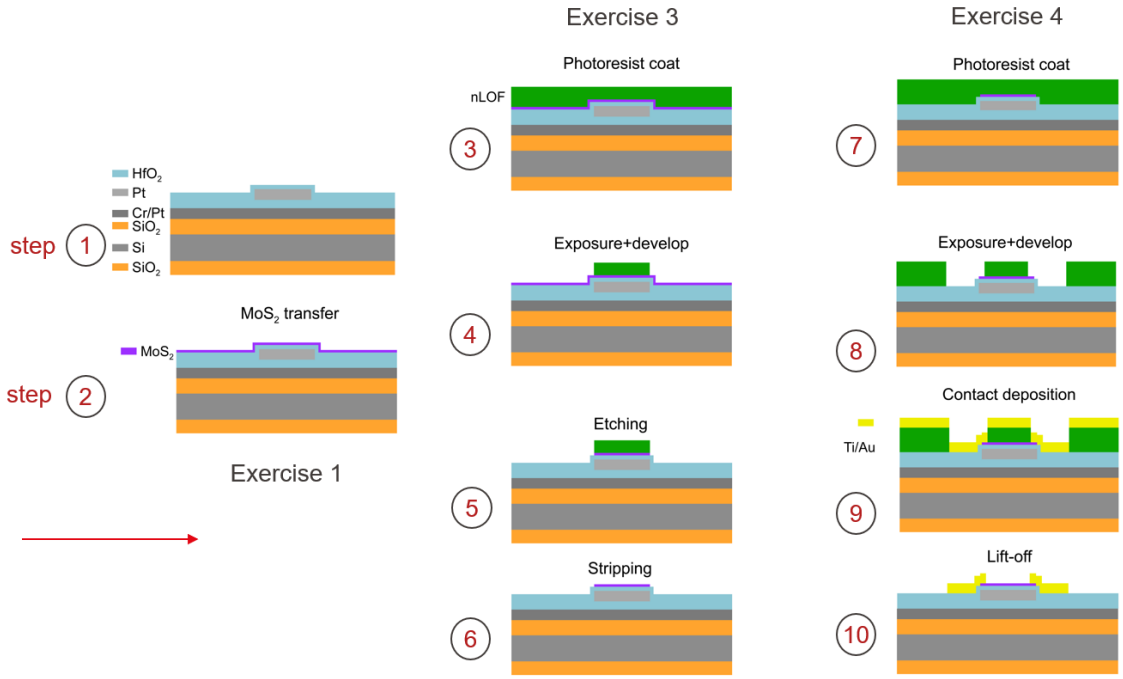


Figure 1. Overview of the complete process flow for the device fabrication in this course. The current exercise (arrow) is between steps 2 and 3 and corresponds to a sample inspection step, these are usually not shown in process flows but are carried out as often as possible in order to facilitate early problem detection.

2. Background

In this exercise, we will use the technique called differential reflectance spectroscopy in order to characterize the 2D material transferred onto the device substrate. This is a relatively simple and rapid technique which can be used to detect a "fingerprint" of the material by recording the spectra of light reflected from its surface. The spatial resolution of the technique is ~1 µm (determined primarily by the microscope) while the wavelength range is 500-1100 nm (1.1-2.5 eV, determined by the spectrometer used). Other optical techniques are in widespread use for the characterization of 2D and other materials such as Raman or fluorescence spectroscopy. The main advantage of differential reflectance spectroscopy is that it is relatively inexpensive, rapid and simple. The use of Raman spectroscopy for example requires the use of lasers, expensive high-resolution spectrometers and filters for removing the laser light from the

resulting spectrum. The requirements for photoluminescence are a bit relaxed but the setups are still an order of magnitude more expensive than that for the differential reflectance technique shown here. Since photoluminescence also requires a direct band gap semiconductor, which in this case means that we could only use it to characterize a single layer of MoS_2 and would not be able to work on thicker structures.

The differential reflectance DR is defined as:

$$DR = \frac{\Delta R}{R} = \frac{R - R_0}{R} \tag{1}$$

where R is the reflectance of the sample as a function of wavelength and R_0 the background reflectance, acquire from a substrate or an empty chip. Reflectance of a material or a surface is the fraction of incident light which is reflected and can be in the range between 0 and 1.

An example of a reflectance and differential reflectance spectra for monolayer MoS_2 is shown on Figure 2.

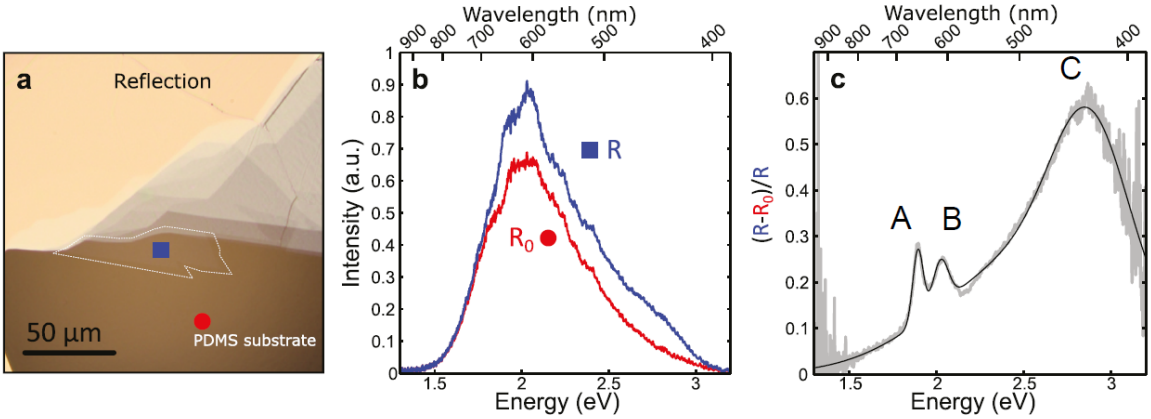


Figure 2. (a) Optical image of an MoS_2 crystal exfoliated on PDMS. The region outlined by white dashed lines is one layer thick. (b) Reflectance as a function of energy and wavelength recorded on the monolayer region (blue rectangle, R) and on the substrate next to it (red circle, R_0). (c) differential reflectance spectrum with characteristic A, B and C exciton peaks. Adapted from [1].

The characteristic exciton peaks (A, B and C shown on Figure 2) are related to resonances in the band structure of MoS_2. Band structure calculation for MoS_2 layers with different thicknesses are shown in Figure 3, left [2]. For bulk crystals and structures with a thickness of more than one layer, the transition between the valence and conduction band which is shortest in energy (black arrow) occurs between points with different wavenumbers and the material is an indirect semiconductor. In the case of a monolayer, the band structure is modified to due a 2D quantum confinement in the vertical direction (the layer itself acts as a potential well for electrons and holes in the material), the shortest transition now occurs at the K point between same wavenumbers and the material is a direct band gap semiconductor. More precise calculations (Figure 3, right), show that there is a small splitting of the valence band, on the order of 150 meV for Mo-containing 2D semiconductors and 450 meV for W-based 2D semicondcutors, due to the spin-orbit coupling. There is also a similar splitting of the conduction band but it is on the order of several meV and is negligible on this scale. A and B transitions then correspond to transitions between either of these two valence bands and the conduction band. The C transition is related to the so-called “nesting” effect, happening when the conduction and valence bands have relative wide regions running parallel to each other so that they can be superimposed (nested).

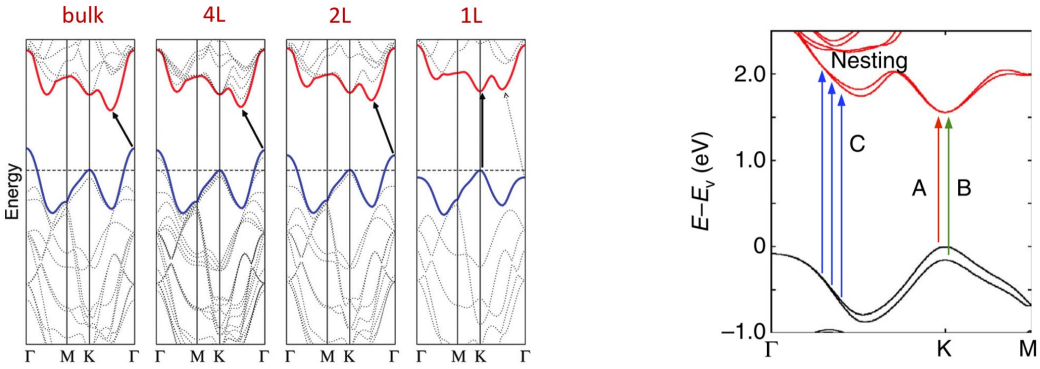


Figure 3. (left) Band structure of MoS_2 with different thicknesses, from bulk to a monolayer (1L) [2]. Right: band structure of monolayer MoS_2 showing the optical transitions and resonances giving rise of A, B and C excitons [3].

The main purpose of this exercise will be to qualitatively verify the quality of the transferred material by checking that its reflectance spectrum contains features typical of monolayer MoS_2, namely A and B excitons at the expected wavelength.

2.1. Description of the setup

The setup consists of a microscope (Figure 4) and optical components mounted on one of the ports of the microscope. A beam splitter on the microscope is used to divide the light reflected by the sample between the two paths. In one path, we have the microscope eye-pieces, allowing you to locate a region of interest on the sample. The second optical path contains another beam-splitter, further splitting the part of the light that was diverted into this branch into a USB camera which will be used to record the image of the sample and on the second path, a multimode optical fiber which transmits the light to a portable CCD spectrometer.

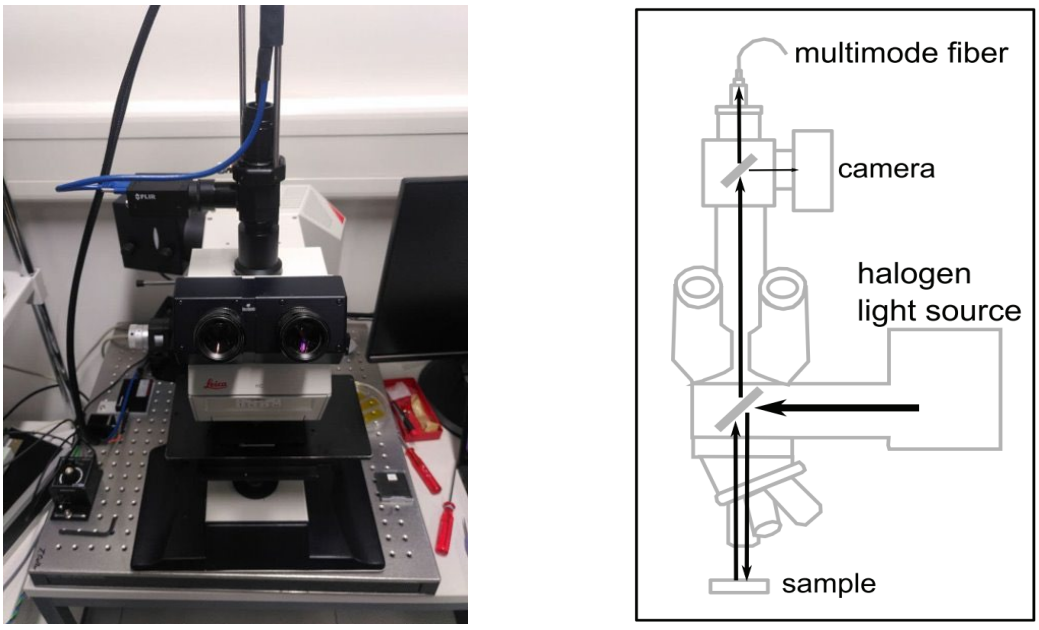


Figure 4. Left: photograph of the microscope used in this setup. Right: schematic of the setup. Reproduced from [1].

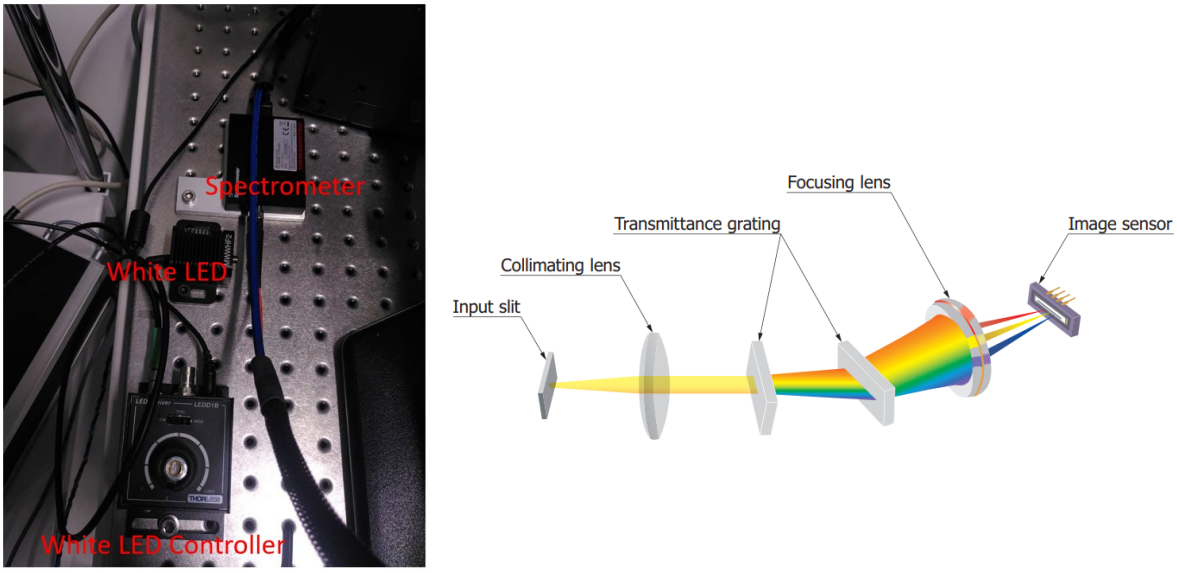


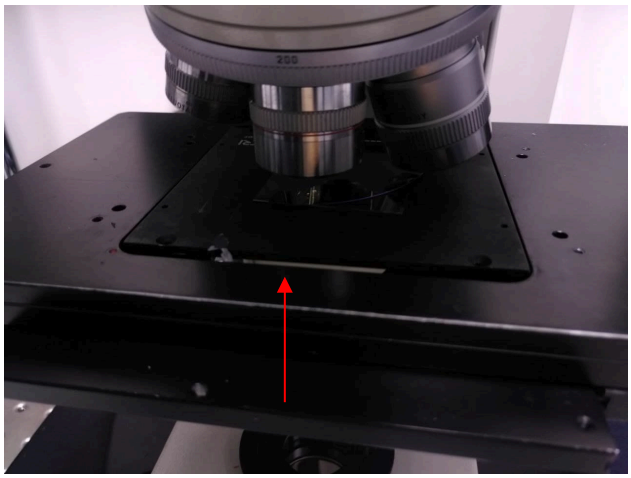
Figure 5. Left: closer view of the spectrometer and white LED light source mounted on the left hand side of the microscope. Right: schematic drawing of the compact spectrometer.

3. Description of experiments and tasks

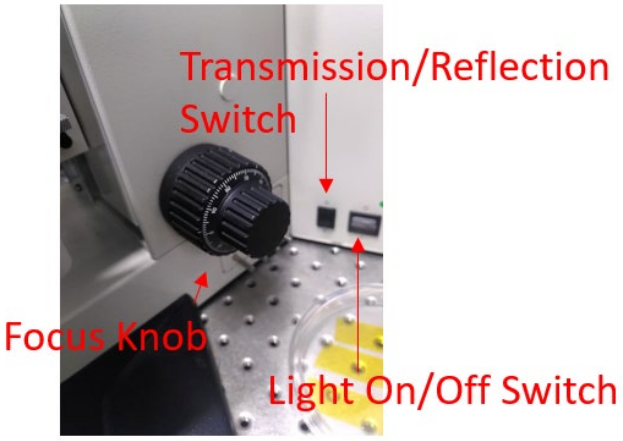
Following is the overview of the tasks and operations to be carried out in this exercise. The main goal is to record differential reflectance spectra of transferred MoS_2 films (both single and double transfer) and compare them to spectra from exfoliated samples (provided by the assistant).

3.1. Set up the microscope and localize an area of interest

1. **Select x5 Magnification Objective Lens (Longest Working distance and focus depth of field)**
2. **Put sample on the sample stage**



3. **Turn on the light**



4. Make sure the reflected light is directed onto the camera

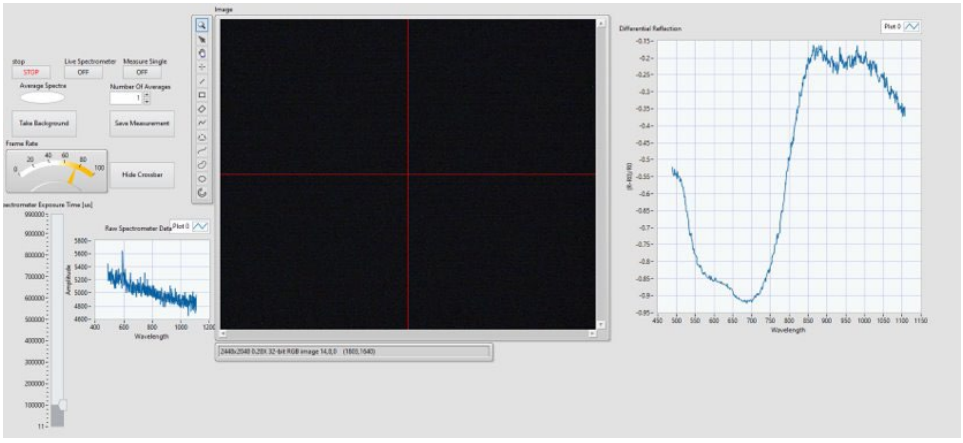
5. Find focus on the sample, and find the region of interest

You can now increase magnification to a suitable objective (e.g. 100x) by tuning the focus for every objective. **Attention:** you need to avoid smashing the objective into the sample – this can destroy both of them. The easiest approach is to first raise the stage by constantly looking at it, until you are a few mm from the objective. You then find the focus by lowering the stage and looking through the eyepiece. A useful trick is also to look at the edge of the sample first, it is much usually much easier to focus on the edge first then on the sometimes featureless sample.

6. (Optional) Check the position of the fiber collection spot on the sample

We assume that light for the fiber and the spectrometer is collected from the center of the sample. To check this, you can you can unplug the fiber from the spectrometer and plug it into the white LED. As you turn the LED ON and increasing its intensity, you will be able to see if the white LED spot coincides with the crossbar center. If this is not the case, ask the TA to help you with the alignment procedure.

7. Adjust the exposure time and light intensity



While looking at the camera feed in the Labview code, move the sample using the knobs on the X-Y translation stage, so that the crossbar in the camera feed coincides with the feature of interest on the substrate. Adjust Exposure Time (in software) and light Intensity (on the

microscope) so that the signal the on spectrometer (Raw Spectrometer Data plot) is not saturated but also has high intensity (10kcounts<I<60kcounts).

3.2. Record the differential reflectivity spectra from transferred samples

1. **Save the background reflectivity spectrum (R_0)**

Click "Take Background" in the labview window, to save the background reflectivity.

2. **Record the spectra from the sample**

Move the crossbar onto the sample and click "Measure Single" or "Live Spectrometer".

You can now save the reflectivity spectra by clicking "save measurement" and specifying file path and name. You should record spectra from several regions of interest on the sample, at least 10 different spots, representing the region of the sample that will form the active area of the devices.

3. **Record the differential reflectivity spectra for the second sample with two transferred MoS_2 layers**

4. **Record the differential reflectivity spectra for the sample with exfoliated MoS_2**

4. Summary of experiments and tasks

1. Record differential reflectance spectra of single and double-transferred MoS_2 layers
2. Record differential reflectance spectra of exfoliated monolayer MoS_2
3. Record differential reflectance spectra for exfoliated MoSe2
4. Record differential reflectance spectra for exfoliated WSe2

5. Questions for the report

In the report, please comment on the following:

1. Show the distribution of A, B and C exciton energies in the respective samples.
2. How big is the valence band splitting energy you obtain from your measurements?
3. How big is the difference in exciton energies between exfoliated and transferred samples?
4. How does the sample with two transfers compare to the sample containing bilayer MoS_2 (figure 3a in ref [1])? Why?
5. Is there a difference between exfoliated MoS2 and MoSe2? Why?
6. Is there a difference in the valence band splitting between the different materials? Why?

6. References

[1] R. Frisenda, Y. Niu, P. Gant, A. J. Molina-Mendoza, R. Schmidt, Rudolf Bratschitsch, J. Liu, L. Fu, D. Dumcenco, A. Kis, D. P. D. Lara, and Andres Castellanos-Gomez, *Micro-Reflectance and Transmittance Spectroscopy: A Versatile and Powerful Tool to Characterize 2D Materials*, J. Phys. Appl. Phys. **50**, 074002 (2017).
[2] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, *Emerging Photoluminescence in Monolayer MoS_2*, Nano Lett. **10**, 1271 (2010).
[3] D. Kozawa, R. Kumar, A. Carvalho, K. K. Amara, W. Zhao, S. Wang, M. Toh, R. M. Ribeiro, A. H. C. Neto, K. Matsuda, and G. Eda, *Photocarrier Relaxation Pathway in Two-Dimensional Semiconducting Transition Metal Dichalcogenides*, Nat. Commun. **5**, 4543 (2014).