Mechanical exfoliation and characterization of 2D materials

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Abstract: In this work, mechanical exfoliation of two-dimensional materials has been performed through the "scotch-tape" method with the objective of producing few-layer flakes and characterize them via optical and atomic force microscopy. The studied materials were MoS_2 and $PtSe_2$ and the substrate used for characterization was Si coated with SiO_x. MoS_2 showed good adhesion to the substrate and some few-layer flakes were obtained and analysed, with results suggesting a correlation between both methods of characterization. On the other hand, $PtSe_2$ exhibited poor adhesion onto the substrate and flakes were thick and broken unevenly, making it very difficult to characterize, indicating that alternative methods for producing flakes, or other substrates for their transfer should be explored in order to achieve better results for this material.

Keywords: materials physics, atomic force microscopy, optical microscopy, van der Waals materials
SDGs: ODS 7.3 and ODS 9.4 and 9.5.

I. INTRODUCTION

In the last two decades, especially since the discovery of graphene in 2004, the field of two dimensional (2D) materials has grown and developed enormously, notably because of their mechanical, optical and electronic properties and applications. In this work we will focus on the so-called transition-metal dichalcogenide (TMD) materials, specifically on MoS_2 and $PtSe_2$. Exfoliation via the "scotch-tape" method was performed on samples of both materials to obtain single and multilayer flakes and then characterized with optical microscopy (OM) to assess the number of layers of promising flakes. Later, atomic force microscopy (AFM) was also performed to verify their actual thickness and correlate the results of both methods of characterization.

In 2D materials, atoms within the same layer are covalently bonded, while layers are held together by van der Waals interactions. This characteristic allows us to peel off layers without damaging their structure, hence, making the obtention of single or few-layered flakes possible [1]. While this peeling off is mostly "random", as we cannot control the amount of material that sticks into the tape and then transferred onto the substrate, there are methods to improve the amount of material transferred as it will be explained in sections where MoS_2 and $PtSe_2$ exfoliation is described.

The most common methods of characterization of 2D materials are costly (e.g. AFM, scanning tunnelling microscopy, Raman spectroscopy…); that is why, in this work, an alternative and cheaper method of characterization that provides a good approximation on the number of layers was investigated. We have chosen OM as the main method of characterization. If effective, it would reduce the number of flakes to be analysed by other methods, as the not promising flakes would be previously discarded, reducing the time of characterization with expensive equipment and consequently making the process much more resource efficient.

II. EXPERIMENTAL PROCEDURE

A. MoS_2 and $PtSe_2$ exfoliation

There are different methods to produce single or few-layer flakes of 2D materials, for example, chemical vapor deposition and molecular beam epitaxy among others [1]. Most of these methods are complex and require advanced and costly equipment, so a most cost-efficient method had to be used. This is why the exfoliation process was selected for this study, which will be explained in the following. After each step, a number correlating to those shown in FIG. 1 is written in brackets. In this case, the "scotch tape" method was the selected one. It is a mechanical exfoliation process in which layers of the bulk crystal are peeled off by adhesive tape. Because the interlayer cohesion is mediated by weak van der Waals forces, by sticking the tape to the surface of the bulk material (1), some layers can be easily extracted (2). From there, one can continue to peel off layers of the material from the tape with another strip of tape (3). By following this procedure three or four times, a strip which is expected to have flakes with a very low number of layers (from one to some dozen) can be obtained (4). Then, the strip is stuck onto the substrate of choice for its transfer, making sure that the flake of interest is sandwiched between the substrate and the tape (5). Finally, with a cotton swab, pressure is applied for some minutes (2-5 minutes normally) to ensure an efficient transfer (6). In the end, tape is removed, and flakes are now transferred onto the substrate (8), the surface of which, has been previously cleaned with isopropanol to eliminate possible sources of contamination. Apart from this, an additional

step was introduced in the procedure described above to maximize the number of flakes transferred onto the substrate. As mentioned in [3], by heating the substrate while the tape is still stuck in it (7) and afterwards peeling it (8), the total surface of material transferred to the substrate increases considerably. In our case, the best results of transferred area with low adhesive (from the tape) contamination were at 80ºC for 90 seconds and then letting it cool down for the same amount of time before the tape was removed. Note that the obtention of monolayer, bi-layer or few-layer flakes utilizing this method is purely a matter of chance, as there is no concrete way of knowing how many layers have been transferred to the substrate.

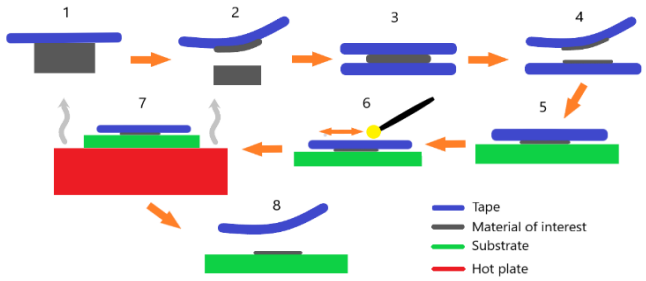

FIG. 1: Illustration of the experimental process for the mechanical exfoliation and transfer. Description of each step is done in the main text.

The substrate of choice was Si coated with 440 nm thick SiO_X and the two materials of study were MoS_2 and $PtSe_2$, Graphene was also used during the training sessions to become familiar with the exfoliation and transfer procedure. The set up for the exfoliation process can be seen in FIG. 2 in the appendix section.

B. Characterization

As mentioned above in I, OM was employed to estimate the number of layers of the flakes that had been successfully transferred to a substrate, and afterwards, AFM was performed to obtain high precision measurements and compare them to the OM results. To make a qualitative analysis of the flakes and estimate the number of layers of each, a colour contrast study of the OM images was conducted. In OM, white light illuminated the sample from above. Part of this light is reflected to the eyepiece lens directly from the flake, the other, is transmitted and refracted through the flake-substrate system. In every interface some light is reflected and some refracted, making it possible to calculate the reflective and refractive indexes through the Fresnel coefficients as described in [2]. Note that each material has its own indexes of reflexion and refraction, so the colour seen for different materials in the same conditions would differ, since light propagates differently through them. In our case, all the flakes will appear of the same colour, as a colour correcting software was applied to the images to facilitate visual detection of different layers. Another factor that changes the indexes, is the number of layers of the sample. This means that a change in thickness causes a detectable variation on the contrast and intensity of the observed flake, allowing us to characterize the samples and determine the number of layers of it. If the flake has very few layers (approximately 1 to 6), the registered intensity is lower than the one of the background (seen in a purple/darker colour in OM images, as in FIG. 3(a)), its indexes stay stable (with little variations yet consistent) and the intensity step between layers remains constant. However, when the flake is thicker than ~7 layers, its indexes begin to change drastically, and the intensity increases till the point of surpassing the one of the background (seen in a bright/white colour in the contrast images). The threshold (in number of layers) between these two behaviours is not clear, at least from an experimental side, so it can only be estimated through statistical analysis of lots of samples. Note that once the intensity goes up, for some layers, it will be close to the one from the background, so flakes with 9 or more layers could falsely be giving readings of intensities that would be expected from flakes with 1 to 4 layers only. AFM was performed on those samples to verify the actual number of layers. As for the OM characterization process, firstly, an optical survey is done throughout the substrate and potential flakes are identified. Then, to quantify the number of layers and determine their thickness, an intensity profile is obtained from the image taken of the flake. Other nearby flakes are also examined to make a statistical study and determine the difference in intensity between layers. By doing spectrometry on channel G (green light), which is the most sensitive light to these changes, we were able to get those intensity profiles and determine the intensity step between layers. By comparing the intensity of the flake versus the one from the background and knowing the step between layers, we were able to estimate the number of layers on each flake. Finally, the most promising flakes were taken to AFM to verify their thickness and determine if the estimations from OM were accurate or not. The results will be discussed on the following section.

III. RESULTS AND DISCUSSION

In this section, the results from the characterization of both MoS_2 and $PtSe_2$ will be discussed and analysed. However, the results from the training with graphene will be briefly commented first.

The camera and software used were from OPTIKA microscopes. It is worth mentioning that these instruments were a new acquisition in the laboratory, and, as a result, no one in the research team was familiarized with the software, so we used the training to get acquainted with it. At the beginning of the study, size and magnification of the images were not calibrated, and thus, images from graphene flakes have no scale bars. Also, image processing for these samples was incipient, so that the lines of the intensity profile were added with image editing. For MoS_2 and $PtSe_2$, images do include both features.

A. Graphene

To practice the process of exfoliation and start characterising some samples, graphene was used, as it is a well-studied material and protocols for its exfoliation and characterization are well established [3], [6]. The results of the study, summarized in FIG. 2, suggest that the intensity jump between layers correspond to 5 arbitrary units (a.u) of intensity as seen in FIG. 2(a). This is concluded based on how graphene breaks down (layer by layer) and seeing the very little difference in contrast, indicating that the transition seen corresponds to two consecutive layers.

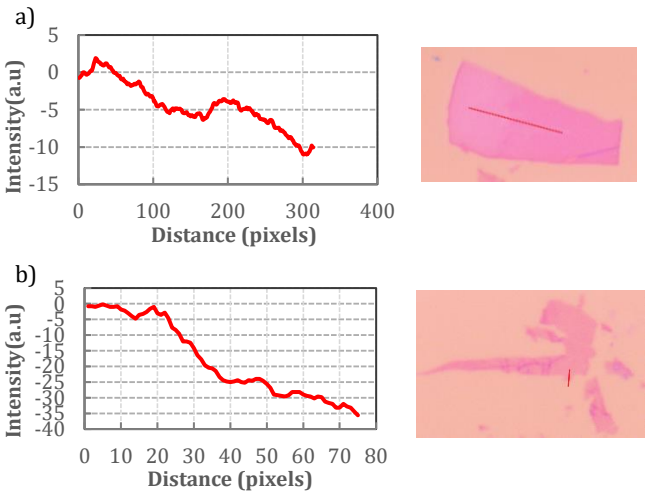

FIG. 2: Intensity profiles of OM and their corresponding flakes (left panels). The red line superposed on the flakes indicates the path of spectrometry and the origin of intensities corresponds to the intensity of the background. a) This flake and its intensity profile was studied to determine the intensity jump between layers. b) This flake was studied in contrast with the background to determine its thickness.

Knowing the intensity of the jump, the number of layers of the flake in FIG. 2(b) can be inferred by contrasting with the background. Analysing the profile, it was determined that the flake in FIG. 2(b) contains a region composed of 5 layers, and then, it transitions to another area with a thickness of 6. As seen, especially on the flake of FIG. 2(b), the transfer to the substrate does not produce a perfectly homogeneous (in layers) flake. Instead, the exfoliation can produce unexpected ruptures on the crystal, generating flakes with multi-number of layers and imperfections on them. That is the reason darker strips can be seen in FIG. 2(b) throughout the flake. The small ripples visible in the profiles are due to imperfections on the flake and to the measurement error of the instrument.

B. MoS_2

Two exfoliation sessions were performed for this material. In each session, a total of three or four substrates with material were produced. The first one was following the method described in FIG. 1 without heating the tape-substrate system (step 7). Samples of this session were mostly thick, but thinner regions could be found and studied. The second one was performed with the full method, and it increased the total area of material transferred as well as the quality of the flakes present: the material transferred tended to be thinner and the flakes bigger. A comparison between samples of these two sessions can be found in FIG. 8 (supplementary material section). The results of the statistical study suggest that the intensity step between layers for MoS_2 flakes with 6 or less layers is of 5 a.u of intensity. As commented above, for flakes with more than 6 layers, the indexes of reflection and refraction change, and so does the intensity jump. For this range of layers (7+ layers) a study of the intensity jump was not performed, yet some results indicate that for layers close to the threshold, the jump is reduced in half. It can be seen that the upper part of the flake in FIG. 3(a) is darker than the rest of it, indicating larger thickness. Thus, it has a lower intensity in comparison to the other region of the flake, which is brighter in contrast and its intensity is closer to the one from the background. This change in 5 a.u of intensity between layers was the minimum detected, as measured in several flakes, it was assumed to be the step between two consecutive layers. A total of three flakes were taken to the AFM for characterization. The first two were really promising, according to their OM profiles, but resulted in thicker flakes of about 10 to 15 layers (see FIG. 9 & FIG. 10 in the appendix section). As aforementioned, when the refractive indexes change, intensity increases. This behaviour begins at an intensity lower than the one of the background, meaning that for some number of layers, the intensity registered would still be below it, giving the false reading of a low-layer flake when it is actually thick. For the last characterized MoS_2 flake (FIG. 3(b)), the intensity

profiles of the OM showed two different layered regions. The first one presented a drop of 30 a.u of intensity, indicating a 6-layer region, whereas the second, exhibited a 25-drop, suggesting a 5-layer region.

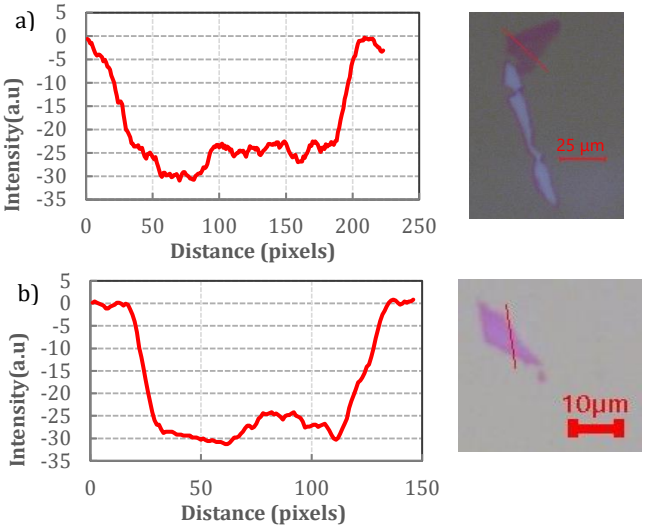

FIG. 3: Intensity profile of two MoS_2 flakes obtained by OM (left) and their corresponding images(right). The spectrometry line goes from top to bottom and the origin of intensities corresponds to the intensity of the background. The red line depicts the area where the profile is taken.

Spectrometry via AFM, shown in FIG. 4, revealed that this flake had 3 different layered zones. In literature, it can be found that monolayer MoS_2 thickness is about 0.75 nm [4].

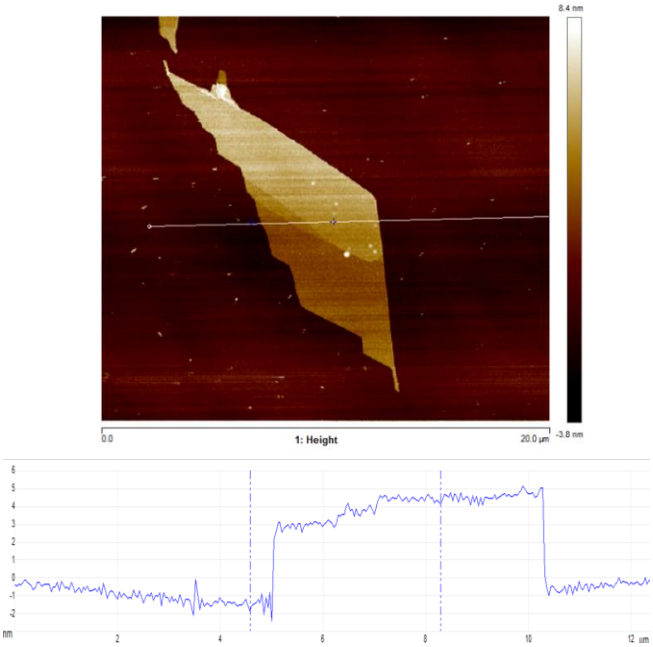

FIG. 4: Image of a multi-layered MoS_2 flake obtained by AFM (top) and its corresponding height profile (bottom). The horizontal white line in the image represents the path of analysis of the profile below.

In our measurements, the step between consecutive layers appears to be of 0.75 nm, consistent with a monolayer jump. The thinnest layer was 4.5 nm thick, which corresponds to 6 layers. This result is in agreement with the prediction of the OM. The other two layers, measured 5.25 and 6 nm respectively, indicating zones of 7 and 8 layers. During characterization, a light spot was observed in the middle of the images, affecting the profiles and intensity differences were noticed when using different magnifications for the same light source (FIG. 11 & FIG. 12).

C. $PtSe_2$

For this material, only one session of exfoliation was performed, in which 4 substrates were obtained using the full method described in FIG. 1. The amount of material transferred to the substrate was very low compared to the other two materials, and the flakes were small (2-4 µm in average size) and very thick. All of them appeared as white and bright on the OM images, and the intensity of their profiles was above the background, indicating that no few-layer flakes were produced. A single flake exhibiting some contrast was found and the intensity of its OM profile was below the background (FIG. 13), but given that no statistical study could be performed, no hypothesis about its thickness could be formulated. AFM revealed a flake with a thickness of approximately 600nm, as depicted in FIG. 5. Considering that the thickness of a monolayer found in other articles is 0.5 nm [5], this flake would have approximately 1200 layers.

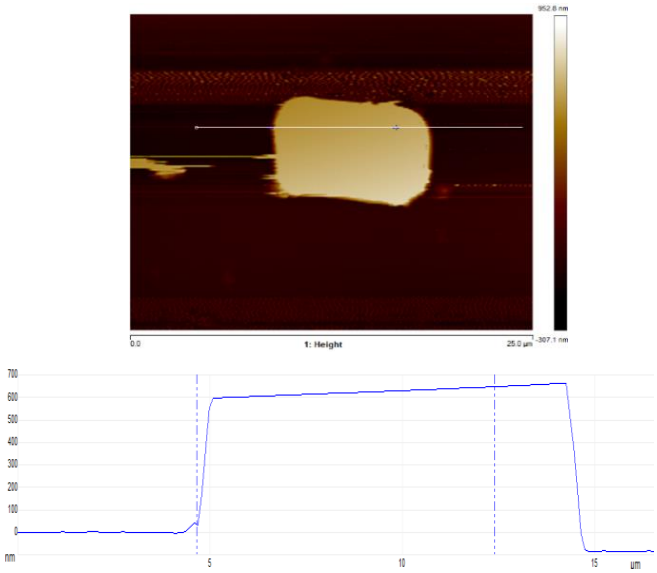

FIG. 5: Image of a $PtSe_2$ flake obtained by AFM (top) and its corresponding height profile (bottom). The horizontal white line in the image represents the path of analysis of the profile below.

IV. CONCLUSIONS

- The results of the study of MoS_2 on Si/SiO_2 substrates of 440 nm suggest that the system (material-substrate) is adequate to obtain a large quantity of few-layer flakes (1-15 layers) with relatively large size (5-15 μm long). A considerable quantity of 5 and 6-layer flakes were visualized with OM, which is a good result as it constitutes a large base of samples to carry out a statistical study and characterize promising flakes. Unfortunately, no mono or bi-layer flakes were found in this work, but this could be due to the randomness character of the exfoliation method. The characterization process and analysis of OM seems to correlate with the results obtained in AFM for flakes of 6 layers or less. As it is in the range of interest, we conclude that it could be a viable option to study this material. It is worth mentioning that the resolution of OM has not proven to be able to distinguish some parts of flakes with consecutive layers to the ones surrounding them, as shown in FIG. 3 and FIG. 4, and caution is advised as areas of 7 to 15 layers could be detected as few-layered zones (as depicted in FIG. 9 & FIG. 10). That is why we encourage to verify the results of OM with AFM
- As for $PtSe_2$, results indicate that the adhesion of the material to the substrate is not adequate, given that the quantity and quality of the flakes transferred were not ideal to be characterized. No jumps in the intensity profiles allowed for the determination of step-size changes between layers. To improve this, other substrates such as gold could be tested for better adhesion, flake quality and colour contrast. In addition, other methods like chemical vapor deposition and molecular beam epitaxy could also be considered to enhance the yield of few-layer flakes on the substrate.
- All in all, this work manifests the difficult task of producing few-layer flakes of TMDs and its characterization. It highlights the need of improving the technique of exfoliation, whether in finding more suitable substrates for specifical materials or by introducing more steps in the process to eliminate possible sources of contamination and enhancing the adhesion of material onto the substrate [3]. It demonstrates the need to explore other methods of producing few-layer flakes and their characterization, such as Raman spectroscopy

Acknowledgments

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Exfoliació mecànica i caracterització de materials 2D

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Resum: En aquest treball, s'ha dut a terme l'exfoliació mecànica de materials bidimensionals per mitjà del mètode "scotch-tape" amb l'objectiu de produir flocs de material amb poques capes i caracteritzar-los via microscòpia òptica i de forces atòmiques. Els materials estudiats han estat el MoS_2 i el $PtSe_2$ i el substrat utilitzat per la seva caracterització Si recobert de SiO_X. El MoS_2 ha mostrat bona adhesió al substrat i s'han obtingut i analitzat alguns flocs amb poques capes, amb els resultats suggerint l'existència de correlació entre els dos mètodes de caracterització. D'altre banda, el $PtSe_2$ ha exhibit una pobre adhesió al substrat i els flocs obtinguts han resultat ser gruixuts i amb presencia de trencaments desiguals, dificultant molt la caracterització i indicant que altres mètodes per produir flocs o altres substrats per la transferència del material haurien de ser explorats per tal d'obtenir millors resultats per aquest material.

Paraules clau: física de materials, microscòpia de forces atòmiques, microscòpia òptica, materials de van der Waals.

ODSs: Aquest TFG està relacionat amb els següents Objectius de Desenvolupament Sostenible (SDGs):

Objectius de Desenvolupament Sostenible (ODSs o SDGs)

1. Fi de la es desigualtats		10. Reducció de les desigualtats	
2. Fam zero		11. Ciutats i comunitats sostenibles	
3. Salut i benestar		12. Consum i producció responsables	
4. Educació de qualitat		13. Acció climàtica	
5. Igualtat de gènere		14. Vida submarina	
6. Aigua neta i sanejament		15. Vida terrestre	
7. Energia neta i sostenible	X	16. Pau, justícia i institucions sòlides	
8. Treball digne i creixement econòmic		17. Aliança pels objectius	
9. Indústria, innovació, infraestructures	X		

El contingut d'aquest TFG, part d'un grau universitari de Física, es relaciona amb l'ODS 7, i en particular amb la fita 7.3, ja que la recerca de materials bidimensionals contribueix al desenvolupament de noves tecnologies més eficients energèticament. També es pot relacionar amb l'ODS 9, fita 9.4, degut a que l'estudi de les propietats bidimensionals contribueix al desenvolupament de tecnologies més netes, sostenibles i eficients, i també amb la 9.5, donat que promociona l'avenç de la investigació científica i n'impulsa la innovació en l'àmbit de ciència de materials.

SUPPLEMENTARY MATERIAL

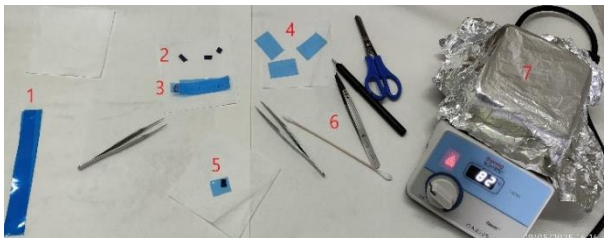
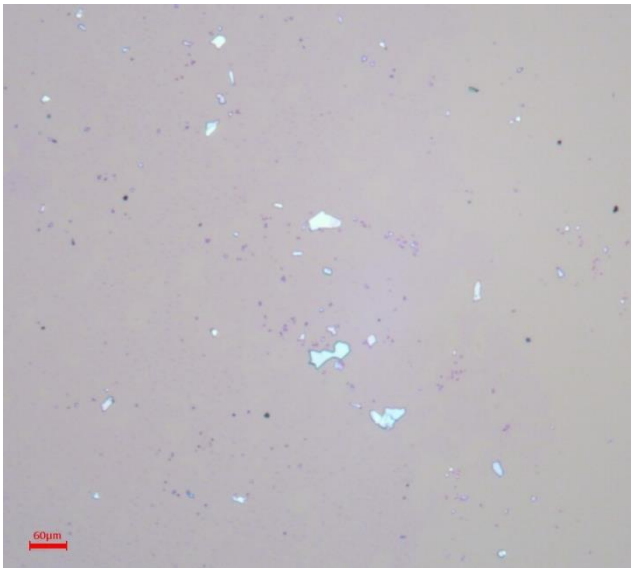


FIG. 6: Image of the tools and equipment used to obtain and transfer the flakes to the substrates. On the left, it can be seen the adhesive tape(1), in the centre, Si/SiO_X substrates(2) and the original strip obtained directly from the bulk sample(3) and three secondary pieces of tape containing few-layer flakes (4), tape stuck into a substrate in the process of transferring the flakes (5), and on the right, some manipulation tools(6) and a hotplate(7).

FIG. 7: An image of the optical microscope (left) as well as the source of light used to illuminate the samples from above (right).



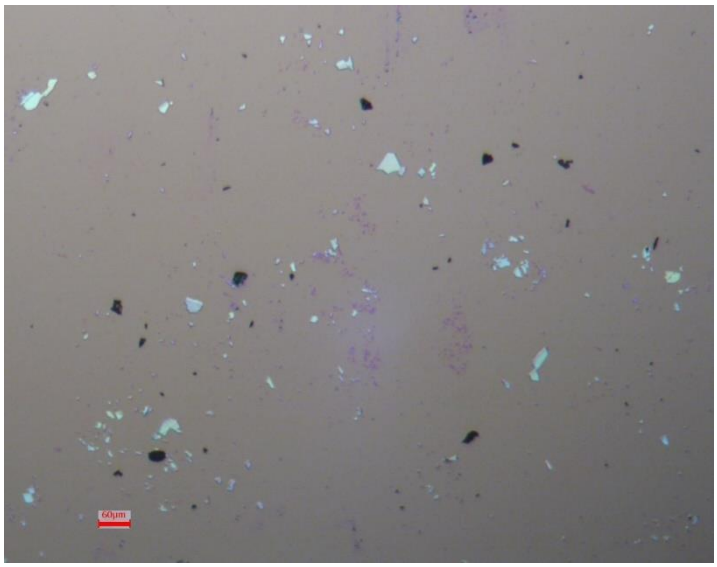
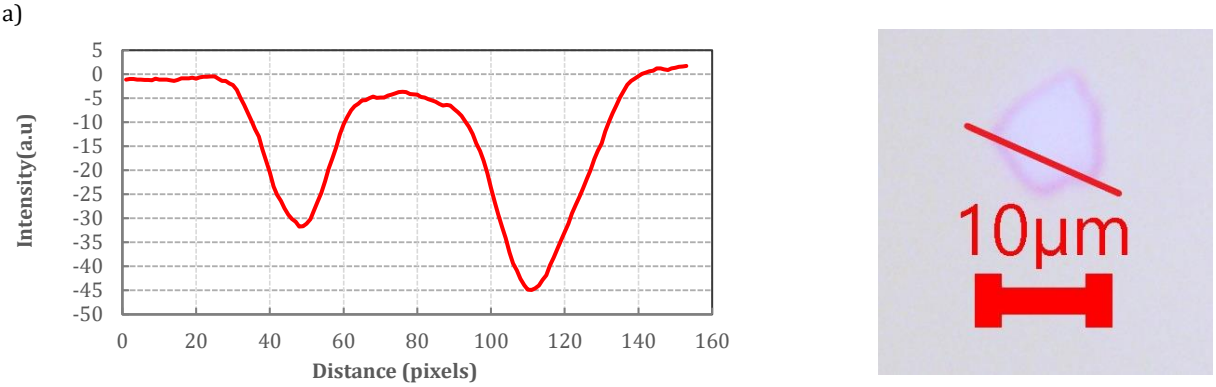


FIG. 8: On the left, an example of a sample of MoS_2 obtained without heating the substrate before exfoliating ("cold sample"). On the right, another sample of MoS_2 but obtained heating the substrate before exfoliating ("hot sample"). It is noticeable that in the "hot sample", there is much more surface of material and there are more thin flakes (purple/darker ones) and they are bigger compared to the ones of the "cold sample".

a)



b)

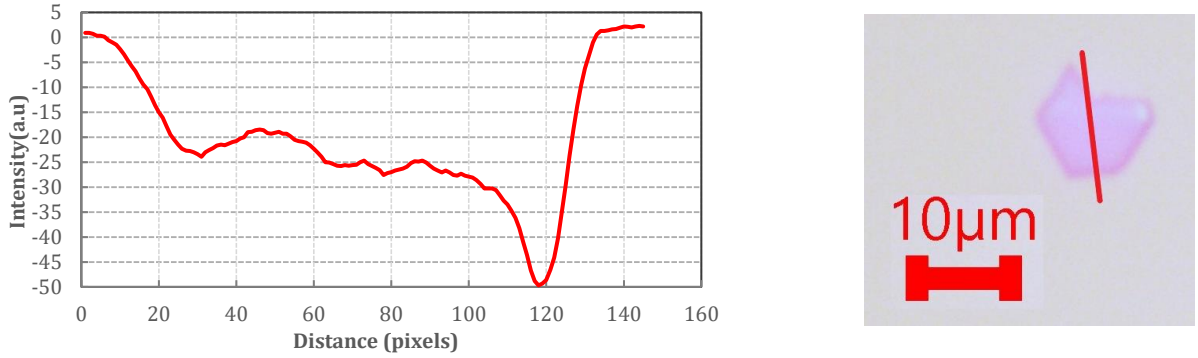


FIG. 9: Intensity profiles of the two MoS_2 flakes characterized with OM and AFM. The spectrometry line goes from left to right and the origin of intensities corresponds to the intensity of the background.

a) b)

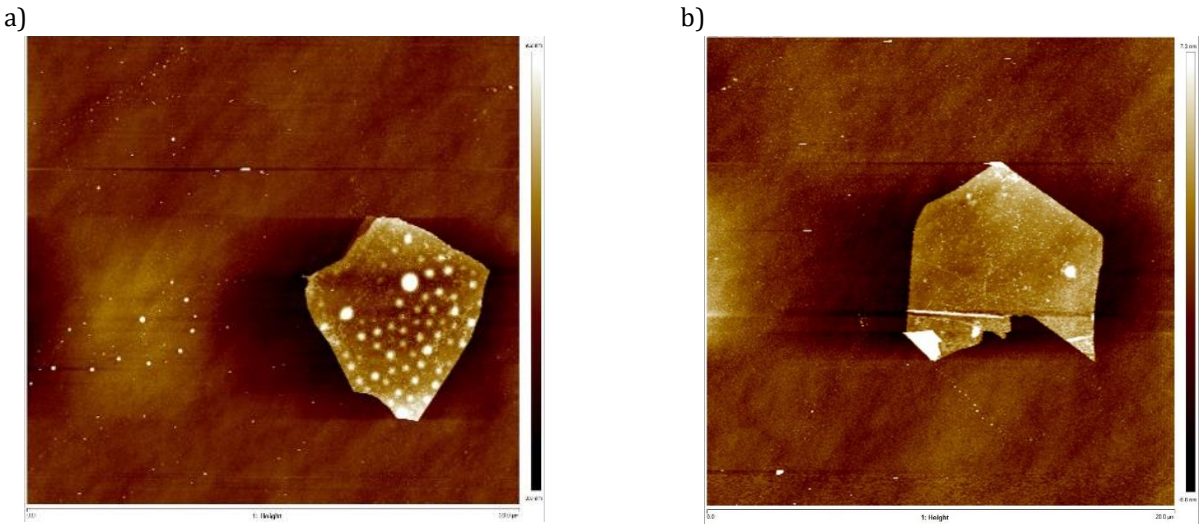
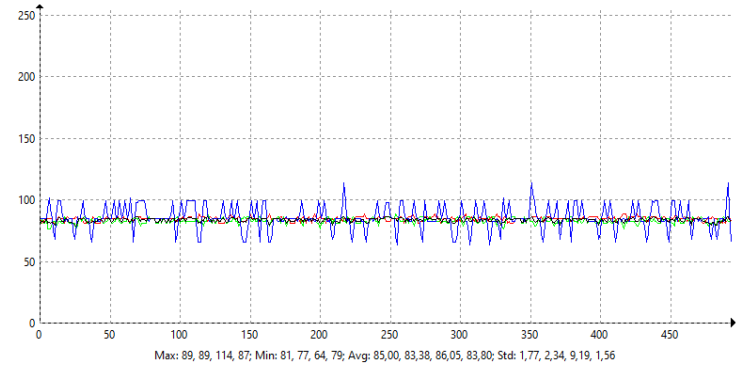


FIG. 10: Images of multi-layered MoS_2 flakes obtained by AFM corresponding to the flakes of FIG. 9.

a)



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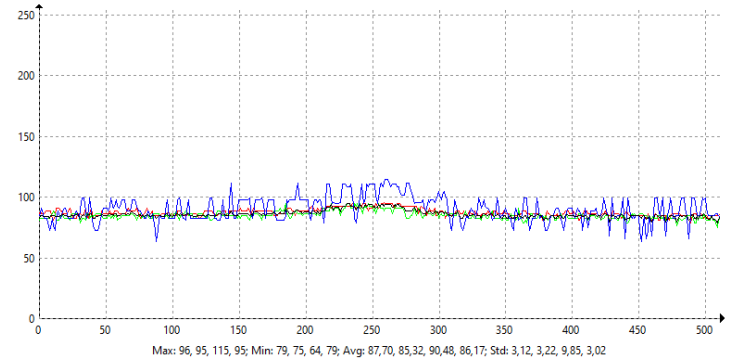


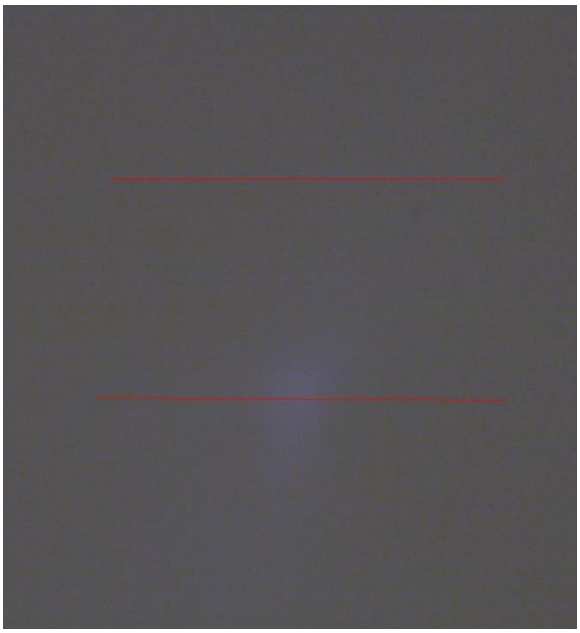
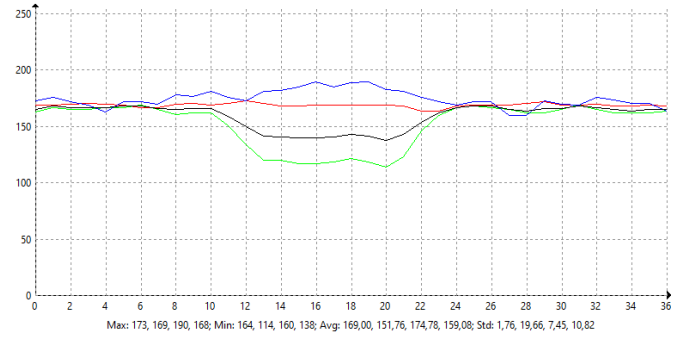


FIG. 11: Image of the background with two measures (right), the upper one corresponds to the intensity profile a) and the other to b). Note that the light spot does indeed affect the intensity profile registered.

a)



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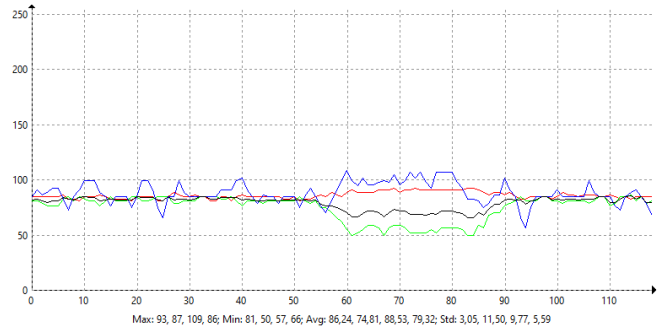

FIG. 12: Intensity profiles in the RGB channels and brightness (black) of the same sample. On a) the magnification used was x20, and in b), x50 was applied. Note the difference in the general level of intensity and the jump that the flake produces.

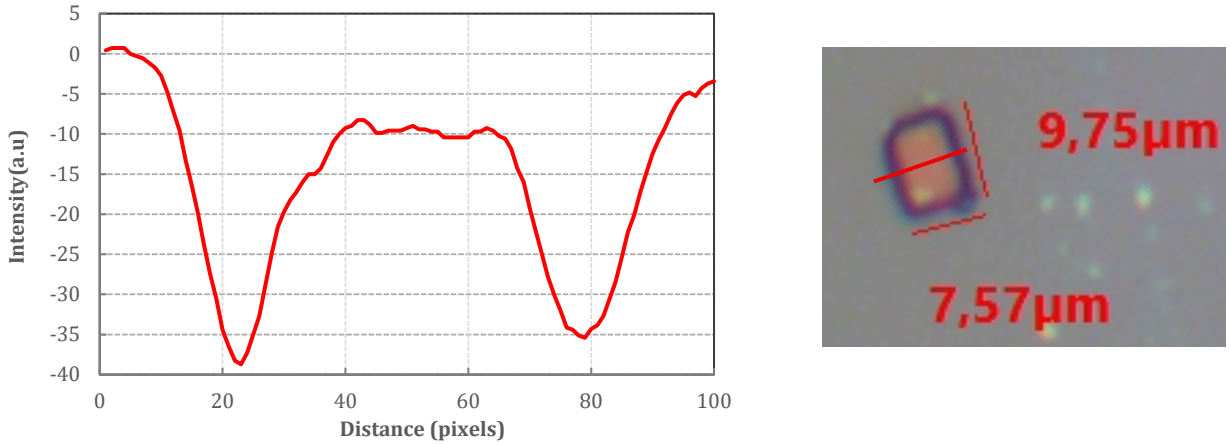

FIG. 13: Intensity profile of the $PtSe_2$ flake characterized by OM (left) and the corresponding image taken on OM with exact measures of the flake (right). The spectrometry line goes from left to right and the origin of intensities corresponds to the intensity of the background. The red line depicts the area where the profile is taken.