



UNIVERSITEIT VAN AMSTERDAM



Bachelor Thesis Natuur- en Sterrenkunde

Creating strain and defects in 2D transition metal dichalcogenides: a deterministic approach towards single photon emitters

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19 June, 2026

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Credits & Period: 15 EC from 17 March, 2026 to 19 June, 2026

Abstract

To be able to fabricate single photon emitters (SPEs) deterministically, the effects of strain and defects on 2D WSe₂, a transition metal dichalcogenide (TMDC), are studied. Optical properties are measured using photoluminescence (PL) (at room temperature and down to 77 K) and Raman spectroscopy (at room temperature). After successful exfoliation of a monolayer of WSe₂ using a gold-assisted exfoliation method, monolayer areas are stamped onto nanostructures to apply strain and irradiated with an electron beam to induce defects. For strain, a lowering of exciton emission energy is observed, and shifting of Raman peaks, both in accordance with literature. The fabrication of narrow nanowrinkles, which contributes to the deterministic placement of strain in a 2D TMDC, is also realised. For defects, a lowering of intensity in PL and a shift in Raman peaks is observed, confirming that defects are present in the material. In further research, a more precise defect creation process could be used, alongside measurements at lower cryogenic temperatures, to reach narrow, SPE-like PL emission. Overall, this work confirms the effects of strain and defects in a 2D TMDC, and paves the way for deterministic creation of SPEs in WSe₂.

Popular Samenvatting

Pas iets meer dan tien jaar geleden is er een nieuw fenomeen ontdekt in halfgeleiders die maar één laag atomen dik zijn: *single photon emission*. Halfgeleiders zijn materialen die een *band gap* hebben in de mogelijke energieën die elektronen in het materiaal kunnen aanslaan, waardoor het pas geleidt als een elektron over deze energie-*gap* is gesprongen. Als een elektron deze sprong maakt, door een foton te absorberen die een laser op het materiaal schijnt, komt de elektron in de hogere energietoestand, en blijft er een 'schijn'-deeltje achter in de grondtoestand, een gat. Deze twee kunnen aan elkaar koppelen door hun tegengestelde ladingen, en worden zo een elektron-gatpaar, of een exciton. Als het elektron daarna weer in de laagste energietoestand komt waarin het kan zijn, bovenin de *band gap*, kunnen het elektron en het gat recombineren, waarna het een foton uitzendt: dit heet photoluminescentie (PL). Dit foton is een *single photon*, en kan worden gebruikt in bijvoorbeeld een quantumcomputer. De reden waarom er 2D-materialen worden gebruikt, is omdat fotonen makkelijk kunnen worden gedetecteerd, omdat er maar een paar atoomlagen zijn. Hét probleem van deze *single photon emitters* (SPE's) is echter dat het exciton op een vooraf bepaalde plek moet worden gebracht, zodat het kan worden gebruikt in toepassingen. Om de SPE's op een gekozen plek te krijgen, wordt de energiestructuur van de halfgeleider aangepast. Dit wordt gedaan door een combinatie van het oprekken (of indrukken) van het materiaal, en het beschadigen van het materiaal, zodat er bijvoorbeeld gaten in de atoomstructuur ontstaan. In ander onderzoek lukt het om een SPE te maken op deze manier, en zelfs om deze in chips te plaatsen. Om meer te weten te komen over de afzonderlijke mechanismen tijdens het proces van een SPE wordt er in dit onderzoek gekeken naar wat het effect is van rek en beschadigingen op een bepaalde 2D halfgeleider: wolfraam diselenide (WSe_2). Het materiaal is op kleine structuren geplaatst om het op te rekken, en er zijn beschadigingen aangebracht door een elektronenstraal op het materiaal te gebruiken. Door te kijken naar hoe bijvoorbeeld het signaal van recombinerende excitons (het PL-signaal) verandert, wordt het mogelijk om te zien wat er met het materiaal gebeurt. Zo is er in dit onderzoek waargenomen dat de emissie-energie van een elektron daalt als er rek wordt toegepast, en dat de sterkte van het PL-signaal omlaag gaat als er beschadigingen worden aangebracht. Deze uitkomsten helpen op de weg naar het maken van deze SPE's op plekken waar ze gewild worden: het geeft een beeld van hoe het materiaal verandert tijdens het proces naar SPE's. In verder onderzoek kunnen er lagere meettemperaturen worden gebruikt, omdat SPE's zich meestal alleen tonen op een temperatuur van 4 Kelvin, of net daar boven.

Contents

Abstract	1
Popular Samenvatting	2
1 Introduction	4
2 Theory	6
2.1 Transition metal dichalcogenides	6
2.2 Excitons, photoluminescence and single photon emission	7
2.3 Photoluminescence characterisation	10
2.4 Raman spectroscopy	13
3 Methods	15
3.1 Monolayer fabrication	15
3.2 Strain field generation	16
3.3 Defect creation	17
3.4 Experimental setup for optical measurements	19
4 Results & Discussion	21
4.1 Sample 1: Confirmation of strained WSe ₂	21
4.2 Sample 2: Monolayer & bilayer WSe ₂ characterisation	26
4.3 Sample 3: Combined effects of strain and defects	28
5 Conclusions & Outlook	34
Acknowledgments	35
References	36
A Appendix	38
A.1 Additional monolayer exfoliation results	38
A.2 Additional results for sample 3	39

1

Introduction

Single photon emission, in which a material emits only one photon at a time with a specific wavelength, has been a much discussed topic over the last years [1]. The nature of a single photon emitter (SPE) enables numerous useful applications, for example in the development of quantum technology, to create qubits in quantum information systems. In the past, a few methods of producing hosts for SPEs have already been shown, for example quantum dots [2]. These methods rely on a production process of SPEs in which deterministic placement is challenging, holding back the site-specificity that is needed to integrate the process into already existing technology, for example telecommunication [3].

Promising candidates for the deterministic production of SPEs are two-dimensional (2D) materials, in particular transition metal dichalcogenides (TMDCs), which are semiconductors and have a direct band gap in their monolayer form. Because layers of atoms are only held together by their Van der Waals interaction in between planes, it is easy to exfoliate one layer of atoms off the bulk crystal. Due to the thickness of only one (or a few) atoms, photons are easily extractable, site-specific creation of SPEs becomes possible, and the integration into existing technology becomes simpler [2].

To be able to fabricate SPEs deterministically in a 2D TMDC, two things are needed: strain and defects [4]. When tensile strain is applied to a layer (or two layers) of 2D material, the band gap shrinks because of the atoms being further apart, creating a place in the material for excitons to funnel to. In combination with the creation of energy states below the conduction band due to a defect, both strain and defects can couple to one another, resulting in states that produce SPE sites [2]. Only one exciton is emitted because of the exciton-exciton interaction: excitons repel each other out of the created quantum trap [5]. The strain and defects can be engineered to be localised, resulting in an SPE that can in principle be placed in a 2D TMDC, wherever one would want the SPE to be.

During the last ten years, research has confirmed that a combination of strain and defects can indeed deterministically create SPEs [2, 6, 7]. Integration with optical components, like waveguides, has been realised [8], and electric tunability, to change the emission energy of an SPE, as well [9]. Tying into previous research to fabricate SPEs deterministically, the goal of this thesis is to focus on the contributions of strain and defects in 2D tungsten diselenide (WSe_2). By analysing both photoluminescence and Raman spectroscopy data, the following research questions are investigated: *What are the optical signatures of strain and defects in WSe_2 , and how do these contribute to deterministic fabrication of single photon emitters?*

This thesis starts with an introduction to 2D TMDCs, excitons, strain, defects, photoluminescence and Raman spectroscopy. After this, the methods used will be explained to conduct the experiments: monolayer exfoliation, strain generation and defect creation. Then, results are shown and implications are discussed: the effects of strain and defects on optical properties. Lastly, the conclusion follows.

2

Theory

2.1. Transition metal dichalcogenides

Transition metal dichalcogenides (TMDCs) are a class of materials that have a chemical composition of the form of MX_2 : one transition metal atom M (tungsten, for example), and two chalcogen atoms X (sulphur or selenium, for example) [10]. The TMDC that is used for this thesis is tungsten diselenide (WSe_2), of which a single layer is shown in Fig. 2.1.

Because the interactions between the atoms are much weaker between different planes of the material than inside a single plane, it is easy to create a monolayer of a TMDC. This is done by exfoliation of a single layer off the bulk material [11], which is described in the Methods chapter. The two-dimensionality of the material also makes it possible to integrate the material into already existing technology and extract photons more efficiently [2].

WSe_2 is a semiconducting material, which has a band structure that has a separation between the valence band (VB) and the conduction band (CB): a band gap. This band gap is indirect in the bulk material, which means that the top of the VB and the bottom of the CB do not have the same momentum value in reciprocal space (see Fig. 2.2). If an electron were to be excited from the VB to the CB and fall back again, both a photon and a phonon would have to be emitted to overcome the energy and the momentum gap, respectively [12]. When the material transitions to only one layer of atoms, the indirect band gap changes to a direct one, which means that no phonon is required for the transition to occur. This makes it easier for photons to recombine to the VB, which makes the photon generation process more efficient [7].

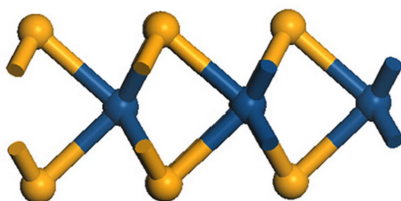


Figure 2.1: A monolayer of WSe_2 , with the tungsten atoms in blue and the selenium atoms in orange. Figure adapted from [13].

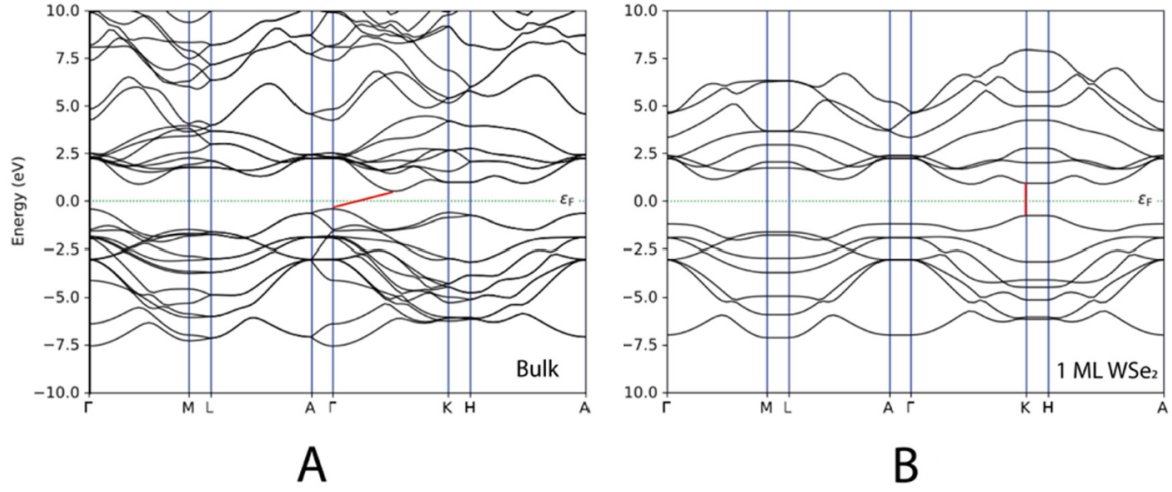


Figure 2.2: **A.** Bulk WSe₂ with an indirect band gap, and **B.** monolayer WSe₂ with a direct band gap. Figure adapted from [14].

2.2. Excitons, photoluminescence and single photon emission

As mentioned before, it is possible to excite an electron from the VB to the CB. The way to do this is to provide the system with a photon of sufficient energy to absorb. This can be done by using a laser. When a laser shines on the material, an electron absorbs the energy of a photon from the laser, causing the electron to be excited to the CB. This process is schematically shown on the left in Fig. 2.3. Because of the fact that electrons will naturally settle into the lowest possible energy state, and because of the presence of the band gap, almost all electrons will be in the VB when there is no excitation, leaving the CB empty. When an electron is then excited into the CB, a hole is left behind in the VB. Because of their opposed charge, the electron and hole can couple to one another by their Coulomb interaction, which results in an electron-hole pair: an exciton [15].

Because the energy of a laser can be higher than the band gap energy, the electron might end up a bit higher in the CB. Then, the electron relaxes to the bottom of the CB by emitting phonons. Separately, the hole does the same, but to the top of the VB. This process is shown by the curved arrows in Fig. 2.3. Because of their opposed charge, the electron and hole couple to one another, forming an exciton. The energy of an exciton is given by

$$E_{exc} = E_{gap} - E_{binding}, \quad (2.1)$$

with E_{gap} the band gap energy and $E_{binding}$ the binding energy. The band gap energy is the energy difference between the top of the VB and the bottom of the CB, which is also the energy that is required to create the electron-hole pair. The binding energy is the energy due to the Coulomb interaction between the electron and hole [15]. The resulting exciton energy lies below the band gap energy, as shown in Fig. 2.3. Since the binding energy is partly governed by the possible excited states n of the excitons, and decreases with higher excited state, the binding energies for different excited states are discretely separated. The resulting possible exciton levels are shown in Fig. 2.3. The binding energy largely affects what energy the resulting exciton will have. In one work [16], the binding energy in monolayer WSe₂ at

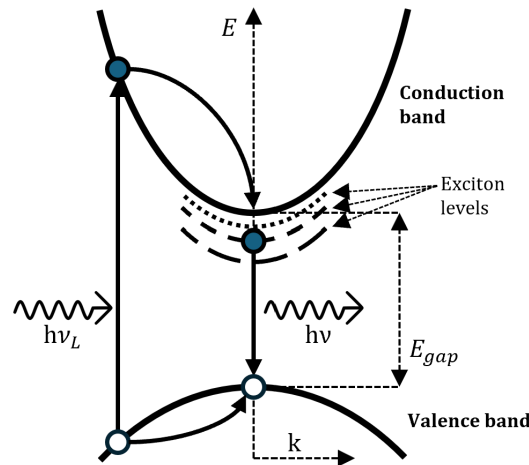


Figure 2.3: The process of photoluminescence. An electron gets excited into the conduction band and forms an electron-hole pair, after which it relaxes to just below the conduction band and recombines radiatively.

4 K was measured to be 0.79 eV, with a band gap of 2.53 eV, resulting in an exciton energy of 1.74 eV.

When an electron and a hole recombine, a photon is emitted. The process of excitation and recombination of electron-hole pairs is called photoluminescence (PL) [15].

Alongside excitons, different kinds of interactions between electrons and holes can be created after excitation. If an exciton couples to an additional electron or hole, a trion can be formed, consisting of either two electrons and one hole, or one electron and two holes. If two excitons couple to each other, a bi-exciton can form. These different created particles also contribute to the PL spectrum of emitted photon energies in a semiconductor [17].

If an individual exciton is funnelled to the bottom of the conduction band and couples to a lower energy defect state within the band gap, there is the possibility to emit a single photon when recombining, with a specific wavelength belonging to it. This process is called single photon emission [6]. The localisation of an exciton can be done in a number of ways, but the most promising combination of processes to fabricate these single photon emitters (SPEs) deterministically is by creating strain and defects in the material. Both together can alter the band structure and availability of electronic states of the material, which can be used to localise an exciton and create SPEs [18].

The concept of applying local strain to a 2D material is visualised in Fig. 2.4. When a single layer of WSe₂ is placed onto a material that has ‘bumps’ on it, called nanostructures, the monolayer will deform. This deformation will create local strain in the material, which results in a change of the band structure at that position. Tensile strain shrinks the band gap, and compressive strain widens it. The tensile strain might act as a mechanism to funnel excitons to a certain position, as shown in Fig. 2.4b. In combination with an energy state within the band gap, the exciton can couple to this state and emit a photon. Thus, at strained regions, the chance that there will be an SPE is higher than at unstrained regions [6]. The reason why only one exciton can couple to such a state inside the band gap and not more is the exciton-exciton interaction. The Coulomb force is repulsive between two excitons, preventing that more than one exciton can couple to a defect state [5].

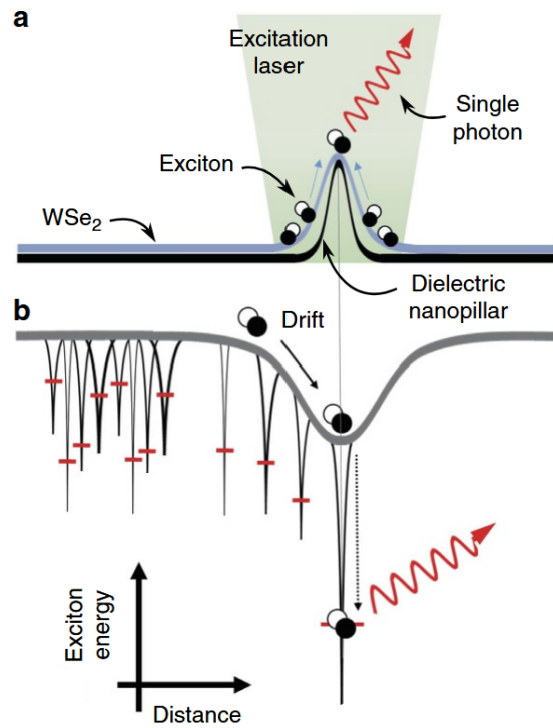


Figure 2.4: Applying strain to a monolayer of WSe_2 . **a.** A monolayer is deformed by a nanostructure, causing excitons to funnel there. **b.** The band gap becomes smaller due to the strain. Excitons funnel into the created trap. Figure adapted from [6].

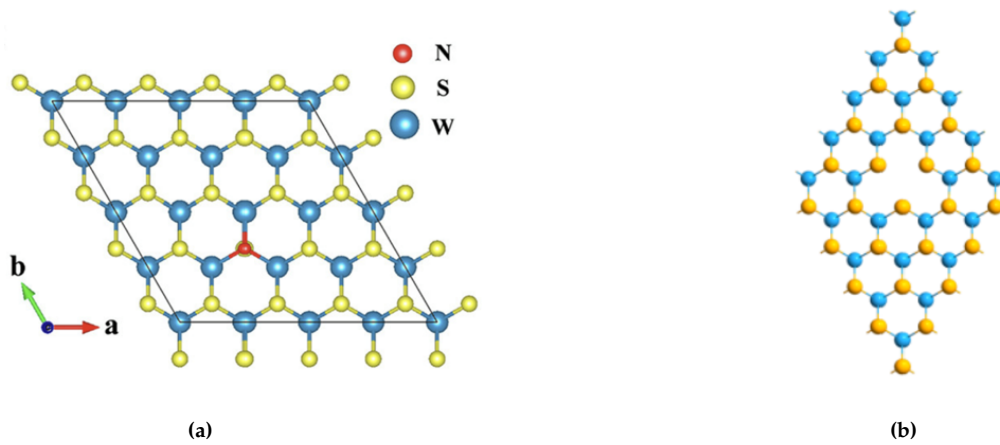


Figure 2.5: The two main categories of defects in a 2D TMDC: **(a)** impurities and **(b)** vacancies. In panel **(a)**, a sulphur atom is substituted by a nitrogen atom in WS_2 . In panel **(b)**, a tungsten atom is removed from WSe_2 . Figures adapted from [19] and [2], respectively.

The reason why strain fabrication is such an important process for the creation of SPEs is the site-specificity. Because nanostructures can be placed at pre-determined positions, along with a carefully placed monolayer of material on top, the position of an SPE can be engineered. This is useful for integration into quantum technology [6]. The fabrication process of an array of nanostructures, to induce strain, will be discussed in the Methods chapter.

Alongside strain fabrication, inducing defects in 2D materials is also required to be able to deterministically create SPEs. A material can have defects in a number of different ways, but the main types can be grouped into two categories: impurities and vacancies [4]. An impurity in a material is a substitution of an atom by another atom. For example, in Fig. 2.5a it is shown that in WS_2 , a sulphur atom is substituted by a nitrogen atom. Creating impurities can be done in numerous ways, but one of them is a plasma treatment [19].

An atom can also be completely removed from a material, causing a vacancy. A method that is widely used to achieve this is electron beam irradiance [2, 7]. An electron beam is directed at a specific position of the material, for example at strained regions, and knocks out one or a few atoms. An example of the remaining lattice structure is shown in Fig. 2.5b.

After a defect is created, the availability of electronic states in the band structure changes. A defect creates extra electronic states for an exciton to be in, which are within the band gap [4]. In combination with applying strain, defect fabrication in a 2D material can thus be used as a method to create SPEs in a controlled way. An exciton can be funnelled to a strained area, at which it can couple to a defect state and emit a single photon.

2.3. Photoluminescence characterisation

After excitation of a TMDC, photons within a range of energies are emitted. Together, these photons make up the PL emission spectrum [15]. A typical PL spectrum for a pristine monolayer of WSe_2 at room temperature is shown in Fig. 2.6a. This spectrum is characterised by a Lorentzian line shape with a line width of ~ 40 meV. The PL spectrum of a monolayer of TMDC exists of two main contributors: excitons and trions. Because the binding energy between the three components of a trion (an electron, a hole, and an additional electron or hole) is higher than the two components of an exciton, the resulting trion emission energy becomes lower than the exciton energy. The peak at a higher energy (fitted in green) in the corresponding PL spectrum can therefore be considered to be excitonic. The smaller peak (in red) at a lower energy than the exciton is associated with the trion contribution [20]. These red and green peaks are fitted to the data to get a clearer insight to the specific contributions to the PL spectrum. The fitting procedure of both peaks is described in section 4.1. A reason why the trion peak is lower and broader than the exciton peak is the different dynamics between both. A reason for broadness of the exciton peak is the interactions with charges around excitons, causing it to have a different, broader energy range [21]. Since a trion is positively or negatively charged, instead of neutral (which an exciton is), there might be stronger interactions with charges than excitons, with a broader emission energy range as a result. The lower intensity of the trion peak can be associated with the fact that trions decay more non-radiatively than excitons do. Since a PL signal is the signal from radiatively decaying excitons and trions, the exciton peak is higher than the trion peak [22].

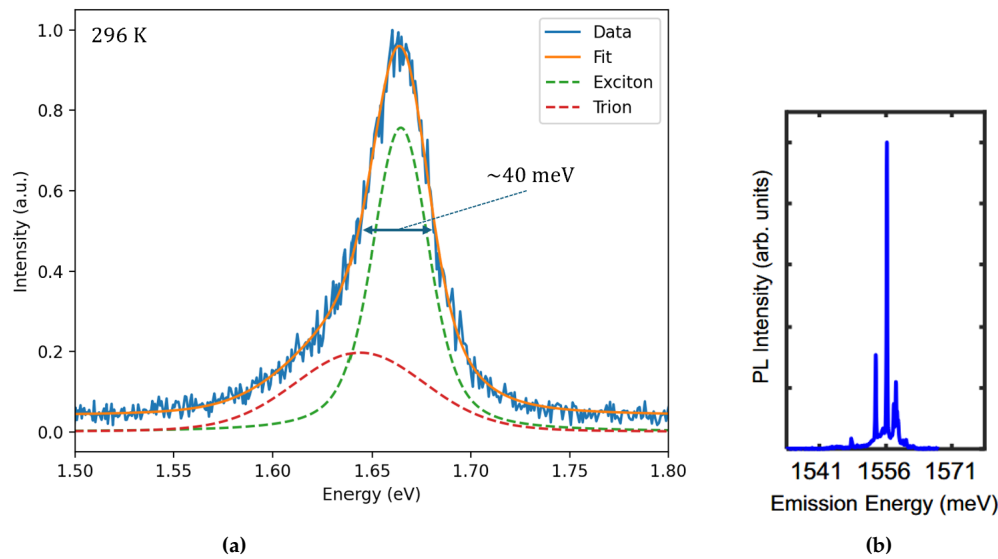


Figure 2.6: (a) A PL spectrum for a pristine monolayer of WSe₂ at room temperature. The width of the peak is ~ 40 meV. The data is fitted to a double Voigt curve; this is described in section 4.1. The red curve can be associated with trion contributions, and the green curve with excitons. (b) An SPE PL spectrum at 5 K, with one distinct narrow peak (width ~ 75 μ eV). Panel (b) adapted from [2].

The PL spectrum of an SPE looks vastly different. The broad range of PL energies is in the case of an SPE reduced to a single (or sometimes double) sharp peak of PL, centered at one corresponding energy: the energy of the defect state within the band gap, which the exciton couples to. An example of the PL spectrum of an SPE is shown in Fig. 2.6b [2]. The sharp peak, on average only 75 μ eV wide, is the PL peak that is associated with SPEs, and is created by applying both strain and defects to the material. An additional necessity for the creation of these narrow peaks is to cool the material to cryogenic temperatures. When the material is cooled, the exciton-phonon scattering inside the material is decreased. This effect entails interactions between excitons and phonons in the material, causing an exciton to emit with a different energy after interacting with a phonon. This scattering process is reduced at lower temperature, making the range of possible exciton energies narrower, until it is as narrow as Fig. 2.6b [23, 24]. It has been shown that usually, the combined effect of strain and defects in order to find SPEs can only hold up to 30 K [4].

Characterising the PL emission spectrum is crucial in the process of understanding what the separate effects of strain and defects are on a monolayer of a TMDC. To be able to transition to a deterministic SPE fabrication process, the separate contributions of strain and defects to the PL spectrum need to be studied, to get insights about whether local strain and local defects are created at a pre-determined position.

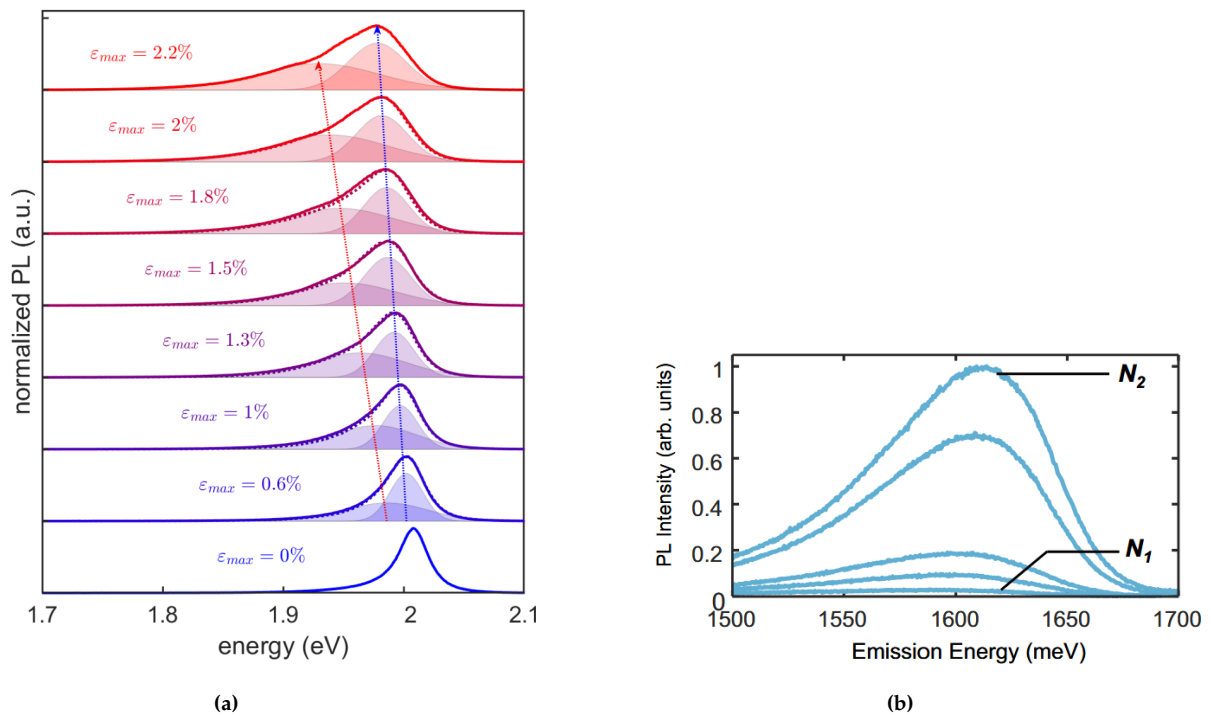


Figure 2.7: (a) The PL spectrum shifts to a lower energy when strain is applied to a monolayer of WS₂ at room temperature. The fitted peaks under the curves are the trion (left) and exciton (right) contributions [20]. (b) When defects are induced, a ‘defect band’ becomes visible at cryogenic temperatures (here at 5 K). As the electron irradiation dose increases (from N₁ to N₂), the amplitude of this band increases as well: there are more defect states [2]. Figures adapted from [20] and [2], respectively.

Strain

As mentioned, the band gap of WSe₂ becomes smaller when tensile strain is applied. Because of this, the electron and hole are closer in energy, which results in a lower photon energy when the electron and hole recombine. This is directly visible in the PL spectrum of a strained monolayer. In Fig. 2.7a, Harats *et al.* [20] showed that applying strain does indeed shift the exciton and trion contributions to the PL spectrum to a lower energy. With increasing mechanical strain ϵ , the PL peak shifts to lower energy. It is also observed that the trionic contribution to the PL spectrum is shifted more than the excitonic part, as is also visible in Fig. 2.7a.

Defects

With the creation of defects in a material, the availability of electronic states within the band gap goes up. These new energy states become visible in the PL spectrum at cryogenic temperature. As seen in Fig. 2.7b, a 2D TMDC which is irradiated with an electron beam has a so-called ‘defect band’: a range of PL energies that originate from defects. As the electron dose increases, the amplitude of this defect band emission increases as well. This is explained by the electron beam making more defect sites for the excitons to couple to [2].

2.4. Raman spectroscopy

A different way of examining the effect of strain and defects on a monolayer of a TMDC is to analyse the shifts in its Raman peaks. When a photon is sent from a laser to a material, it sometimes interacts with phonons, which are vibrations of the atomic lattice. The frequency of the photon changes because of the phonon, resulting in a shift between the incoming and outgoing photon frequency. This shift is called a Raman shift, and can be calculated by

$$\bar{\nu} = \frac{10^7}{\lambda_0} - \frac{10^7}{\lambda_1}, \quad (2.2)$$

with $\bar{\nu}$ the Raman shift in cm^{-1} , λ_0 the incoming photon wavelength and λ_1 the outgoing photon wavelength, both in nm. The cm^{-1} is the conventional unit to express Raman shift, hence the factors of 10^7 in the equation [15].

Because each material has a different atomic structure, resulting in different phonon interactions, each material has one (or more) Raman peaks specific to that material: their ‘finger prints’. The peaks that are associated with WSe_2 are shown in Fig. 2.8a. The atomic vibrations for WSe_2 are in the out-of-plane direction, and one work reported the energy of these vibrations to be on the order of 10^{-7} eV/atom [25].

For a different kind of TMDC, molybdenum disulphide (MoS_2), Parkin *et al.* [26] showed that the Raman peaks shift when sulphur vacancies are induced by an electron beam. This is shown in Fig. 2.8b. As the electron dose increases, the shifts increase as well. Although these shifts are observed for a different kind of TMDC than the one being used in this thesis, the shift might also be visible for the Raman peaks of WSe_2 . The Raman shift, along with the ‘defect band’ in the PL spectrum, thus forms a complementary probe of the effect of defects in 2D WSe_2 .

It is also possible to see the effect of strain in the Raman peaks. Dadgar *et al.* [27] showed that Raman peaks also shift when applying increasing strain to a TMDC. For example, the high Raman peak in Fig. 2.8a shifted from 251.6 cm^{-1} to 250.5 cm^{-1} when going from 0% to 3% tensile strain. For both strain and defects, the shift in Raman peaks is on the order of $1\text{-}10 \text{ cm}^{-1}$ [26, 27].

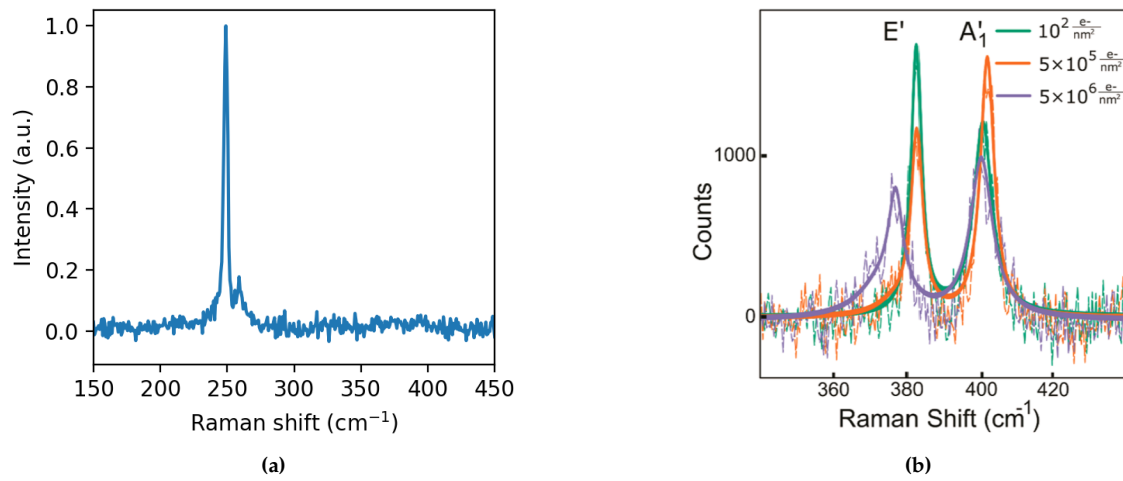


Figure 2.8: (a) The Raman peaks for a pristine monolayer of WSe₂. The higher peak is centered around 248.9 cm⁻¹, and the small peak is centered around 258.8 cm⁻¹. (b) Raman peaks shifting in a monolayer of MoS₂. Higher electron dose makes the peaks shift and change in intensity. Panel (b) adapted from [26].

3

Methods

3.1. Monolayer fabrication

For the fabrication of a monolayer of WSe_2 , a gold-assisted exfoliation method is used, which is inspired by the work of Velický *et al.* [11]. The process is schematically shown in Fig. 3.1. The reason behind this method is the smoothness of the gold. Because the gold is deposited on a smooth silicon wafer, the gold smoothens as well. The smoothness of the gold helps with picking up the monolayer from the bulk material: it makes sure that the exfoliated monolayer is as large as possible, and the Van der Waals interaction makes sure that only one layer of WSe_2 atoms interacts with the gold layer.

First, a piece of thermal release tape (TRT) is cut into a square shape, after which it is pressed on top of the wafer consisting of a silicon substrate, a layer of gold, and a layer of polymethyl methacrylate (PMMA), which is a polymer that protects the gold and provides mechanical stability. Then, a piece of bulk WSe_2 is obtained by the scotch tape method. This is a method in which a piece of bulk material gets cleaved between two pieces of tape, resulting in a thinner piece of material. After cleaving, the stack of TRT, PMMA and gold is lifted off of the silicon wafer, and pushed down on the WSe_2 . After pushing the stack down on the bulk material, the resulting stack is carefully lifted off of the bulk material, and there will (ideally) be a large area of monolayer of WSe_2 on the bottom of the gold. In the literature used [11], the monolayer areas are up to the order of a few millimeters. The stack with the monolayer attached to it is then placed onto a quartz substrate (SiO_2).

It is important to know what the size of the created monolayer is, because a large enough area of it is required to maximise the number of SPEs later on. Therefore, after the stack of materials is placed onto the substrate, the fabricated monolayer is inspected under a microscope. Monolayer areas of a minimum of $50\text{ }\mu\text{m}$ by $50\text{ }\mu\text{m}$ are chosen to use during the rest of the research. These are selected by eye using the microscope, looking for a certain colour and opacity the layer has: the thinner the layer, the more light it lets through.

Having identified a substrate containing a $50\text{ }\mu\text{m}$ by $50\text{ }\mu\text{m}$ monolayer of WSe_2 , the rest of the used materials has to be removed. First, the sample is placed on top of a hot plate, which causes the TRT to release. After that, the stack is dipped into a few solvents in the following order: acetone for 1 minute, 2-propanol (IPA) for 15 seconds, gold etchant (KI) for 2 minutes, water for 10 seconds, a second water for 10 seconds and IPA again for 10 seconds. The acetone makes sure that the PMMA is etched, and the water and IPA after the gold etchant make sure that there is minimal residue from the etchant. After a quick dry with a nitrogen gun, the final result is reached: monolayer WSe_2 on an SiO_2 substrate.

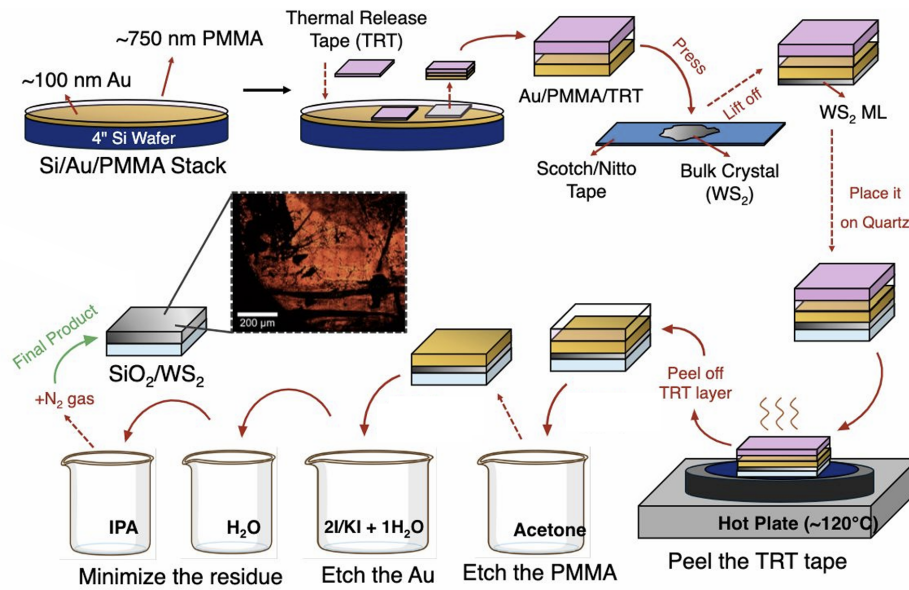


Figure 3.1: A visualisation of the gold-assisted exfoliation process. This graphic differs slightly from the written text: the order of liquids used is different, and the material used for this thesis is WSe_2 , not WS_2 .

3.2. Strain field generation

To create strain in the material, arrays of nanostructures are used. One of the most widely used methods for creating arrays of nanostructures is electron beam lithography (EBL) [2, 6, 7]. A substrate is coated with e-beam resist, after which a pattern is written in it, using a tightly focussed beam of high energy electrons. After developing the resist, the patterned resist remains on the substrate, in the form of nanostructures. A nanostructure shape that is used often is a cylindrical nanopillar (NP), ranging from 40 to 200 nm in height. A challenge with this shape of nanostructure in terms of creating well-positioned SPEs is that the strained area is created around it. As seen in Fig. 3.2a, strain in the form of nanowrinkles, where the material is ‘folded over’, is created in an arbitrary direction, somewhere around a NP. To overcome this, Paralakis *et al.* [7] designed shapes of nanostructures which are different, and might help the strained points to be in a certain direction, instead of randomly oriented around the strain area. The concept of one of the shapes, a three-pointed star (TS), is seen in Fig. 3.2b. The vertices of the star deform the monolayer, which results in nanowrinkles, inducing strain. At these specific places, the PL spectra should shift, as theory predicts [20].

In this thesis, multiple arrays with different shapes of nanostructures are used to create strain fields. One of the patterns used in EBL to create such an array is shown in Fig. 3.2c. A $20\ \mu\text{m}$ by $20\ \mu\text{m}$ area is visible, showing multiple arrays of NPs, along TSs, a five-pointed star (FS) and bow ties (BTs). The latter three shapes are adopted from Paralakis *et al.* [7]. Along the vertices of these shapes, strain is expected to become visible (at the three points of the TS, at the five points of the FS, and in between the two vertices of the BT). The height of the used nanostructures is 160 and 200 nm for the first and third fabricated sample, respectively.

To get a monolayer on top of the fabricated nanostructures, a dry-transfer technique is used [28]. By pressing a stamp (heated to $70\ ^\circ\text{C}$) made out of polyethylene (kitchen wrap) on the monolayer WSe_2 and heating the stamp (with WSe_2) to $140\ ^\circ\text{C}$, the material clings to

the stamp. Then, after cooling the stamp to 70 °C again, the stamp (with WSe₂ attached to it) can be pressed down on the nanostructures and heated to 150 °C, after which the stamp gets dragged away from the stamp area, which leaves the WSe₂ at the area. Then, the residue of the stamp gets removed. What is left, is a stack of two parts: the nanostructures with the monolayer WSe₂ on top.

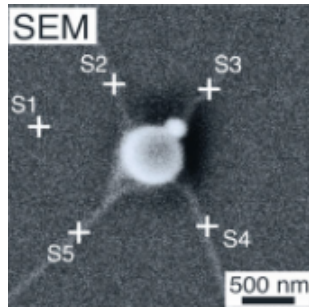
Hexagonal boron nitride encapsulation

It is possible to use the process of stamping a material to create stacks of 2D materials. These are called heterostructures [4]. The concept of layering 2D materials is used in this thesis. By stamping a thin layer (~13 nm) of hexagonal boron nitride (hBN) on top of the used monolayer of WSe₂, the monolayer is mechanically supported by the extra layer [2]. Potential damages from stamping the material on nanostructures are prevented in this way.

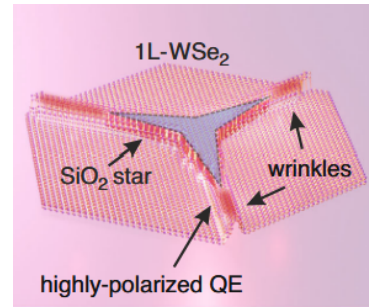
3.3. Defect creation

As shortly mentioned in section 2.2, defects can be created by using an electron beam. This is also used for this thesis. By varying the kinetic energy of the electrons (measured in keV) and the electron dose (measured in electrons per area, or Coulomb per area), the amount of atoms that get knocked out by an electron beam, creating defects, can be controlled [4]. A balance between the two (energy and number of electrons) has to be found to reach an efficient vacancy production process. In literature, a variety of different energies and electron doses are used, with varying results. For example, Parto *et al.* [2] used a range of doses from 8×10^4 to 10^6 electrons/ μm^2 with an electron energy of 100 keV. Successfully created defects by electron beam irradiance has also been shown by Xu *et al.* [18], using a dose of around 10^5 electrons/ μm^2 and electron energy of 30 keV. Clearly, there is no straightforward recipe for using an electron beam to induce defects yet.

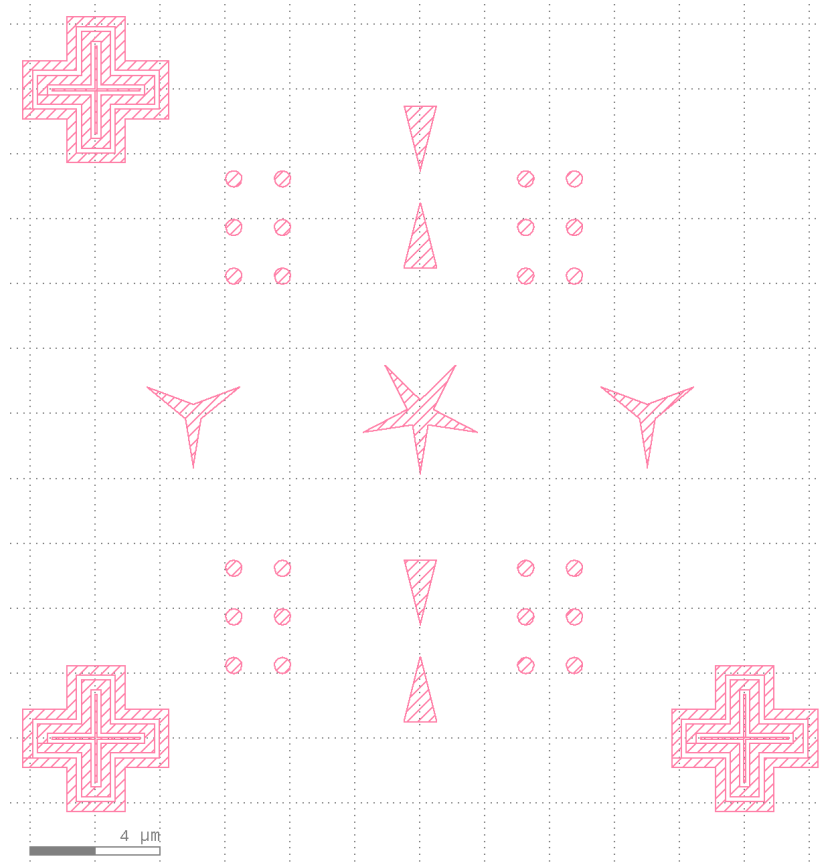
To be sure that the probability of knocking out atoms is sufficiently high, a large electron dose is used for this thesis, ranging from $1.000 \mu\text{C}/\text{cm}^2$ to $\sim 100.000 \mu\text{C}/\text{cm}^2$ (on the order of 10^7 - 10^9 electrons/ μm^2). The energy of the electrons used ranges from 50 to 100 keV.



(a) A scanning electron microscope (SEM) image of a NP with different orientations of created strain. Sites S2-S5 display shifted PL spectra. Figure adapted from [7].



(b) A visualisation of the effect of a TS on a monolayer. The monolayer deforms at the vertices, creating nanowrinkles. Figure adapted from [7].



(c) One of the used arrays of nanostructures. There are NPs, TSs, BTs and a FS visible. The big areas in the three corners are alignment markers for the EBL tool. One square is $2\ \mu\text{m}$ by $2\ \mu\text{m}$.

Figure 3.2

3.4. Experimental setup for optical measurements

The characterisation of the mentioned optical properties in sections 2.3 (PL) and 2.4 (Raman shifts) is performed by using the WITec alpha300 confocal Raman microscope, of which a schematic is shown in Fig. 3.3. A laser with a wavelength of 532 nm is used in the setup. The laser is used to excite the WSe₂ and produce PL, and the laser photons scattered by the material lattice (Raman shifts) are also measured. These processes happen at the same time, but different settings of the WITec are optimised to record the two different signals independently. A sample is mounted on a piezo stage, which can be moved using the WITec software, with nanometer precision. The laser travels through a few beam splitters and is then focused by an objective. For most measurements, an objective of 100x magnification (with a numerical aperture of 0.9, which means that the maximum working angle is $\sim 128^\circ$ [29]) is used, to ensure the highest resolution when the laser is focused on the sample. The laser hits the sample, and the emitted and scattered light travels back through the objective, via a dichroic mirror which filters out all wavelengths below the laser wavelength of 532 nm, to a spectrometer, which collects the signal. It is also possible to move a camera into the beam path, and look at the sample and take pictures. For taking these pictures, additional objectives of 5x, 20x and 50x magnification are used, alongside an LED as a light source.

Using the piezo stage, a map of spectra can be taken as well. By selecting an area on the sample, the WITec can take PL or Raman spectra for each pixel in the given area. In this way, spatial differences of PL and Raman data in different areas of the sample can be investigated. This is needed for the characterisation of shifts of PL peaks at different positions due to strain, for example.

Cooling the sample

To be able to get a narrow SPE-like PL signal, the exciton has to remain trapped in a certain position of the material. However, the trapping potential, which is the potential by the created quantum trap (by strain and defects), is not high enough to confine an exciton at room temperature: the thermal energy of the exciton might overcome the potential barrier. Therefore, the thermal energy of the exciton has to be reduced for the exciton to be well confined inside the quantum trap [2]. This is done by using a Linkam stage (Linkam THMS600), which can be mounted in the WITec setup, so that PL emission and Raman shifts can be measured in the same way as before. A schematic of the Linkam stage is shown in Fig. 3.4. A pump (Pfeiffer Vacuum HiCube 700 Classic) is used to pump out the air from the stage, creating a vacuum (with a pressure range of 10^{-4} - 10^{-12} mbar). After, nitrogen, which has a temperature of 77 K, is let into the stage (in gas form), and cools down the sample. To get to a stable temperature, the Linkam stage is heated by electrical resistance, to counterbalance the cold. The temperature is read out by a sensor, which is linked to the Linkam software. The sample is mounted inside the stage, after which it can be looked at by the WITec microscope through a small window.

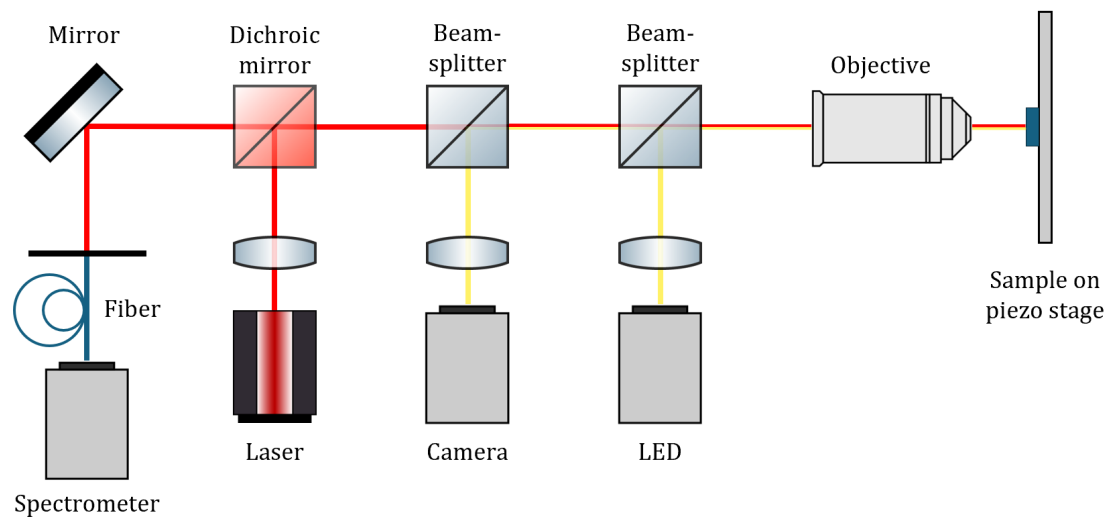


Figure 3.3: A schematic of the WITec setup used, with the laser light in red and the LED light in yellow. When the light travels back through the setup to the spectrometer, the dichroic mirror filters out all wavelengths below the laser wavelength (532 nm).

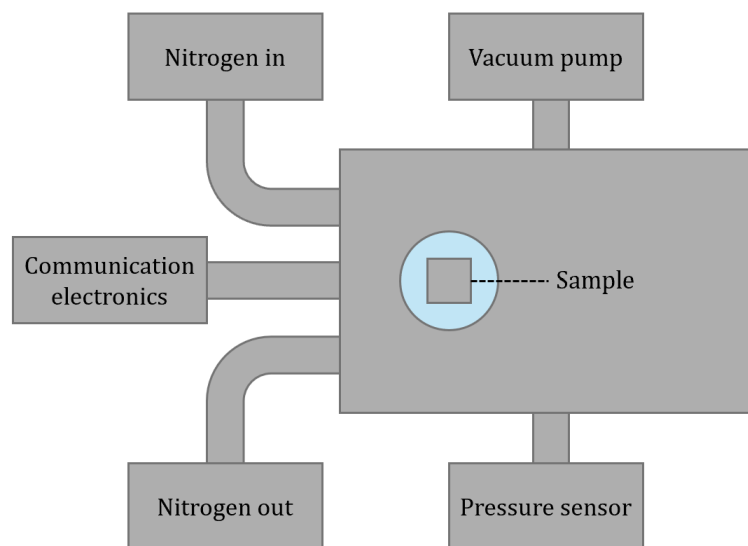


Figure 3.4: A schematic of the Linkam stage, which is used to cool down a sample.

4

Results & Discussion

Three different samples are prepared using the exfoliation and stamping methods described in section 3.1. The monolayer WSe₂ used in each sample was first characterised via PL measurements immediately after exfoliation. Each sample then underwent different treatments to investigate the effects of strain and defects. The first sample was stamped onto an array of nanostructures to apply strain, the second sample was irradiated by an electron beam to induce defects, and the third sample has had a combination of both. In this chapter, the results and implications of these treatments are discussed.

4.1. Sample 1: Confirmation of strained WSe₂

The bare monolayer for sample 1 after the exfoliation procedure is outlined in Fig. 4.1. In the middle of the picture, a large continuous area of WSe₂ is seen in red, which was an ideal candidate for stamping on nanostructures, since the whole array of nanostructures would be covered. Additionally, some few-layer and bulk pieces of material are seen.

After monolayer fabrication and characterisation, the material was stamped onto nanostructures. The array of nanostructures is shown in Fig. 3.2c. The area that was picked up by the stamp is highlighted in blue in Fig. 4.1. The area that was left is shown in Fig. A.1. The stamped area on top of the nanostructures is shown in Fig. 4.2. The first thing to notice is that the monolayer is ripped. After removing the stamp residue with oleic acid, parts of the monolayer ripped, for an unknown reason. Fortunately, some areas of monolayer were left, also on the nanostructures.

In Fig. 4.2, a green square is visible. Inside this green square, PL spectra were measured. The area used is 25 μm by 25 μm , and the spectra were taken in a grid of 100 by 100 pixels. This means that once every 0.25 μm , a PL spectrum of the corresponding position was taken. To get an insight of the trion and exciton contributions in the PL spectra, the data was fitted to two Voigt curves. A Voigt curve consists of a convolution of a Lorentzian and a Gaussian curve, given by

$$V(x; \sigma, \gamma) = \int_{-\infty}^{\infty} G(x'; \sigma) L(x - x'; \gamma) dx', \quad (4.1)$$

with G being the Gaussian contribution, and L being the Lorentzian contribution, which are given by

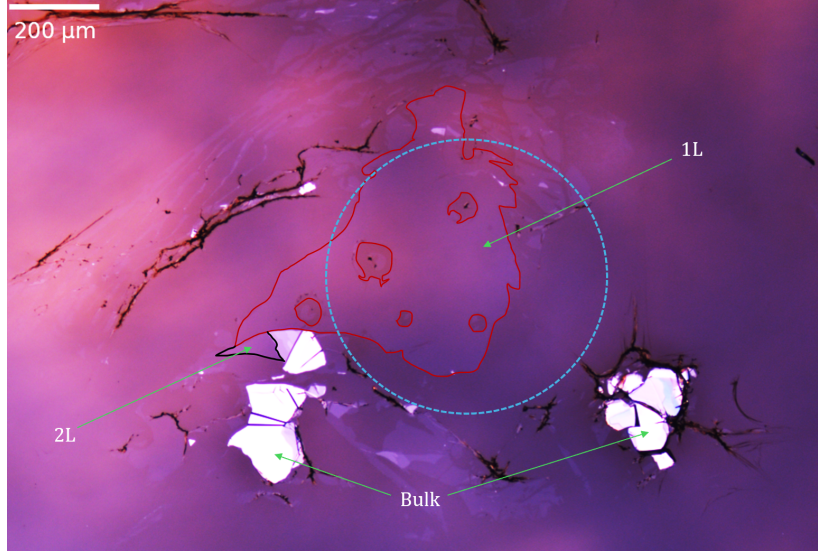


Figure 4.1: WSe₂ on a SiO₂ substrate, with a continuous monolayer outlined in red, a piece of bilayer outlined in black, and some pieces of bulk material. The blue area indicates the area that was stamped.

$$G(x; \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2}\right), \quad L(x; \gamma) = \frac{\gamma/\pi}{x^2 + \gamma^2},$$

respectively. In these equations, σ is the standard deviation of the Gaussian curve and γ is the half-width at half-maximum (HWHM) of the Lorentzian curve [30].

The Lorentzian and Gaussian contributions can be explained by the atomic structure of the material. In a material, the interactions between light and the material itself are dominated by electrons, either bound to the atoms or free electrons. Since displaced electrons can be considered to be electric dipoles, the interaction between a light wave and the atomic lattice (with electrons) can be described by oscillating dipoles. Considering that these oscillations can be damped because of atomic vibrations, the system can be described by a damped harmonic oscillator. Solving the differential equation of motion for this system, the resulting energy distribution for the excitons and trions (consisting of electrons) is a Lorentzian curve [15]. When the material is not pristine, and has local variations, inhomogeneous broadening takes place, causing the emitted energy to be broader than the Lorentzian curve. To account for this broadening, a Gaussian component is added to the fitting curve.

Because both excitons and trions have different energies, two combined Voigt curves are fitted to the data. However, equation 4.1 cannot be computed numerically. Therefore, an approximation is used, given by

$$V'(x; \sigma, \gamma, A, x_{cen}) = A \cdot \frac{\Re(w(z))}{\sigma\sqrt{2\pi}}, \text{ with } z = \frac{(x - x_{cen}) + i\gamma}{\sigma\sqrt{2}}, \quad (4.2)$$

where A is the amplitude of the curve, σ the standard deviation of the Gaussian component, γ the HWHM of the Lorentzian component, x_{cen} the central energy of the fitted curve, and $w(z)$ the Faddeeva function, which is a complex error function [30]. The parameters A , σ , γ

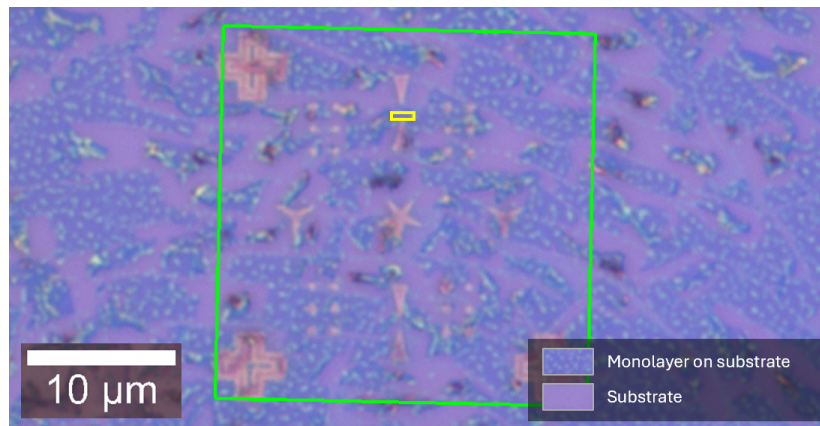


Figure 4.2: Ripped monolayer of WSe₂ on nanostructures made by EBL. The green square is the PL measurement area, and the yellow box corresponds to the red box in Fig. 4.3a.

and x_{cen} are given to the fitting software (curve_fit from scipy.optimize) as fitting parameters. To not only get two separate Voigt curves out of the fitting procedure, but also a combined fit, the trion and exciton components are added to one another, with an offset component.

When comparing central energies of a Voigt curve at different positions, the energy might shift. This energy shift is an indication of strain, since strain lowers the exciton emission energy [20]. The plotted central energies around the yellow box in Fig. 4.2 are shown in Fig. 4.3a. Firstly, the areas in white are either areas where there is no monolayer present, or where the exciton fit failed. Failing of the exciton fit sometimes happens when the data is out of the bounds of the exciton fit parameters: in that case, only a trion peak gets fitted. Secondly, the bluer pixels are those with lower exciton energy, and can be associated with strain. Throughout the whole area of 100 x 100 pixels, there are bluer areas visible but no nanostructure that could have caused strain. It is not clear why these bluer pixels are in these regions, but a possibility could be that these areas are strained because of the ripping of the material during the stamping process. A promising line of pixels at which the exciton energy is lowered is indicated with a red box. This red box corresponds to the yellow box in Fig. 4.2, at which strain could have been applied deterministically due to the bow tie shaped nanostructures around it [7]. The data and fits of these four pixels are plotted in Fig. 4.3b. Since the pixels gradually move in between the bow tie shape in Fig. 4.2, it is expected that the local strain alters the exciton emission energy. This is exactly what is visible in Fig. 4.3b, similar to literature [20]. It seems that if the monolayer stays intact, stamping on nanostructures does indeed apply deterministic strain to the material.

As mentioned, a narrow, SPE-like PL peak is only observed at cryogenic temperatures. Since this sample was strained, and SPEs happen at strained positions (in combination with defects), PL measurements have been taken at varying temperatures, to get an insight in how the PL emission changes when cooling down, to observe a narrowing of PL signal. The sample was cooled using the Linkam setup. After that, single spectra of PL were taken at roughly the same position: in between the upper bow tie in Fig. 4.2, as before. The PL spectra for four different temperatures are shown in Fig. 4.4. A couple of things can be observed. Firstly, the center energy of the PL peak shifts to higher energies when the temperature is lowered. This is consistent with literature [23]. When the material is cooled, the atomic

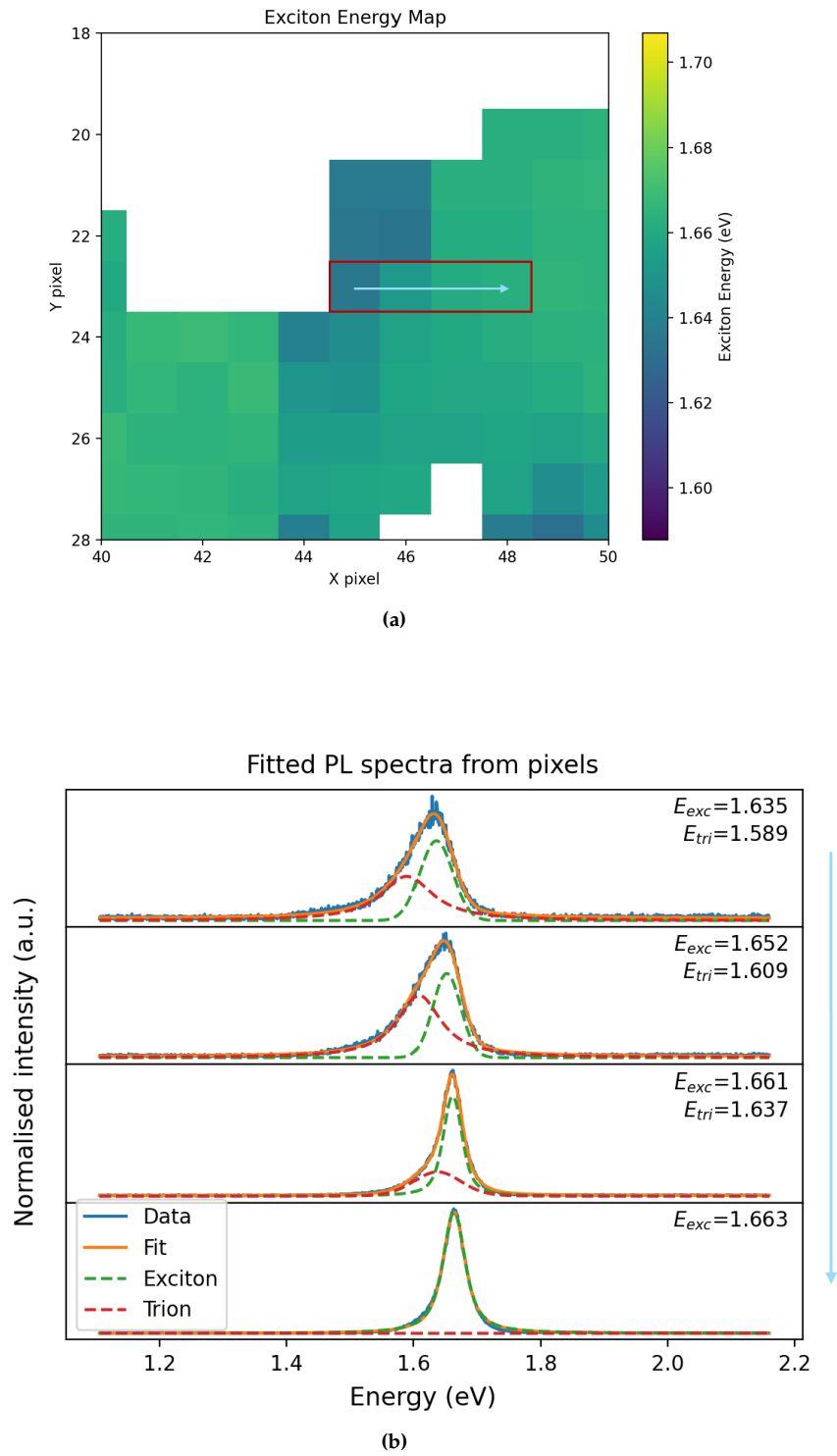


Figure 4.3: (a) Fitted exciton energies (x_{cen} for the exciton curve of equation 4.2) of the pixels taken around the yellow box in Fig. 4.2. The red box in this Figure is the same area as the yellow box in Fig. 4.2. (b) Normalised PL intensity as a function of energy, with fits, for the pixels indicated in Fig. 4.3a. In the strained area, the PL peak shifts to the left and trionic contributions become bigger, similar to Fig. 2.7a. The blue arrows in (a) and (b) indicate which pixels are which in both panels.

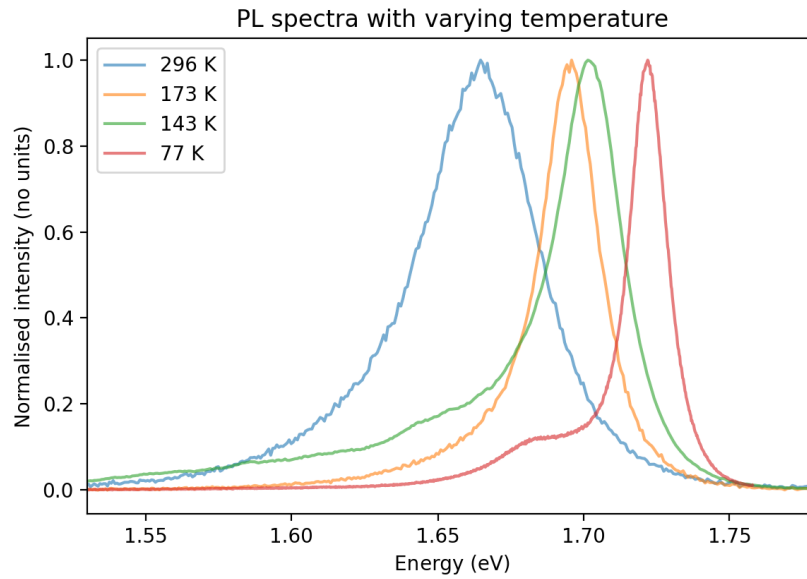


Figure 4.4: Normalised PL intensity as a function of energy, at different temperatures. The peaks shift to higher energy when decreasing the temperature. The laser power is not measured, but is not changed during the four measurements.

lattice contracts, and this makes interactions between the atoms larger. This results in a bigger band gap and a bigger exciton emission energy. Secondly, the peak gets narrower as the temperature decreases. This is also in line with literature and has to do with phonons: when the material is cooled, the exciton-phonon scattering (as mentioned in section 2.3). This results in a narrower PL peak [23, 24]. Thirdly, a second peak, albeit small, becomes visible when the temperature is decreased, at a lower energy than the main peak. This lower peak could be the trionic contribution of the signal, that becomes more visible at lower temperatures. It could also be a defect band (similar to Fig. 2.7b), induced by the ripping of the material [20]. Because the sample moved by small amounts (a few micrometers) inside the Linkam stage when cooling it down, the positions at which the PL data were taken are not certain to be exactly the same. If it would be certain that all four spectra were taken at exactly the same position, the intensity of the PL peaks at different temperatures could be investigated. One would expect that the PL intensity becomes higher when decreasing the temperature, since excitons are not hindered by the exciton-phonon interaction anymore, resulting in more excitons funnelling to a specific energy, making the intensity higher.

All in all, the spectra behave as expected, but no signatures of SPEs are observed. If this approach is combined with deterministically e-beam irradiated areas to try and make an SPE, there could be a more distinct defect band, similar to Fig. 2.7b. The temperature also needs to be even lower, since the sharpest peaks of PL that are associated as SPE-peaks are mostly observed at temperatures below 30 K. The exciton-trion peak, which now still dominates the spectra, will then also be highly suppressed, since excitons and trions will get captured in the created quantum trap by strain and defects more efficiently, emitting within a narrower energy range [2].

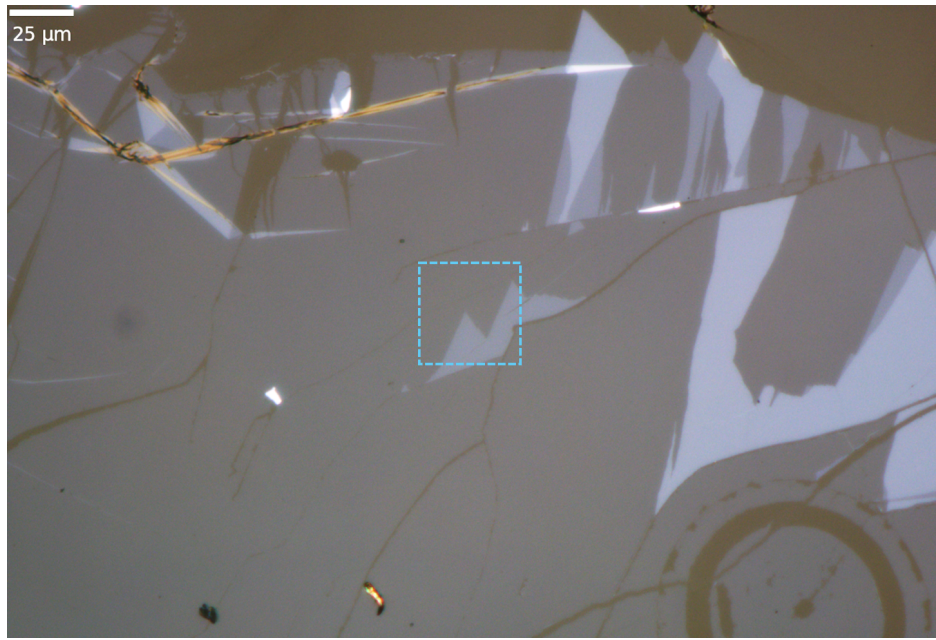


Figure 4.5: Image of a part of the second sample. In the middle, a piece of bilayer WSe₂ is visible, surrounded by monolayer. In blue, the estimated electron beam irradiation area (as shown in Fig. 4.6) is highlighted.

4.2. Sample 2: Monolayer & bilayer WSe₂ characterisation

To get an insight in the effects of only inducing defects (and no strain) in the material, a second sample was fabricated. The exfoliated monolayer of WSe₂ for this sample is shown in Fig. 4.5. Afterwards, the sample was irradiated with an electron beam. After choosing an area on the sample to irradiate, a pattern was chosen to test different doses of electrons. In Fig. 4.6, this pattern is visible. An electron energy of 100 keV, and a varying dose ranging from 1000 to 1800 $\mu\text{C}/\text{cm}^2$, of the order of 10^7 electrons per μm^2 , was used. As seen in Fig. 4.6, the doses were applied on an array of circles. These circles were all 2 μm in diameter. After visual inspection of the integrated PL emission spectra, as seen in Fig. 4.7, no clear effect of the electron beam was observed. An explanation for this could be that the alignment of the irradiation went wrong, and a different than expected area on the sample was irradiated.

However, since the area that was supposed to be irradiated contained a piece of bilayer material (as shown in Fig. 4.5), a comparative characterisation between monolayer and bilayer WSe₂ has been done. The difference between the PL emission peaks is seen in Fig. 4.8a. A typical monolayer PL emission peak is visible, with a high exciton contribution and a smaller trion contribution on the left of it. The bilayer emission peak is roughly half in height, and has a much broader energy range. The broader energy range is in line with literature: in bilayer TMDCs, the trion contribution becomes bigger than the exciton contribution [31]. The reason for this is uncertain. The smaller height can be explained by the fact that bilayer WSe₂ does not have a direct band gap anymore, making it less efficient for photons to be emitted from the material [13].

There is also a difference in Raman shift that can be observed between monolayer and bilayer WSe₂. As seen in Fig. 4.8b, the bilayer Raman peak is slightly shifted to the

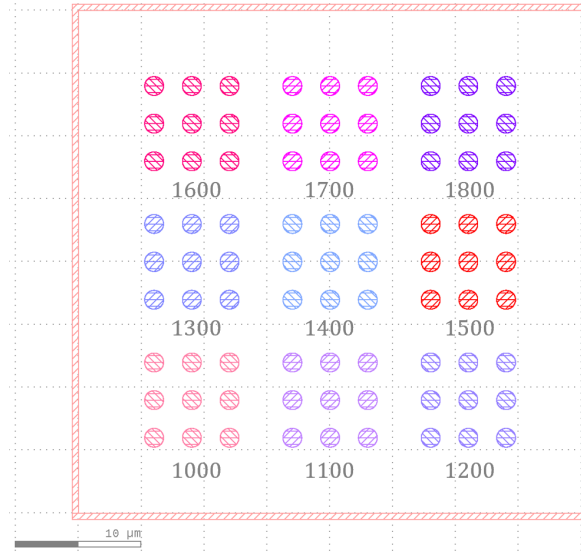


Figure 4.6: The electron beam irradiation pattern for sample 2. Each set of 3x3 circles represents a different dose, ranging from 1000-1800 $\mu\text{C}/\text{cm}^2$. The border has a dose of 1000 $\mu\text{C}/\text{cm}^2$.

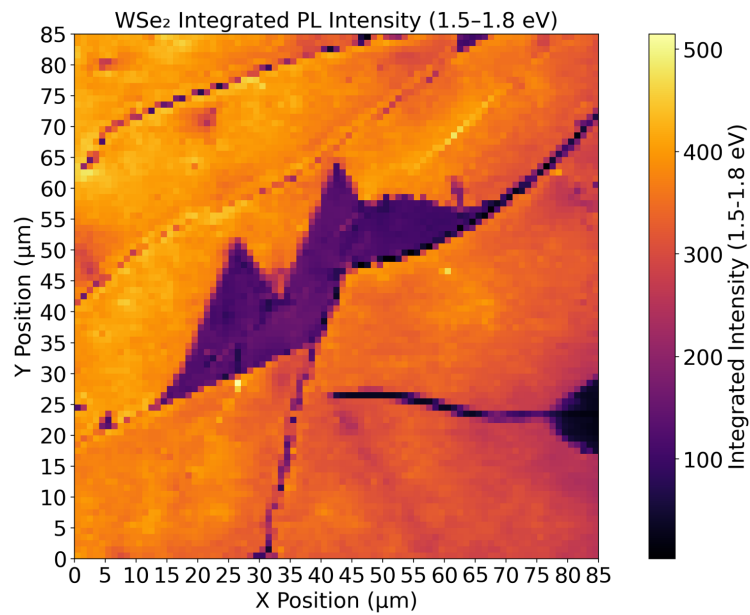


Figure 4.7: Integrated PL intensity between 1.5 and 1.8 eV for an area of sample 2 (laser power: 103 μW). A lowering of PL intensity is visible for the bilayer area in the middle of the Figure. A lowering of intensity because of induced defects by the electron beam is not visible.

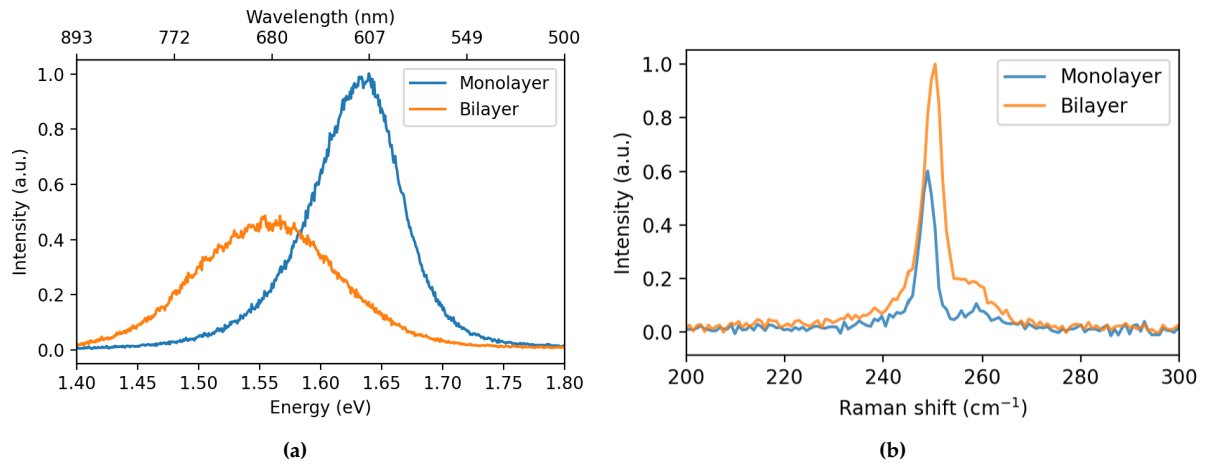


Figure 4.8: (a) PL emission and (b) Raman scattering from monolayer and bilayer WSe₂. Clear distinctions between mono- and bilayer signals are visible. The used laser powers are (a) 262 μ W and (b) 40 μ W.

right ($\sim 2 \text{ cm}^{-1}$), and both the bigger and smaller peak have increased in intensity. This is also what it expected according to literature [25]. Physically, there are more atoms to scatter off of, which increases the detected photons, and therefore the peaks. The small shift in Raman peak when going from mono- to bilayer can be explained by the out-of-plane phonons (of the type A_{1g}) vibrating with different energies, because of interaction between layers [25].

4.3. Sample 3: Combined effects of strain and defects

To get an insight in the combined effect of strain and defects on the optical properties of the material, the third sample was fabricated. The result of the exfoliation of the third sample is shown in Fig. A.2. After the exfoliation of a monolayer of WSe₂, the material was stamped on nanostructures. To protect the monolayer from ripping, as happened to the first sample, and to improve potential SPE quality, a $\sim 13 \text{ nm}$ layer of hBN was stamped onto the WSe₂/nanostructure array, resulting in a heterostructure of hBN, WSe₂ and nanostructures. The thickness of the hBN was measured using a reflectance spectrum of the hBN flake while sitting on a silicon substrate. The spectrum is compared to a transfer matrix model (TMM), which provides the theoretical reflectance of the hBN flake on the silicon substrate as a function of the hBN thickness. The thickness of the hBN flake is determined from the theoretical thickness of the hBN in the TMM model, that best fits the experimental reflectance spectrum that is measured [32]. The design for the array of nanostructures is shown in Fig. A.3. Similar to the first sample, NPs, TSs, FSs and BTs are chosen as nanostructures, but this time in a greater quantity. Out-takes of the stamping procedure are shown in Fig. A.4. After stamping, the residue of the stamp was removed by air plasma. The air plasma would have also eaten away the WSe₂, but since the hBN was placed on top of it, the WSe₂ remained. The fabricated heterostructure is visible in Fig. 4.9. The hBN/WSe₂ stack was only partly stamped on the nanostructure array: an upper array of NPs, a lower array of NPs, a FS and one tip of a TS. The colouring of the image gives away that the material draping over the nanostructures has happened successfully: in between the nanostructures, there is a different colour than outside of the nanostructures, indicating a different height

of the material. This result is remarkable, since literature reports that a much thinner layer (around 1-5 nm) of hBN is needed to be able to generate strain [2]. However, it seems that a 13 nm layer of hBN also creates sufficient strain.

To get a quantitative insight of this visible strain creation, a height profile was measured using an atomic force microscope (AFM). The AFM picture is seen in Fig. 4.10a. On the left side of the picture, the hBN/WSe₂ stack is stamped on top of the nanostructures. The right side of the picture shows bare nanostructures. On the left, there are strained areas (wrinkles) visible in between the NPs, in mostly a vertical direction. The reason why the wrinkles are more prevalent in the vertical direction than the horizontal direction is unclear, but the direction of dragging away the stamp after stamping might play a role. The stamp was dragged in a horizontal direction, which might have caused the horizontal wrinkles to have flattened out. There are also wrinkles visible on the tips of the FS and along the tip of the TS. The height of the nanostructures turned out to be the same height as the designed nanostructure array, as expected: 200 nm.

After this, the height map data was used to calculate the geometric strain of part of the sample. The strain derivation can be found in section A.2.3, and is based on how much a material contracts or compresses after it is stamped onto an array of structures. The result of this calculation is shown in Fig. 4.10b. The narrow wrinkles in between the NPs are visible and have areas of localised strain, as wanted. There is also a heavily strained wrinkle visible along the tip of the TS, and along the upper left NP. Along the edges of the FS, strain is also visible. The value of 3% strain is promising for SPEs, since this is higher than the amount of strain that is used in a previous work: 0.6% strain for successful SPE-fabrication [6].

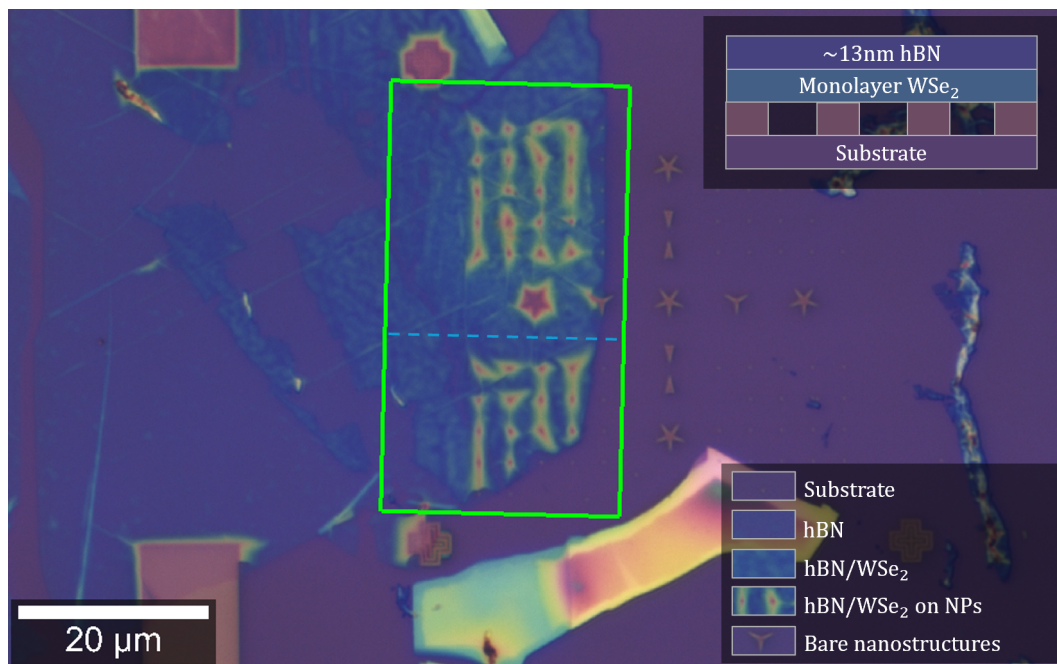


Figure 4.9: A picture of hBN/WSe₂ stamped onto nanostructures. In green, a PL data collection area is visible. Everything inside the green area and above the dotted blue line has been irradiated by an electron beam. In the top right corner, a schematic cross section of the heterostructure is shown. The cubes in between the monolayer and the substrate are the nanostructures.

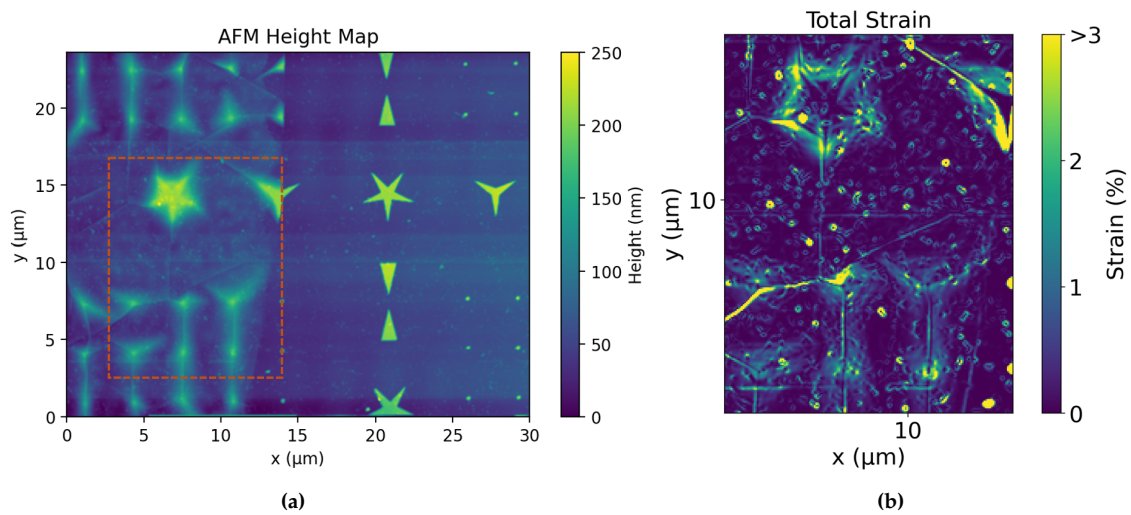


Figure 4.10: (a) AFM height map of a part of sample 3. A hBN/WSe₂ heterostructure is stamped onto nanostructures on the left, creating strain. On the right, there are bare nanostructures visible. The dotted rectangle indicates the area for which strain was calculated. (b) Calculated strain for the rectangular area in (a), using the calculation mentioned in section A.2.3. Narrow strain is visible between NPs and at the edges of the TS and FS.

After studying strain, the material was irradiated with an electron beam. Because the irradiation pattern that was used at the second sample (as seen in Fig. 4.6) did not become visible, a uniformly irradiated large rectangular area was chosen for this sample. In Fig. 4.9, the dotted blue line indicates one of the borders between the irradiated and non-irradiated area: the area of nanostructures above the line was irradiated with a dose of 10^9 electrons/ μm^2 , and the lower part of nanostructures was not.

Then, PL characterisation of the sample was done, both before and after the e-beam irradiation, to study the impact of irradiation on PL. The irradiated PL data was taken of the green rectangle in Fig. 4.9. Because the green rectangle is $25\ \mu\text{m}$ by $45\ \mu\text{m}$ in size, and data was taken of an area of 100 by 180 pixels, a PL spectrum was taken every $0.25\ \mu\text{m}$. The non-irradiated PL data was taken of a similar rectangular area with the same resolution. What is worth mentioning is that before the sample was irradiated with the electron beam, a layer of conductive polymer, a polyaniline (All-Resist Electra 92), was put on top of the sample. This is needed to prevent the sample from charging up completely and deflect the electron beam. After the irradiation, the conductive layer was initially still on there. In the PL signal, however, a dramatic lowering of intensity was seen (this is shown in Fig. A.5). This lowering can be partly explained by carbon contamination of the conductive layer, causing the PL signal to not get through properly. Therefore, the conductive layer was removed, PL measurements were taken, and the PL signal was of significant intensity again.

For each pixel of taken data, the integrated area below the PL peak was taken, in the energy range 1.4-1.8 eV. The resulting integrated intensities, for both before and after e-beam irradiation, are shown in Fig. 4.11. A few things can be mentioned. First, both before and after irradiation, the PL intensity seems to be the highest on top of the nanostructures. This makes sense, since the strain is the highest at these positions, increasing the exciton funnelling and therefore emission. Second, the PL intensity for the whole sample has dropped after

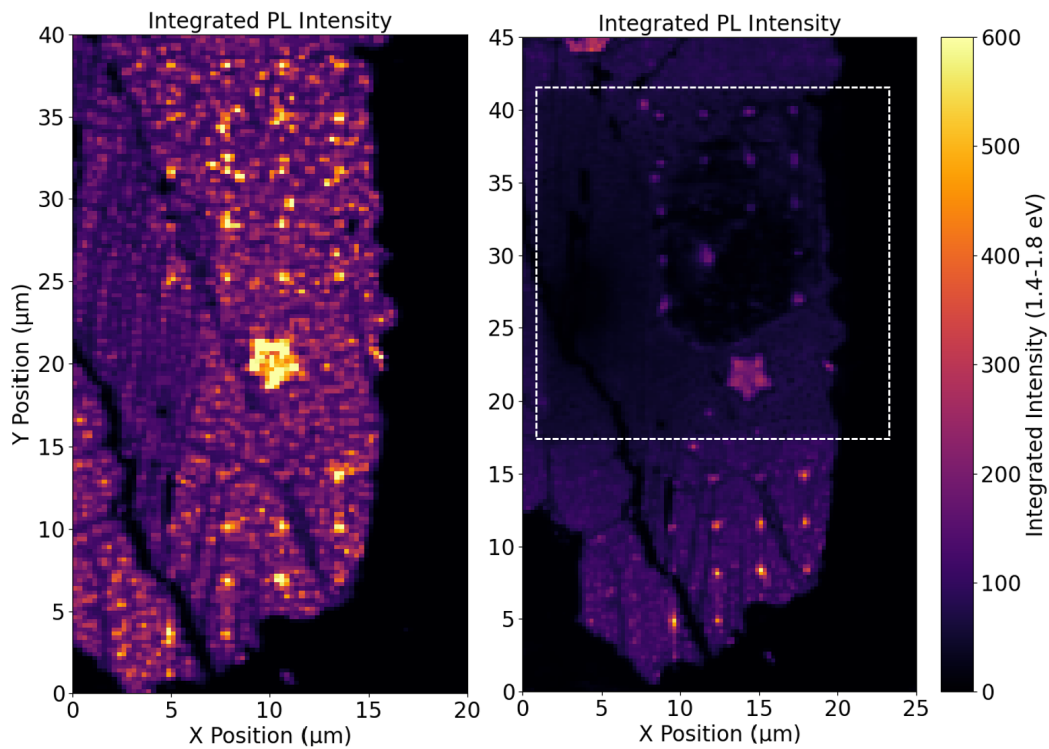


Figure 4.11: Integrated PL intensity of sample 3 before (left) and after (right) electron beam irradiation. The white rectangle highlights the irradiated area. The intensity is the highest at the nanostructures. For both measurements, a laser power of $100 \mu\text{W}$ are used.

irradiation. Before the irradiation of the rectangular area in white in Fig. 4.11, the whole sample was irradiated with a lower dose to get a scanning electron microscopy (SEM) image, to make out the position of the nanostructures on the sample. After this, the area as indicated before was further irradiated. The effect of irradiation is clearly visible in the PL map: a distinct differences between the irradiated and non-irradiated area can be seen. Inside the irradiated area, it is seen that the PL drops even more, or completely disappears, in between the NPs. An explanation for this could be that the combined effect of defects and strain might have resulted in the material being damaged too much, causing PL intensity to drop through non-radiative channels.

Subsequently, several lines of pixels were taken across the wrinkles, to see if there is strain visible in the form of PL peaks shifting, as seen for the first sample. A PL scan along a line of pixels is shown in Fig. A.6. Unfortunately, a shift in peaks has not been observed for this sample. This could be explained by the fact that the wrinkles are so narrow, that the PL resolution of $0.25 \mu\text{m}$ was not enough to capture the shift: for the most part, the unstrained areas around the wrinkles were measured.

To get another insight on the effect of strain and defects, Raman spectroscopy was done on this sample. The position of the Raman peak of WSe_2 per pixel is shown in Fig. 4.12. The area taken for the Raman peaks is smaller than the area for the PL: an area of $10 \mu\text{m}$ by $20 \mu\text{m}$ is chosen, in a grid of 40 by 80 pixels. In both maps, the FS is visible. A few things can be mentioned about this Raman map. First, the Raman peak of pristine monolayer WSe_2

lies around 249.5 cm^{-1} [25]. A majority of the pixels indeed show this. Second, there are parts of the material that do not have a distinct Raman peak for WSe_2 ; these are the white areas. These areas seem to be centred around the nanostructures, so they are most likely at the areas with the most strain. It is not expected that the Raman peak disappears when there is strain [27], so this could be a failure in the setup used. It might be that the material bent so much, that the laser did not land on a flat surface, resulting in scattered photons in all sorts of different angles than the signal collection pickup angle (which is the same as the laser angle). This disappearance of signal would then also be observed when taking PL measurements, but this is not the case; the reason for these white areas appearing is therefore not clear. Outside of these white areas however, in the strained areas, there is a small shift of peaks visible (the turquoise coloured pixels), which is in line with literature [27]. Third, the Raman shifts seem to be the highest at the area that was irradiated with the electron beam. The combined effect of strain and defects might have altered the lattice even more, causing this larger shift, because of a larger change of atomic vibrations. Lastly, a Raman peak shift caused by defects only is not visible in the Figure, unlike what was seen in literature for MoS_2 [26]. If an unstrained, not irradiated part of the sample is compared with an unstrained, but irradiated part of the sample, a shift in Raman peaks is not observed. However, there is a drop in Raman peak intensity visible between the irradiated and non-irradiated area (this is shown in Fig. A.7).

To conclude this sample, AFM, PL and Raman characterisation show that there are numeral effects of strain and defects at the same time. For strain, it was observed that stamping the material onto nanostructures creates physical strain, but a shift in PL spectra was not observed. Slight shifts of Raman peaks also confirm strain. For defects, a large area was irradiated with an electron beam, resulting in dropping intensity in both PL and Raman spectra. At certain areas of the material, the intensity quenched completely; this might be because of too many defects. The observed shift in Raman peaks in MoS_2 after only electron beam irradiation was not observed for this sample of WSe_2 , but a combined effect of strain and defects is visible as a larger shift in Raman peaks.

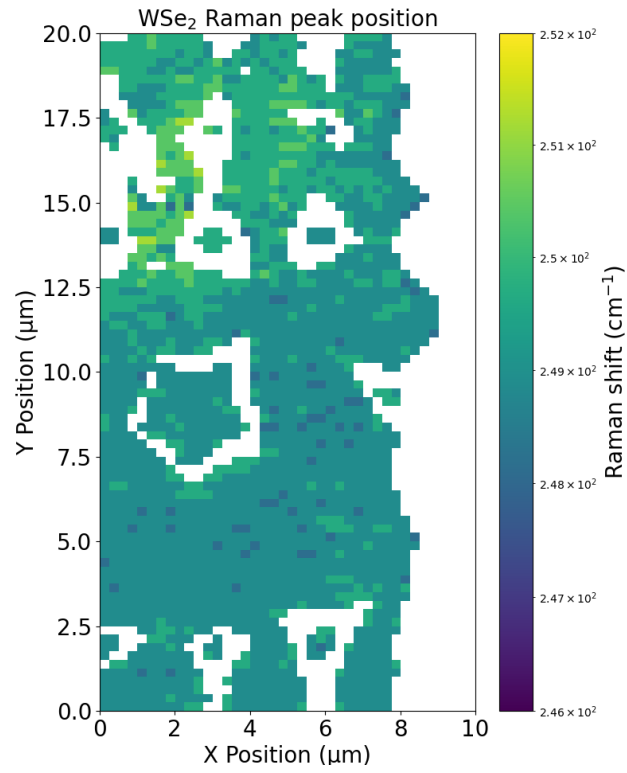


Figure 4.12: Heat map of Raman peak positions of WSe₂ in sample 3. Outlines of the FS and NPs are visible.

5

Conclusions & Outlook

As part of the process to deterministically fabricate SPEs in a 2D TMDC (WSe_2) this research was conducted. The separate and combined effects of strain and defects were characterised. This has been done mainly using PL and Raman spectroscopy. Using a gold-existed exfoliation technique, three samples of monolayer WSe_2 were obtained. The first sample confirmed that strain lowers the exciton emission energy, resulting in a PL spectrum shift, in line with literature. For the third sample however, this was not observed. Additionally, temperature-dependent measurements were done on the first sample, to get insights in how PL data would change when cooling down the sample, which is needed for SPE-fabrication. This showed blueshift and narrowing of PL data, which is expected for WSe_2 . The second sample was irradiated with an electron beam, but this area was not visible in any of the data taken. The third sample did show visible strain when taking AFM data, in contrast to the PL data. Slight shifts in Raman peaks, caused by strain, were also visible. Alongside strain, the effects of defects were also analysed. A drop in PL and Raman intensity was observed in an e-beamed area, but PL quenched completely at some places. This could be because of a too high defect density. A combined effect of strain and defects resulted in a bigger Raman shift than only inducing strain. A defect band in the PL signal was unfortunately not visible. This can be explained by the fact that the measurements were done at room temperature, and not at cryogenic temperature.

Further research could focus on a more systematic way of inducing defects in the material. Adding markers around an area that will be irradiated helps finding the area afterwards. Varying electron doses could prevent the material from getting damaged, such that a sweet spot of electron dose can be found. To make sure that the obtained data is free of abnormalities, such as dirt or ripping of the material, the material could also be encapsulated by hBN on the bottom, to have the WSe_2 ‘sandwiched’, and therefore pristine, between two layers of protection. Furthermore, during the strain creation process, more strain-aligning nanostructures could be used, instead of the arrays of NPs that were used now, which still do not reach the accuracy that is needed to place these strained areas. An array of BTs could be a way to precisely localise strain. Lastly, the material could be cooled down to 4 K, to compare the observed SPE peaks in literature to the samples used here, and ultimately, this approach to deterministically created SPEs could be confirmed to be successful.

Acknowledgments

I would like to thank all people who helped me during this project, in particular the people from the SPE team: Alvaro Loya Villalpando, David van Houten, Alexander Hendriksen, Richter Florusse, Jorik van de Groep, Peter Schall and Laurens Siebbeles. I would also like to thank the people who helped when I got stuck on some things in the lab: Bernardo Dias and Anne Claude. Lastly, I want to thank my dear friends and family, who kept listening to me when I was rambling on about the project.

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A

Appendix

A.1. Additional monolayer exfoliation results

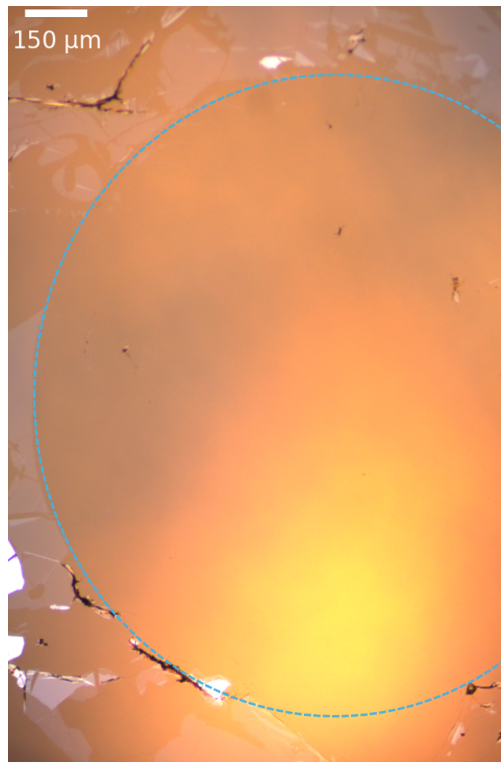


Figure A.1: Picture of the substrate of sample 1 after stamping. The stamped region is shown in blue, and is the same region as in Fig. 4.1. Around the stamp region, the monolayer that was left is visible.

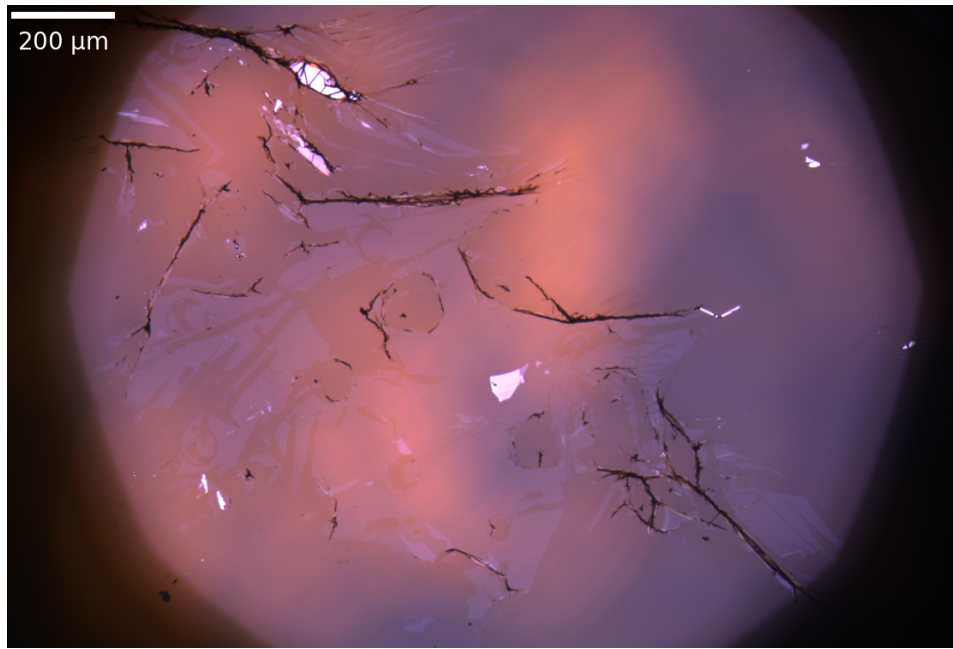


Figure A.2: Picture of exfoliated monolayer WSe₂ for sample 3. Large consecutive areas of monolayer are visible, along some pieces of multi-layer material.

A.2. Additional results for sample 3

A.2.1. Design of nanostructure array

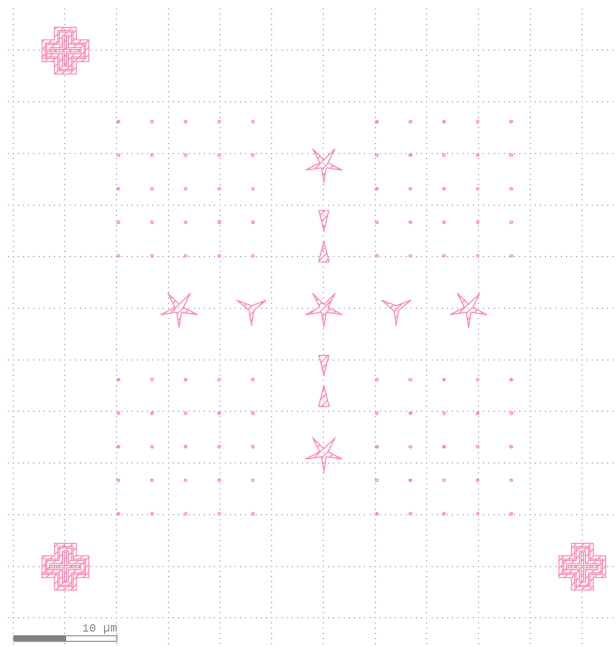


Figure A.3: The design of the nanostructure array of sample 3. NPs, TSs, FSs and BTs are visible. The crosses in the corners are alignment markers.

A.2.2. Stamping procedure

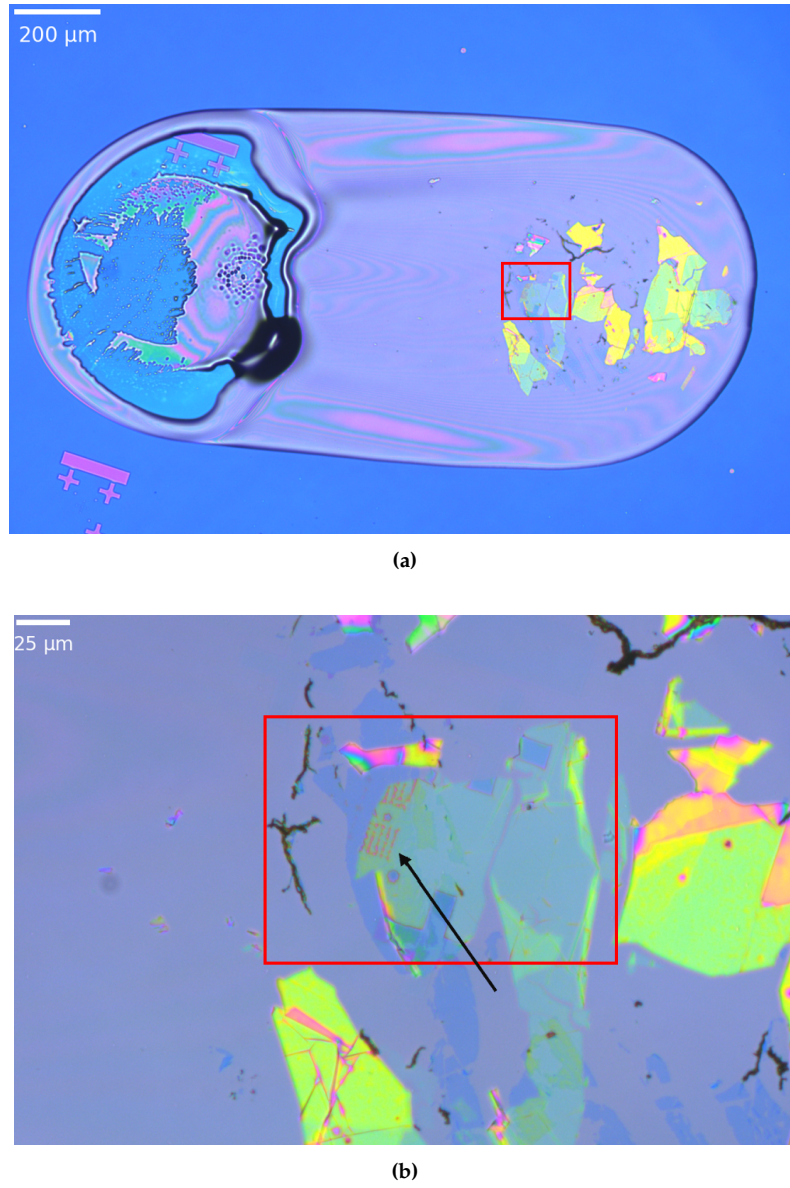


Figure A.4: Stamping sample 3 on top of nanostructures. (a) The residue of the stamp on the sample after the stamp is dragged away from the stamped materials on the nanostructures. The red area is the same as the red area in (b), where the hBN/WSe₂ is visible on top of the nanostructures; NPs are indicated with a black arrow.

A.2.3. Geometric strain derivation

Consider a small flat piece of monolayer WSe₂. If only the x-direction is considered right now, it has length dx . Then, it is stamped onto a nanostructure. Because the material bends over a structure, the material might contract or expand to a new length, ds . Now, the strain in the x-direction can be calculated by

$$\epsilon = \frac{ds - dx}{dx}. \quad (\text{A.1})$$

The Pythagorean theorem states that $ds^2 = dx^2 + dz^2$, and since $dz = \frac{\partial z}{\partial x} dx$, ds can be written as

$$ds = dx \sqrt{1 + \left(\frac{\partial z}{\partial x}\right)^2}.$$

For small slopes, a $\sqrt{1+a}$ term can be approximated by a first order Taylor expansion to $1 + \frac{a}{2}$, so

$$ds \approx dx \left(1 + \frac{1}{2} \left(\frac{\partial z}{\partial x}\right)^2\right).$$

Substituting this back into equation A.1 gives

$$\epsilon_{xx} = \frac{1}{2} \left(\frac{\partial z}{\partial x}\right)^2. \quad (\text{A.2})$$

Physically, this expression can be seen as the change in length in the x-direction, when the material is being contracted/expanded in the x-direction. If the second dimension is taken into account, similar equations to equation A.2 can be added for changes in length in one direction after contracting/expanding in a different direction, resulting in a geometrical strain tensor:

$$\epsilon = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} \\ \epsilon_{yx} & \epsilon_{yy} \end{pmatrix}.$$

Of this tensor, the norm can be calculated, which is the total strain used for Fig. reffig:sample3 strain calculated:

$$\|\epsilon\| = \sqrt{\epsilon_{xx}^2 + \epsilon_{yy}^2 + 2\epsilon_{xy}^2},$$

where it is assumed that $\epsilon_{xy} = \epsilon_{yx}$, because of hexagonal symmetry in the lattice.

A.2.4. Comparison between PL intensities before and after removing conductive layer

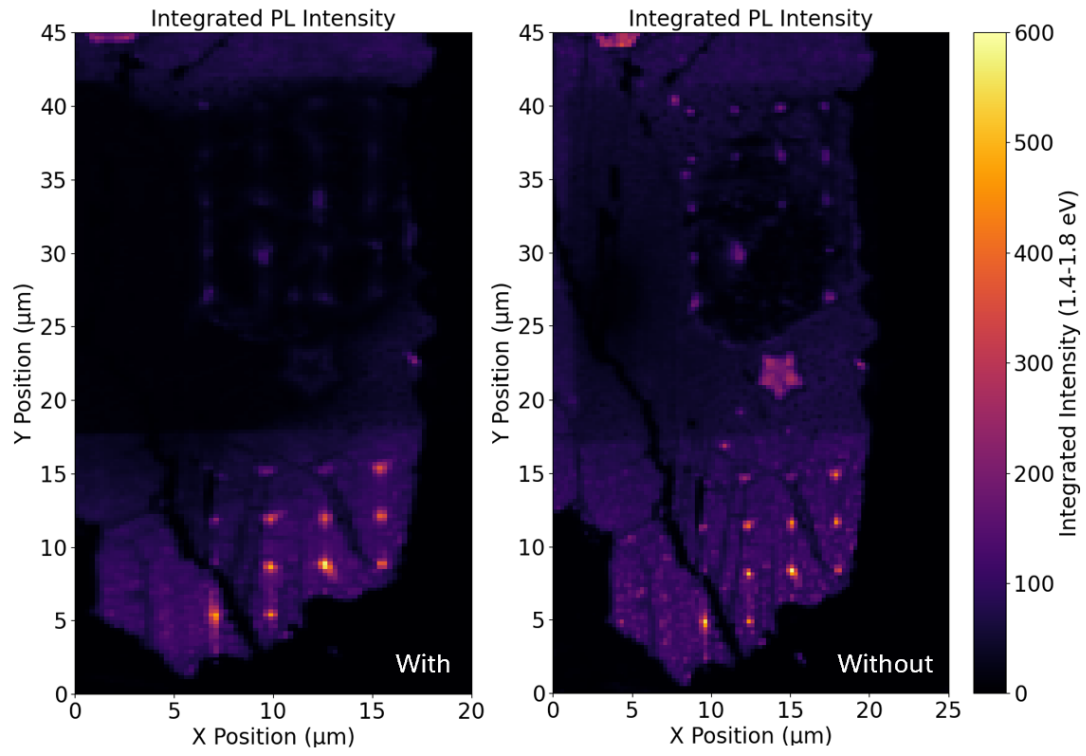


Figure A.5: Integrated PL intensity between 1.4 and 1.8 eV for sample 3, after it was irradiated with an electron beam. The left panel shows the PL intensity with a conductive layer of electra still there, and the right panel shows the PL intensity without this conductive layer. The laser power used for both is 100 μ W.

A.2.5. Fitted PL spectra along line of pixels

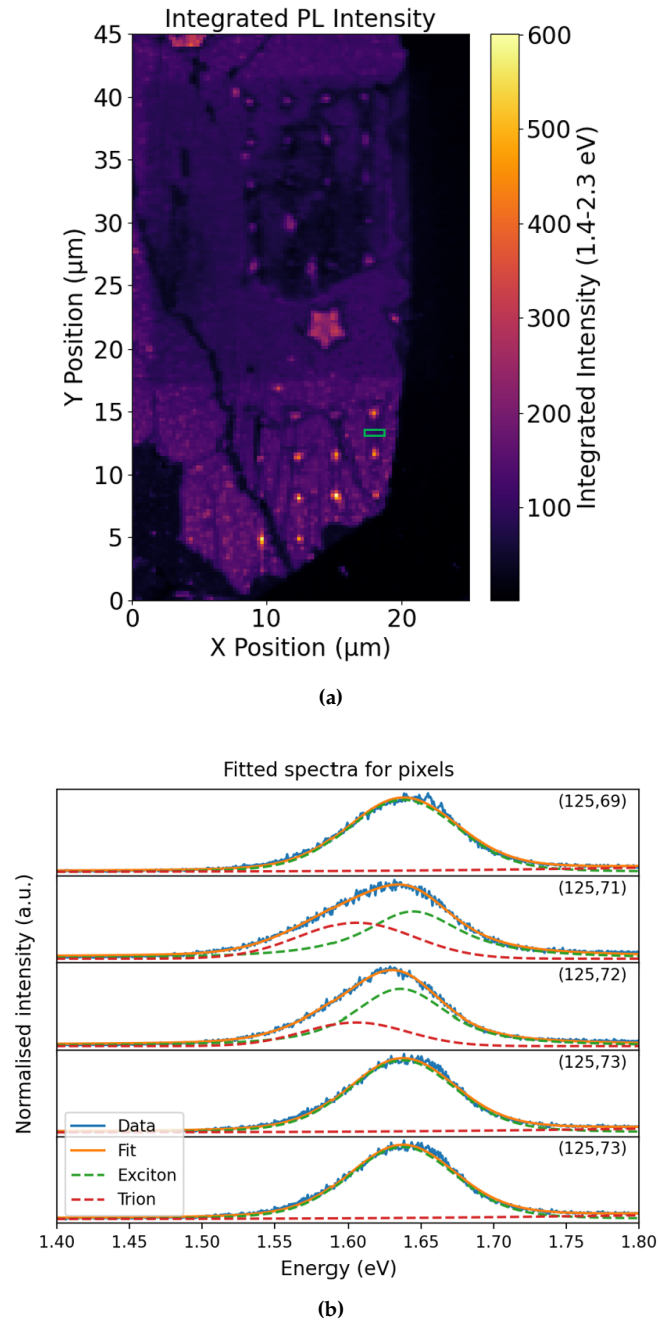


Figure A.6: (a) Integrated PL intensity of sample 3 after irradiation (same plot as the right panel in Fig. 4.11, laser power: $100 \mu\text{W}$), but now, a line of pixels is selected in between two NPs. (b) Fitted PL spectra of the line of pixels showed in (a). A distinct shift in PL peaks, as visible in Fig. 4.3b, is not visible.

A.2.6. Lowering of Raman peak intensity

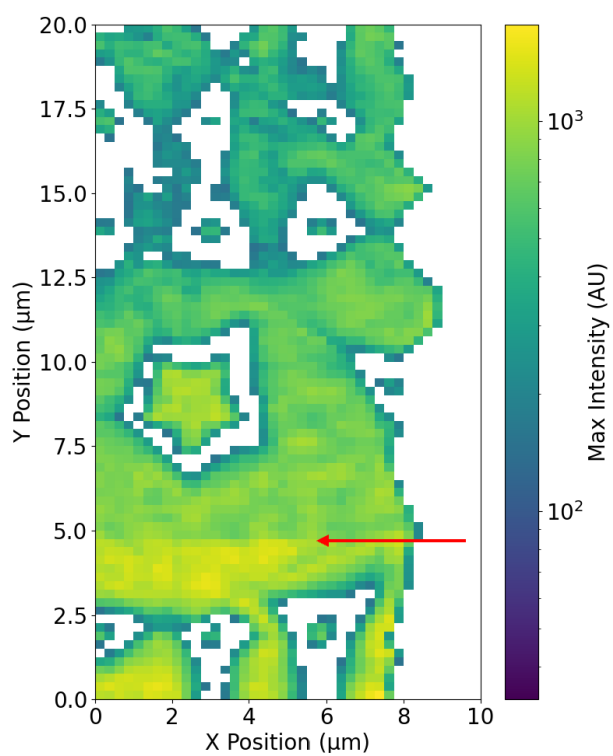


Figure A.7: Maximum Raman peak intensity map for a part of sample 3 (laser power: $105 \mu\text{W}$). The difference in maximum intensities between the irradiated and not-irradiated area is visible along the red arrow: the intensity drops from yellow to green.