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Master's Degree in Nanotechnologies for ICTs Thesis

Lateral Conversion TMD synthesis: investigating sub-20 nm features, Material Quality and Optical Device Design

Supervisors Dr. TEVYE KUYKENDALL Prof. FABRIZIO GIORGIS Dr. AIDAR KEMELBAY Candidate MARCO D'ALESSANDRO



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Abstract

The research presented in this master's thesis delves into the synthesis and characterization of transition metal dichalcogenides (TMDs), with a particular emphasis on WS_2 , renowned for its exceptional properties among TMDs. The primary objective of this study was to investigate the reduction of TMD features down to 20 nm utilizing a bottom-up lithographic approach employing block copolymers to create the desired features and a lateral conversion growth mechanism to convert a uniformly deposited metal oxide layer to the desired TMD. To analyze the resulting material, a transfer method onto TEM grids was developed. Scanning transmission electron microscopy (STEM) and Raman spectroscopy were used for initial TMD characterization and to optimize the transfer technique. Further microstructural analysis was made possible using high-resolution transmission electron microscopy (HRTEM). The results gained from this analysis provided valuable information about the structure and properties of the synthesized WS_2 , and gave insight into the synthetic parameters of the conversion process. Building on this work, it has been investigated the design performance of an optical device using the lateral conversion method. Finite-difference time-domain (FDTD) simulations were used to develop a model of a distributed Bragg reflector (DBR) based on WS_2 . DBR structures were then fabricated and compared with silicon nitride (SiN) for performance evaluation. The fabrication of the designed optical device took place in a controlled environment within a cleanroom, examining different approaches to treat the substrates. A systematic study on the dynamics of the conversion technique was conducted to ultimately assess the optimal growth conditions. To gauge the effectiveness of the device, thorough characterization was carried out through white light measurements.

Looking ahead, the prospects of this research encompass optimizing the synthesis methods of such a structure, and deeply understanding the dynamics of the reactions and the subsequent changes produced in the morphology of the material. An interesting application would involve the generation of Bloch Surface Waves (BSW) on top of the dielectric stack, whose design is investigated at the end of the dissertation. The design and fabrication of an optical device using this synthetic method will establish a foundation for potential future applications in advanced optoelectronic systems.

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Thesis Outline

The thesis is structured to encompass distinct yet interconnected sections that collectively contribute to elucidating the research objectives. An initial literature review is presented to better frame the research objectives. Subsequently, a description of the materials, synthetic and characterization methods is presented. The results of a systematic study of synthetic parameters are then highlighted, providing insights into material growth dynamics. These synthetic insights are then applied to the exploration, design and fabrication of Transition Metal Dichalcogenides integrated into optical devices. This structured approach enhances both the chronological flow and the global comprehension of the subject matter:

- Chapter 1 introduces 2D materials, TMDs and their potential applications.
- Chapter 2 provides a theoretical background of the topics of the thesis. In particular, special attention is given to the physical and electrical properties of 2D materials, their synthesis methods, and also the fundamental principles behind the characterization and transfer methods are presented.
- Chapter 3 is devoted to the description of the TMD lateral conversion synthesis method used in this research and characterization of the resulting materials. The fabrication process flow is outlined, and an in-depth investigation into the effects of temperature on the reduction and conversion steps is presented. The transfer methods necessary for detailed TEM characterization is described, being complemented by Raman spectra and scanning electron imaging techniques. Together with high resolution TEM, insights into the synthetic method and resulting TMD microstructure are discussed.
- Chapter 4 provides a theoretical background on the optical devices and their relative simulations performed in Lumerical. A description of the geometry and the expected results is provided.
- Chapter 5 is dedicated to the description of the fabrication process of the DBR performed in the cleanroom. An overview on optimization steps is given, as well as the ultimate synthesis of the samples.
- Chapter 6 reports the results obtained for the optical devices after the dedicated measurements. A discussion is also proposed, to investigate possible improvements.
- Chapter 7 summarizes the work carried out during the project, with an outlook on future perspectives in this research field.
- In conclusion, Appendix provides additional information.

Chapter 1

Introduction: Materials and Applications

1.1 2D Materials

Two-dimensional (2D) materials have gained significant attention in recent years due to their unique properties and potential applications in various fields, from electronics and optoelectronics [1] to energy storage and sensing [2]. In general, they can be described as layered crystalline structures characterized by a strong bonding in the plane, while weak Van der Waals forces hold the crystalline planes together [3]. Compared to bulk solids, layered materials have the advantage of avoiding surface dangling bonds, charge carrier scattering and lattice mismatch, which are limiting factors of bulk materials [4]. The discovery of graphene in 2004 [5] marked a significant milestone in the study of layered structures, leading to a surge of interest in this field. Graphene consists of a single layer of hexagonally arranged carbon atoms, and possesses remarkable properties with respect to bulk graphite [6], being chemically inert and with some specific molecules that can functionalize it, having attracted attention for various applications [7]. The major limiting factor of graphene is the lack of a bandgap, which is an important characteristic when electronic applications come into play, since they rely on the tunability of this attribute. Application of uniaxial strain [8], doping, generating ribbons [9] and alloying it with an insulating layer of hexagonal boron nitride (h-BN) have been attempted to solve the issue [10]. Nevertheless, a resulting reduced graphene mobility is observed. Under this perspective, transition metal dichalcogenides (TMDs) have emerged as a promising class of semiconductors, with tunable electronic and optical properties that make them attractive for use in electronic devices and optoelectronic applications [11].

1.2 Transition Metal Dichalcogenides (TMDs)

Among TMDs, it is possible to find semiconductors $(MoS_2 \text{ and } WS_2)$, semimetals $(WTe_2 \text{ and } TiSe_2)$, metals (NbS_2) and insulators (HfS_2) , with a few examples of low-temperature superconducting materials such as $NbSe_2$ [12]. The generalized formula describing these promising materials is MX_2 , where M represents a transition metal from group 4 to 10, and X is a chalcogen (Fig.1.1). Usually, TMDs



Figure 1.1: Transition metals and chalcogen atoms highlighted in the periodic table [11]

with metals being part of groups 4-7 are found in layered form, having a single layer thickness of 6-7 Å, with the two chalcogen atoms sandwiching the metal atom with a hexagonally packed crystal structure in the plane. Also, it should be noted that the strong covalent intra-layer bond between M and X, combined with weak Van der Waals interactions between the layers, leads to the ability to easily cleave the crystal [13]. The filling of bonding states of TMDs is achieved by the donation of four electrons coming from metal atoms, so that the oxidation states of the chalcogen and the metal are -2 and +4, respectively. Also, the bond length between metal atoms is between 3.15 Å and 4.03 Å, therefore there is a limited energetic overlap between d orbitals of TMDs [11]. Layered TMDs can show two different metal coordinations: trigonal prismatic or octahedral, depending on the thermodynamically favorable combination of metal and chalcogens. As for bulk TMDs, we can find polymorphism since a single layer of MX_2 containing three layers of atoms can appear in two different phases. Usually, we can find 1T, 2H and 3R polymorphs, with the letter standing for trigonal, hexagonal and rhombohedral and the digit in front indicating the number of X-M-X sequences present in the unit cell. In general, a single TMD can be found in different polytypes, with some polymorphisms recurring more often. For instance, the most classic example of TMD is MoS_2 , which can appear in the 2H phase, with aBa bAb stacking sequence (lower and upper case representing chalcogen and metal) when found in nature, whereas a synthetic one shows a 3H phase. However, both polytypes have a trigonal prismatic metal coordination [14]. Moreover, we can identify three separate polytypes for single layer TMDs, namely H-, T- and T'- phases. A hexagonal symmetry (D_{3h}) is identified for the metal coordination of the H- phase whereas octahedral (D_{3d}) for the T- and T'- is distorted. Overall, the trigonal prismatic configuration belongs to the D_{3h} point group, with a 2H semiconducting phase, the octahedral is part of the D_{3d} group, with a 1T metallic phase, and the distorted octahedral has a 1T' metallic phase, which appears as a bulky distortion of the planes (see Fig.1.2).



Figure 1.2: Structural configuration of H,T and T' phases of monolayer TMD [15]

1.3 Applications

1.3.1 Electronics applications

The major excitement for 2D materials comes from their potential application to new generation of electronic devices, based on extremely thin channel layers of field effect transistors (FET). Despite their fragility when exposed to ambient conditions and the dependence of electronic properties on the low concentration of defects in the material, which is difficult to control, recent improvements towards large-scale integration of these materials have been established. Good results have been obtained for MoS_2 FET, with high I_{ON}/I_{OFF} ratio of 10⁷, low subthreshold swing and no short channel effects [16]. Also, the atomic thickness allows the development transparent and flexible devices operated at relatively low voltages [17]. A major issue related to 2D based transistors is represented by the contact resistance arising from the layered channel and the bulky metal contacts. Extensive studies have been done in this perspective, leading to the development of edge contacts to be preferred to top contacts, due to the lowering of the energetic barrier that electrons have to overcome in order to avoid a drastic drop of the drain current [18]. Moreover, the most important companies in the semiconductor industry are trying to progressively achieve miniaturization of electronic devices and these materials may play a central role. Recently, at the 2022 IEEE International Electron Devices Meeting in San Francisco the first demonstration of a monolayer MoS_2 based gate all around field effect transistor (GAAFET) has been presented. Despite the difficulties encountered in the fabrication process, excellent figures of merit were achieved, also demonstrating a higher mechanical stiffness with respect to Si, making its integration more reliable [19]. However, we should take into account degradation of the monolayers in general. By stacking these layers with additional materials it is possible to limit this process and preserve the correct operation of the device.

1.3.2 Optoelectronics applications

The rising demand in data storage and the growth of telecom networks have driven the development of alternative technologies for integration with silicon photonics. It has been shown that it is possible to enhance the generation and modulation of light with 2D materials since they do not suffer from lattice mismatch and can be transferred onto silicon-based devices. Also, the transition from indirect to direct bandgap materials when thinned to single layers makes TMDs suitable for optoelectronic application due to the long exciton lifetimes with respect to other two-dimensional materials such as graphene. A LED based on TMDs and a lasing system are two examples of what has been demonstrated in this field [20]. Another interesting example is the creation of light emitters based on the electrical actuation of coupled waveguides. Indeed, it is possible to create a heterostructure made of a TMD-based light emitting device (LED), which exploits the excitonic recombination, and waveguides made of hexagonal boron nitride (h-BN), exhibiting a good overlap of optical modes [21].

1.3.3 Energy storage applications

It is of remarkable interest that bulk TMDs have been employed as electrodes for lithium-ion batteries, given the easy intercalation of lithium ions in the interlayers. However, their structural instability during the exfoliation and relatively low voltage and energy density are limiting their application as cathode materials. On the other hand, TMD nanosheets are attractive as anodes due to their ability to accommodate structural changes [22]. Nevertheless, their low electrical conductivity still represents a limitation. Morphology and grain size can also affect TMDs as anodes in lithium-ion batteries. To cope with it, MoS_2 /graphene composites have been produced, with promising results in achieving high specific capacity and cycling stability [23]. The cycling stability of TMD electrodes remains challenging, but it can be improved by integration with carbonaceous materials through various methods, such as carbon coating using CVD [24].

1.3.4 Catalysis applications

Nanosheets of TMDs can be advantageous in catalysis reactions given the great stability of these materials against photo-corrosion and their tunable bandgap, allowing the use of MX_2 compounds for light harvesting from visible to infrared wavelengths. Therefore, they can be applied in photochemical water-splitting reactions and for energetic charge transfers. It has been also demonstrated that these performances can be enhanced by hybridizing TMDs with other materials [25]. The major interest is, however, directed at their application in the hydrogen evolution reaction. If the bulk form of TMDs is not really efficient, their miniaturization allows a higher number of active areas for the catalysis [26]. In particular, theoretical calculations have identified the metallic edges of a trigonal prismatic structure of MoS2 to be active for the electrochemical reaction, whereas the basal plane stays inert [27]. This is supported by experimental evidence that the sulfide terminated Mo-edge of 2H MoS_2 plays the central role in the reaction [28].

1.3.5 Valleytronic and sensing applications

Valleytronics is a new field of electronics that relies on the use of the valley degree of freedom of electrons, which can be seen as an analogy to their spin. Different from spintronics, which is based on the spin of electrons, valley tronics focuses on the energy minima or maxima in the band structure of materials, known as valleys. The interest in TMDs comes from the existence of two valleys with opposite circular polarization. It has been demonstrated that TMDs exhibit strong spinorbit coupling, leading to the formation of spin-valley coupled states, which can be manipulated by external stimuli such as the application of strain, magnetic, and electric fields [29]. These characteristics may enable TMD's valley degree of freedom to be employed in valley-based logic gates, memory devices and filters. Having a large surface to volume ratio and high surface mobility, TMDs can be suitable for sensing applications. A first example is represented by the detection of heavy metals, such as Hg^{2+} , which were detected by a FET based on molybdenum disulfide. Since heavy metal ions have a strong specificity towards the sulfur of the TMD and good electron transfer, the in-plane conductivity of MoS_2 appears to be modulated [30]. In another example, the high demand of sensors for diabetic patients has led to the development of a glucose sensitive sensor based on the metallic phase of WSe_2 , demonstrating a good signal to noise ratio and the possibility to integrate metal nanoparticles to increase the response time[31]. TMDs can also be applied to probing of DNA strands after a surface functionalization, which may result in physical changes to the TMD's properties and enable their application to molecular and cancer diagnostics [32].

Chapter 2

Theoretical Background

2.1 Properties of 2D materials

2.1.1 Electronic properties

The transition metal coordination directly affects the electronic structure of the TMD, in particular its d-electron count. It is demonstrated that for the 1H and 1T phases, the non-bonding d bands can be found in between the gap separating the bonding (σ) and anti-bonding (σ^*) bands of the M-X bonds as can be seen in Fig. 2.1. Also, transition metal centres coordinated octahedrally (D_{3d}) can form a degeneracy resulting in $d_{z^2,x^2-y^2}(e_g)$ and $d_{yz,xz,xy}(t_{2g})$ orbitals being occupied by the d electrons. However, the d orbitals of trigonal prismatic coordinated TMDs (D_{3h}) separate into three different groups, namely $d_{z^2}(a_1), d_{x^2-y^2,xy}(e)$ and $d_{xz,yz}(e')$. Overall, the different behavior of TMDs comes from the progressive filling of d bands from group 4 to group 10 in the periodic table. If the bands are partially filled we get a metallic behavior with the Fermi level sitting inside the band whereas if we have full occupation, we get a semiconducting one. Also, it should be noticed that the impact of the chalcogen atom on the electronic structure is negligible with respect to the metal ones, but still a trend can be found. Indeed, there is a broadening of d bands and therefore a reduction of bandgap while increasing the atomic number of the chalcogen. Hence, group 4 TMDs express an octahedral structure, with group 5 showing both octahedral and trigonal prismatic. Group 6 are trigonal prismatic, with group 7 showing a distorted octahedral structure and group 10 an octahedral configuration.

To fully address the electronic properties of TMDs, one should focus on the differences arising between bulky structures and low-number layered ones, in particular monolayers, with a remarkable change expressed by semiconducting TMDs. In Fig. 2.3 analysis conducted on bandgap characteristics of MoS_2 from bulk to few to monolayer is reported. In particular, bulk material shows an indirect



Figure 2.1: Electronic structure bands for different TMDs groups [11].

bandgap semiconductor with a gap of around 1eV with the valence band maximum centered around the Γ point and the conduction band minimum in the middle of $\Gamma - K$ symmetry lines. However, the single layer is a direct bandgap material, with both minimum of conduction and maximum of valence bands at the K point. The transition from indirect to direct bandgap originates from the quantum confinement effect and it is one of the main reasons bi-dimensional materials have gained so much interest in the field [11].



Figure 2.2: TMDs bandgaps from bulk to mono layered structures [11].

2.1.2 Vibrational properties

To study the vibrational properties of materials, Raman spectroscopy is a powerful technique based on light scattering that is able to investigate the internal structure of molecules. When light at a certain frequency impinges on a surface, both elastic and inelastic scattered photons are generated. The vast majority of photons are scattered elastically, hence emitted with the same energy (i.e., frequency) of the incident light. This process is called Raleigh scattering. Nevertheless, a small fraction of photons $(10^{-6} - 10^{-9})$ of the total number) are absorbed putting the molecule in a different vibrational state, with a subsequent interaction with one or more phonons, creating or absorbing them. Depending on that, photons are re-emitted, either at a lower or higher energy than the incident one, hence creating an inelastic scattering. A Stokes shift is observed for scattered photons with a decreased frequency with respect to the incident photon, whereas an anti-Stokes shift is observed if the energy of the scattered photon is observed at higher frequencies. From a probabilistic point of view, Stokes events are much more likely to happen, since anti-Stokes events require the pre existence of phonons, that are not numerous even at room temperature (RT). To be more precise, in the following one can express the Raman efficiency for both Stokes and anti Stokes as:

$$\eta(Stokes) \propto n(\Omega, T) + 1 \text{ and } \eta(anti - Stokes) \propto n(\Omega, T)$$
 (2.1)

with Ω representing the frequency of photons and T the temperature, with n expressing the Bose-Einstein distribution

$$n(\Omega, T) = \frac{1}{\exp\frac{\hbar\Omega}{kT} - 1}$$
(2.2)

The characteristic Raman spectrum is formed by only specific discrete frequencies, arising from the quantization of energetic levels of molecules and phonons, therefore the energetic transitions that electrons can undergo are represented by the following graph, where one can notice the quantum levels associated to vibrational states.



Figure 2.3: Rayleigh, Stokes and anti-Stokes scattering represented by Jablonski energetic diagram. One can notice the fundamental state S_0 with the higher energies vibrational states associated with it [33].

To determine the intensity of the Raman spectrum, the induced dipole moment originating from the polarizability of the molecule's electron cloud as a consequence of the interaction with the oscillating electric field of the incident monochromatic light should be taken into account. Hence, the signal intensity is determined by the variation in polarizability of the molecule, with a stronger signal if the electron cloud is heavily distorted. Also, the vibrational modes of the elements composing a molecule are uniquely determined by the peak position and therefore the spectrum is direct evidence of the functional groups present in the sample. Raman shifts are an intrinsic property of the material and are usually expressed in wavenumbers $(cm^{-1} \text{ as unit})$, deriving from the difference between the inverse of the incident and scattered wavelength. Some information related to the crystallographic quality, induced strain, and number of layers can also be extracted from the spectrum [34].

To get a more quantitative insight into Raman intensities, one should distinguish between Raman active, Infrared active and optically silent modes. A Raman active mode intensity is defined by the Raman tensor, expressed as

$$\mathbf{Rt} = d\sigma/d\Omega \propto \sum_{j} |e_s Rt_j e_i|^2 \tag{2.3}$$

where e_i and e_s are the polarization vectors of incoming and scattered photons, respectively, and Rt_j is the *j*-th Raman tensor of the vibrational mode. Also, for a Raman mode to appear in the spectrum, some conditions should apply: correct scattering configuration, phonon-electron coupling since the intensity is proportional to the square of this interaction and excitation energy, if one wants to enhance the intensity of one particular mode of the sample [35]. Overall, the representation of phonons in bulk MX_2 at the center of the Brillouin zone (i.e., Γ point) can be seen as

$$\Gamma_{bulk} = A_{1g} + 2A_{2u} + 2B_{2g} + E_{1g} + 2E_{1u} + E_{2u} + B_{1u} + 2E_{2g} \tag{2.4}$$

where one can point out A_{1g} , E_{1g} , E_{2g}^1 and E_{2g}^2 as Raman active, whereas the infrared actives are E_{1u}^1 , E_{1u}^2 , A_{2u}^1 and A_{2u}^2 and the others are optically inactive[36]. Since most of the samples that will be treated in this dissertation are made of WS_2 a more in-depth focus on vibrational properties of this material is required. In particular, WS_2 is structured as a trigonal prismatic crystal with an alternance of S-W-S atoms stack. Therefore, a single plane is made of three layers, namely two sulfur layers sandwiching a tungsten layer, as illustrated in Fig. 2.4. In the figure can be noticed that the active modes are E_{2g}^1 and A_{1g} at the Γ point and the LA modes at the M point. The formers are optical phonon modes whereas the latter are longitudinal acoustic modes. E_{2g}^1 represents an in plane mode whereas the A_{1g} is an out of plane vibration of sulfur atoms. Also, LA modes reflect the in-plane movement similar to sound waves. The Raman spectra can be fitted with multiple Lorentzians, to extract the peaks location precisely, represented by the following relation:

Lorentzian fit
$$y = a_0 \left(1 + \left(\frac{x - a_1}{a_2}\right)^2\right)^{-1}$$
 (2.5)



Figure 2.4: Illustration of the trilayered structure of WS_2 and principal Raman active modes. Notice S atoms in green and W atoms in red. [37].

where a_0 is the peak intensity, a_1 peak center position, and a_2 the peak width, namely half of the full width at half maximum (FWHM).

Fig.2.5 shows Raman spectra of WS_2 taken from a test structure where one can notice the Lorentzian fitting of the acquired data. The most important peaks to notice are A_{1g} , 2LA and E_{2g}^1 .



Figure 2.5: Lorentzian fitted Raman spectrum of WS_2 with the most relevant resonance modes displayed

2.2 Synthesis methods

To develop a reliable, scalable and industrially appealing technique to employ TMDs, it is important to study different methods of production of the thin films.

Given the structure of TMDs, showing a strong in-plane covalent bonding but weak van der Waals interactions between interlayers, the materials can be either isolated in a top-down approach or synthesized in a bottom-up manner. The top-down method involves mechanical exfoliation of the bulk TMD crystals whereas the bottom-up is achieved by synthesis of TMD from vapor phase precursors. The following sections provide an overview of the different methods, pointing out major benefits and drawbacks of them.

2.2.1 Mechanical Exfoliation

Mechanical exfoliation was one of the first methods used for the isolation of graphene. This method, referred to as the "scotch tape" method was able to provide samples with very high quality for research purposes. It involves the use of adhesive tape to peel off a few monolayer flakes from a bulk crystal, which are subsequently transferred onto a target substrate. Despite the insightful information attainable from this technique, the lack of control of positioning, shape, thickness and potential contamination of the flakes does not make it suitable for large scalability and mass production in the industry. Therefore, other methods need to be exploited [11].

2.2.2 Liquid Phase Exfoliation (LPE)

Another example of top-down technique is found in the liquid phase exfoliation. It is possible to achieve micrometer dimensions of the flake, making it a scalable technique. Among the LPE techniques, it is possible to distinguish between two methods. The first one is based on the dispersion of powdered nanoparticles in either a solvent of aqueous-based surfactant and then sonicated. The surfactant is able to coat the created sheets to prevent a post re-aggregation relying on the ability to overcome the energy cohesion between surrounding layers. Even if the sonication may affect the lateral dimensions of the manufactured layer, a good yield is still achievable. A nearly 100% yield method is represented by the synthesis of nanosheet from the hydration of lithium intercalated compounds enhanced by ultrasound. The process involves the creation of $Li_x XS_2$ compounds which are the precursor to create the solid form by sonication in water. By controlling the reaction and the Li amount one can control the yield of the process and the obtained TMD phase. The major advantage of this method is the possibility to generate a metallic 1T phase, obtained from a charge transfer process from metallic Li to the TMD, where the water bilayer plays the fundamental role of passivating the residual negative charge. However, also this process has some drawbacks, such as high temperatures, length of the reaction and needs a controlled environment to prevent nucleation of metal nanoparticles [11].

2.2.3 Chemical Vapour Deposition (CVD)

Chemical vapor deposition is a technique employed to deposit thin films from a vapor phase reaction with gaseous precursors. It is possible to deposit a broad range of materials, including metals, insulators and semiconductors. In general, the process involves high temperatures and low pressures, but there are some exceptions. The environmental conditions are crucial to provide the reactant gases with sufficient activation energy to become reactive species in the deposition process. On a molecular scale level, the overall reaction can be separated into multiple subprocesses happening subsequently. In a region with a controlled gas flow, the precursor molecules are transported into the reactor and diffused to the sample surface. At this point, molecules are adsorbed and further diffused on the surface up to their decomposition. Therefore, it can be observed the nucleation and growth of material, incorporating into the thin film. At a final stage, excess molecules or byproducts undergo desorption. It is worth noticing that the process can be limited



Figure 2.6: Cycle process of CVD subsequent reactions happening at the substrate surface [38].

by the reaction rate or the mass transport, whichever is the slowest. Also, the diffusion of the molecules on the surface is strongly related to the temperature of the process, following an exponential Arrhenius trend as expressed by the relation $R = R_0 e^{-E_a/(kT)}$. In particular, the surface reaction rate increases accordingly with temperature until a saturation point, therefore the process is mass transport limited. However, at low temperatures we have a reaction-limited process, as shown by the trend in the figure, where it can be observed the separation of the two regimes. The main advantages of CVD are good step coverage, reliability and conformal coatings, making this technique suitable for microelectronics applications where high aspect ratios structures are created. Among the different types of CVD, we can differentiate between atmospheric pressure CVD, with high deposition rates but lower conformality than the low-pressure CVD deposition, characterized

by good uniformity at expense of a lower throughput. Also, plasma enhanced (PECVD) can be employed to improve the decomposition of precursors by means of physical plasma. Regarding the synthesis of transition metal dichalcogenides, it is important to notice that metals and chalcogens exhibit very different physical properties, therefore making their stoichiometric combination controllable. In particular, transition metals show high melting temperatures (over 2000 °C) and low vapor pressure whereas chalcogens exhibit lower melting temperatures (below 500 °C) with much higher vapor pressures. Four different approaches can be highlighted for TMDs synthesis: the first one is based on precursors' decomposition via thermal process, with a reducing environment preventing oxidation and favoring transformation into MX_2 . To obtain good quality thin films, thermolysis in two steps is performed, consisting of the removal of solvent and annealing to improve crystallinity; the second approach consists of chalcogenation of a pre-deposited metal or relative oxide on a substrate, obtained through various deposition techniques. By controlling the annealing time, it is possible to control the number of chalcogenated layers, since the process is slow; the third possibility is represented by a physical vapor transport of MX_2 powders kept at high temperatures to a target growth substrate by an inert gas controlled flow; the last method, which is also the most common, is based on a vapor phase reaction of two precursors, the chalcogen and the metal oxides, with a fundamental role played by H_2 in the thermodynamics of the reaction [39].

2.3 Transfer methods

In the previous sections, different methods of synthesis were presented. However, some target substrates may not be suitable for some synthesis methods of TMDs, due to high temperatures and other harsh conditions. For this reason, transfer methods have been developed to make the TMDs available for advanced characterization methods and for their use in device applications. The most important elements to take into account when doing a transfer are surface energies and uniformity. Among transfer processes, one can distinguish between wet and dry methods. The wet processes, such as those using solvents or intercalation chemistries are used to reduce the mechanical manipulation of the synthesized film and subsequent induced stresses whereas the dry one does not involve any water or chemicals during the process. Some methods can be a mix between the two, therefore another distinction can be made between those methods involving a support, such as a polymer, and those that do not. The majority of this section will focus on polymerassisted transfer methods. Polymers are involved in this technique due to their good flexibility, uniform contact creation and mechanical strength. An important relation to consider is related to the surface energy of a material, described by the

following Young's equation:

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg} cos\theta \tag{2.6}$$

where θ is the contact angle between solid and liquids, σ_{lg} , σ_{sl} and σ_{sg} are the surface tensions of liquid, between liquid and solid and solids, respectively. The important information is that hydrophobic surfaces show a contact angle larger than 90° with a low surface energy whereas the opposite behavior is displayed by hydrophilic ones. A lower surface energy is associated with a lower adhesion force, therefore a polymer with these characteristics will be removed more easily without leaving residues. At the same time, the surface energy of the target substrate should be higher than the polymer one, to allow for a good adhesion of the film. A commonly used polymer is polymethylmethacrylate (PMMA), which enables to transfer the film on a target substrate after wet scooping. However, the drawbacks of PMMA are that it is hard to completely remove its residues from the surface and they could cause a degradation of optoelectrical properties of the 2D-based materials. For this reason, additional etching or annealing steps to remove residues are required, which could cause wrinkles in the film. Also, the use of strong chemicals can damage the target substrate, hence making this method incompatible with mass production in industry [40]. Dry transfer processes are introduced to be able to obtain a large-scale transfer due to a more easily controlled adhesion between the substrates. A common material used in this context is polydimethylsiloxane (PDMS), a viscoelastic polymer with good flexibility, transparency and low surface energy. These characteristics ensure an easy detachment of the film from the PDMS without the need for wet hazardous chemicals, resulting in a cleaner transfer. The problem with PDMS relies on the difficulty to create a uniform contact with the 2D film, due to surface grains, therefore inducing damages. This issue can be partially solved by using a thermal release tape that can be controlled by a rolling station, however, it can leave some residues on the surface [41]. Previous works have pointed out that a polystyrene (PS) method can be beneficial compared to the PMMA one, since PS forms stronger binding with the film to be transferred, due to a higher hydrophobicity with respect to PMMA. Also, the Young's modulus of PS being larger than that of PMMA, more robust support for the 2D film is provided, reducing wrinkles and cracks. Another advantage of PS is the possibility to peel off the film in water without the need for long-term etching processes in hot solutions (such as KOH) and to avoid bubble generation, which could cause damage to either the sample or the substrate. One disadvantage of PS is that it is more brittle than PMMA, limiting its suitability for large-scale integration. However, for small-scale applications, such as for material quality analysis, it is quite useful. In this work, the PS method is adopted, ensuring an easy and fast way to transfer TMDs to target substrates for further study.

Chapter 3

TMD Patterning, Synthesis and Characterization

3.1 Overview and motivation

The field of two-dimensional materials research has rapidly grown in recent years, with some promising achievements. However, the large-scale integration of these cutting-edge materials remains a challenge. As the final objective would be their implementation in a variety of applications, such as electronics, sensing, and energy storage devices, a reliable and reproducible method to integrate highquality materials is required to exploit their unique properties. Overcoming these challenges is one of the primary goals for studying the lithographically defined lateral conversion synthesis method that is being developed by this group. In this thesis, I will explore the application of this technique to the synthesis of sub 20 nm features using self-assembled block copolymer (BCP) directed lithography, as well as to standard optical lithographically defined structures for applications in optical devices. The BCP patterned structures will be used as a test bed for producing ultra-small features, as well as to study the details of the lateral conversion process and the effects of process parameters on the evolution of the crystalline microstructure during the conversion. TEM is one of the few methods that allows us to study the microstructure at the atomic scale. And since the fabrication process results in the TMD being buried between different layers of materials, scanning probe methods are not feasible. To enable TEM, the sample needs to be ultra-thin, on the order of tens of nanometers. The strategy pursued for this study was to transfer the converted TMDs onto TEM grids using a polymer lift-off process. The development and validation of this transfer method enabled the transfer of BCP-patterned TMDs from the original growth substrate to TEM grids. A series of synthetic experiments were carried out to perform a detailed

study of the effect of temperature during each stage of the two-step reduction and conversion process. Optical microscopy, SEM, Raman, and TEM were used to optimize the transfer process, and perform a detailed characterization of the TMDs. Following the investigation of the synthetic parameters, the optimized conditions were used to integrate TMDs into an optical device, a distributed Bragg reflector mirror (DBR), with the aim of demonstrating the performance advantages of TMDs.

3.2 TMD Synthesis and Transfer

3.2.1 Lateral conversion method

Existing methods of TMD fabrication and integration, such as CVD and mechanical exfoliation, discussed above, still suffer from a number of challenges and limitations. As highlighted in 2.2, mechanical exfoliation is a good way to obtain materials to perform fundamental studies, but it is not suitable for their integration on a large scale. To solve the poor repeatability and exposure to contamination of this method, gas-phase growth methods such as CVD are employed. However, it should be considered that for a complete and reliable integration of TMDs, not only is a controllable synthesis needed, but it should also be possible to tune the material properties either during or after the growth, and the properties need to be preserved throughout the multiple steps of the fabrication process. Therefore, it is desirable to avoid exposure to environmental conditions, and minimize contaminants and structural defects arising from the fabrication process, such as residues coming from lithography or oxidation after passivation of surfaces. In this context, the lateral conversion method described below takes advantage of pre-defined lithography patterned structures, controllable TMD thickness, with a precision down to few layers, and the encapsulation of the 2D materials between two layers of SiO2, which protects the TMD from contamination. The TMD lateral conversion synthesis method was developed by the Kuykendall group [42], and aims to overcome some existing limitations to the large-scale integration of these materials. The lateral conversion process can be broken into two main steps: substrate fabrication and chemical conversion. The general idea of the method is to lithographically define a reactive metal oxide (or metal) layer sandwiched between non-reactive silicon oxide layers. This sandwiched oxide film is lithographically patterned to define the desired features of the final TMD structures, and then etched to expose the edges of the buried oxide layer (Fig. 3.1a). The substrate is then heated in a furnace and the metal oxide is converted to the TMD in a two-step process (Fig. 3.1b-c). First, the oxide is reduced to the metal in the presence of hydrogen gas, and second, the metal is converted to the TMD in the presence of a reactive chalcogen precursor. Because only the edges of the substrate are exposed, the conversion

process proceeds laterally as the gas diffuses from the edge toward the center of the patterned feature. The top three images in Fig. 3.1 illustrate this process. Below each of these illustrations are optical microscopy images of an actual substrate converted using this method. The contrast in the image is due to interference effects and changes in the refractive index of the converted material. A detailed



Figure 3.1: Schematic representation of lateral conversion CVD process, highlighting the three main steps of the procedure. From left to right, lithographic patterning, reduction step, and final conversion[42].

step-by-step description of this process follows. In the first step, a Si wafer with a thermally grown layer of 250 nm thick SiO_2 is used. A metal oxide layer is deposited onto the wafer, which can be expressed with a general formula MO_x . This step is performed by plasma-enhanced atomic layer deposition (PEALD) to guarantee optimal control over thin film thickness and conformality. The thickness can be precisely controlled, typically in a range of 2 to 10 nm, and determines the number of layers of the van der Waals material after conversion. The metal oxide layer is then capped with a few nanometers of SiO_2 , deposited by PEALD to ensure a high-quality interface. An additional 10 - 50 nm of SiO_2 are then deposited by plasma-enhanced chemical vapor deposition (PECVD), which increases the thickness of the capping layer while preserving a reasonable processing time. A representation of the multi-layer structure can be visualized in Fig.3.2.

While the laterally converted reactive layer could be composed of either metal or metal oxide, the latter was chosen because they can be uniformly and conformally deposited by atomic layer deposition (ALD), a widely used fabrication technique. ALD can be described as a CVD reaction split into two halves, aiming at keeping the precursors separated during the different steps. It is a self-limiting process based on surface reactions happening in a vacuum chamber with sequential gas pulses of precursor and co-reactant, repeatedly producing monolayers due to precise control of the number of cycles. As can be observed by the scheme in Fig. 3.3, a



Figure 3.2: Graphical representation of the stack employed in the lateral conversion method. From bottom to top, Si substrate with a layer of thermal SiO_2 on top; TMD layers are grown on the SiO_2 and encapsulated with SiO_2 , both grown by ALD; a final passivation layer of SiO_2 is deposited on top.

cycle is made of exposure to the first precursor, purge of the chamber to evacuate the excess non-reacted precursor or potential by-products, introduction of second precursor and final purge.



Figure 3.3: ALD cycle for Al_2O_3 growth illustration pointing out the controllability of the process

Good ALD precursors have to be volatile with a good stability without decomposition due to high temperatures and should quickly react without damaging the sample surface. An advancement is represented by PEALD, which enables controlling the reactions with a plasma flow, achieving lower temperatures and expanding the ALD window by decreasing the activation energy and limiting the surface contamination [43]. The film is then patterned using standard optical lithography techniques. Photolithography allows for the transfer of a desired pattern onto a substrate by exploiting the interaction of a material, the photoresist, photosensitive with certain wavelengths of the light spectrum. The PR is a mix of different components, but overall can be described as an organic material that is exposed selectively by means of a mask, which is transparent only where the desired pattern is intended to be transferred. The PR can be separated between positive or negative. The former is made soluble after the interaction with light whereas the latter becomes less soluble. This produces an opposite effect when interacting with a developer, which is used to obtain the final patterning. To expose the edges of the encapsulated metal oxide, etching through the stack thickness is required. Etching can be divided into two different approaches: wet and dry etching. The former relies on wet chemical solutions that react with the sample surface when immersed in the bath. Wet solutions are overall stronger and selectively remove very resistant materials, but are also more hazardous and not suitable for any kind of substrate. To eliminate handling of dangerous acids and solvents, dry etching is introduced, gaining in terms of process control and versatility. Dry etching is based on gas or vapor sources typically ionized, either plasma or non-plasma assisted. In general, the dry approach allows to obtain great directionality of the etching with high aspect ratios and less undercutting. Nevertheless, some major issues arise from the toxicity of gas and re-deposition of nonvolatile compounds.

After lithographic patterning, the actual TMD reaction can be detailed as follows. The gas-assisted reactions are performed in a furnace: the tool is a "OTF-1200X-4-RTP" compact rapid thermal annealing furnace composed of a 4" quartz tube (see Fig.3.4). The system is heated by a halogen light with a power of 10kVwith a heating rate of 120° C/s. The cooling system is made of a recirculating water chiller and the vacuum is reached through pumping. The temperature control is automatic, with an accuracy of $\pm 0.5^{\circ}$ C, and can be programmed by a digital display. The temperature sensor is based on a thermocouple in contact with the aluminum nitride sample holder. The furnace is kept under a controlled environment in a glovebox and the gas flows are provided by a gas stream underneath the glovebox. Indeed, selectors valves are used to switch to Ar supply, to provide a reducing environment with H_2 and to deliver H_2S supply.

The metal oxide MO_x is transformed into MX_2 in a two-step process: first, the oxide is reduced to the corresponding metal, then it is chalcogenated by exposure to H_2X to get the final TMD. More in detail, the reduction step is performed



Figure 3.4: Tube furnace for lateral conversion

by heating the sample in a temperature range of $650 - 750^{\circ}$ C in a gas flow of combined Ar and H_2 at atmospheric pressure for a duration of 2 hours. After that, the chalcogenation is done by inserting a flow of H_2X in the Ar/ H_2 mix at temperatures ranging between $650 - 850 \,^{\circ}$ C at a pressure of 100 torr. To guarantee good conversion, a rapid gas exchange is achieved between the two steps, while at the end of the process, the system is left to cool down at controlled pressure with inert Ar flow.

To summarize, this section has provided motivation to the choice of implementing the lateral conversion approach, elucidating the advantages over traditional synthesis methods, and has detailed the different steps of the fabrication process flow.

3.2.2 Block Copolymer (BCP) lithography

In the electronics industry, there has been a continuous effort directed towards the reduction of lithographically defined feature sizes. As the classical top-down approach reaches its limits, interest in bottom-up methods has been increasing. One particular approach, a directed self-assembly (DSA) of block copolymers (BCPs) has been demonstrated to achieve patterning of features down to a few nanometers. A multi-step process to selectively pattern the two polymers is developed. Indeed, a combination of dry, wet and ion beam etching is required [44]. The most common BCP system is made of PS-b-PMMA, with surface energies of PS and PMMA similar between them and the possibility to easily control the orientation of the domains by tuning them by an external field. A general description of the fabrication process is presented in the following. The BCP pattern is created by depositing the cross-linkable mix between PS-b-PMMA on the surface as a first step by spin coating and subsequent annealing. During the annealing, the cross-linking takes place as well as the creation of a mat layer of the same thickness as the spun layer. Then, e-beam resist is used to coat the sample and e-beam lithography is performed, resulting in the creation of the desired pattern. Another thin layer of PS-b-PMMA is coated, this one going to graft the brush between the mat stripes. After, the BCP film is etched through dry anisotropic oxygen/helium assisted etching, removing the PMMA 2.5 times faster than PS. Hence, a PS pattern is created, serving as a resist mask for the following AlO_x conformal coating by ALD. The AlO_x will serve as a hard mask for the etching of the underlying substrate. After BCl_3 based dry etching the excess AlO_x is removed from the surface, to finally create an interdigitated AlO_x/PS pattern. Subsequently, O_2 plasma eliminates PS and the SiO_2 etching can be performed, by means of $CHF_3/Ar/O_2$ plasma-assisted recipe [45]. The result consists of a successful reduction of the lithographic limit, the entire process being reported schematically in Fig. 3.5. The etched substrate is now ready for further manipulation, in this case it will undergo lateral conversion. The next section will describe the characterization of these features more in detail, but a first overlook of the structures can be observed as a result of the transfer of the BCP-assisted conversion of the substrate onto a SiO_2 substrate, in particular in Fig.3.6 one can see how these small features appear. SEM images report BCP DSA structures on standard electrodes patterned using a standard lithographic mask on the SiO_2 substrate.



Figure 3.5: Process flow graphics of the BCP bottom-up approach. Coating of the original substrate and subsequent patterning of the PS-*b*-PMMA mix are reported. Also, AlO_x coating is described, used as hard mask for the final etching step, resulting in a shrinking of the lithographic limit.



Figure 3.6: SEM images at different magnifications showing the BCP random orientation when transferred on a target substrate.

3.2.3 Poly-Styrene (PS) assisted transfer method

As mentioned in the previous section, the wet transfer method allows to exploit of liquid/solid interactions of the substrate and TMDs with water. Indeed, polystyrene (PS) is relatively hydrophobic, whereas SiO_2 is hydrophilic. This interaction causes the water to penetrate between the layers, lifting off the polystyrene and the TMD, which are more strongly adhered to each other than the TMD is to the substrate. Due to the density and hydrophobic interaction, the polystyrene floats to the surface of the water where it can be lifted out by the target substrate. The experimental method is straightforward, however, the steps need to be carefully executed to preserve the fragile films. The following steps are performed:

- The 5 x 10 mm^2 converted substrates are cleaved into two parts, to generate samples of 5 x 5 mm^2 , which is sufficient to cover the dimensions of the target TEM grid.
- 30 μl of PS (280 kDa, 10 wt%) dissolved in toluene is applied to the top of the sample and spin-coated at 3000 rpm for 45 s with a ramp-up time of 10 s. It is then baked on a hot plate for 30 min at 60°C to let the excess solvent evaporate from the sample before proceeding with the transfer.
- The samples are scratched with a razor along the edges and with a cross pattern in the center to further divide the sample into four smaller squares and to expose the edges to the water intercalation. The four small squares have a dimension sufficient to completely cover the TEM grid without wrapping around it.
- The substrate is immersed in a glass dish with a reasonable amount of deionized (DI) water and let sit until the flake is delaminated, as a result of different surface energies driving water molecules to penetrate between the films. For particularly stubborn films, this step is preceded by a few minutes of exposure to a 7% buffered HF solution dispersed dropwise on the surface of the substrate.
- The flakes, which float on the surface of the water, are lifted out onto the desired substrates and left to completely dry.
- The polymer is dissolved in toluene, carefully dispersing droplets onto the surface and letting the solvent wick through the grid into a tissue so as not to disrupt the deposited structures, washing them away, and concluding the transfer process.

Since this process started as a proof of concept, continuous improvements, and small adjustments were explored throughout the project. Indeed, because the samples were comprised of such small, densely-packed features water molecules appeared to have difficulty intercalating between the layers, making it more difficult to overcome the surfacial energies. To speed up the delamination process, we observed that it was helpful to put the glass dish on a hot plate for a short time (roughly 10 minutes) at a temperature of around 100°C. This led to a great improvement in the time needed to peel off the polymer from the surface without interfering with the grown material. Also, mechanical help to lift the flake was introduced by gently handling a blade to detach all the edges from the surface. However, this approach is not beneficial for the quality of the transferred material, since some residual stress is introduced in the structure, as it will be discussed later in this section. Another approach to improve the polymer lift-off, was to add a few droplets of diluted HF on top of the sample proceeding with the immersion of the chip in water. By etching the SiO_2 surface as the water intercalates between the layers, we observed a more effective removal of the PS film, successfully lifting off and transferring the patterned TMD entirely to the TEM grid. After the transfer onto the target surface, the TEM grid is left to dry on a hot plate at 120°C for 15 minutes. In figure, an illustration of the entire process can be observed, with the cartoon showing the flake floating in water before being transferred onto the target grid. Notice that manipulating such a fragile material is challenging, and the throughput is not always as desired, meaning that the repeatability of the process has to be improved. However, as a first method to give a quality assessment of the grown materials, the results obtained in terms of transferred samples was good enough to enable electron imaging, either transferring a full square or just a part of the flake on the TEM grid.

The objective of this process is to be able to provide a way to characterize the quality of the material in a simple and relatively fast manner. The idea is to take advantage of electron microscopy, in particular - SEM and STEM, to analyze the structures. The choice to use these characterization methods for the preliminary analysis was made to speed up the process, enabling the study of multiple samples during a single session, and requiring less laborious sample handling and alignment required for TEM. In this case, STEM mode of a Zeiss Gemini Ultra55 Field Emission Scanning Electron Microscope (FESEM) is employed. To make a distinction between STEM carried out in the FESEM vs those from the TEM, we will refer to these as FE-STEM. The lacey carbon grids provide a sufficiently thin sample to make transmission microscopy possible. In FE-STEM mode, it is possible to reach accelerating voltages in the electron gun of 30 kV, which is good enough to give a first overview of grain dimensions and distribution. A separate project conducted by the group is to directly grow the TMDs on a platform that allows TEM membranes to be etched into the substrate after growth, allowing TEM analysis to be performed on the as-made sample without transferring it.



Figure 3.7: Graphic illustration of the PS-assisted transfer process: PS is dispensed on the substrate with a pipette, spin-coated, then baked for 30 minutes to let the solvent evaporate. The substrate is submerged in water, and once the difference in surface energies lifts off the flake, it is transferred onto a TEM grid. Notice pictures of the real process of the last two steps.

3.2.4 Study on the induced strain

As expected, the transfer process introduces mechanical damage in the structure, mainly due to the required manipulation to help the flake delaminate from the substrate. In theory, it would be possible to identify the number of layers transferred as well as those remaining on the substrate using Raman spectroscopy. An analysis of the resonant peak positions could be conducted, allowing the determination of whether the flake is made of single or multiple layers, also referring to their relative Raman intensity. By reducing the number of layers, the vibrational modes soften as a result of a decrease in the interlayers interaction, which would cause a decrease in the frequency of the A_{1g} peak and, unexpectedly, an increase for the E_{2g}^1 one. However, in this case, this study cannot be extensively examined, since the induced strain on the surface leads to a macroscopic effect on the Raman spectrum, which leads to an overall redshift of the peak positions. To give a quantitative description of this effect, the analysis is done by comparing the Raman spectra of the substrate
before and after the transfer, as well as the TEM grid signals. The objective is to find a remarkable difference in terms of both intensity and peaks' position in the substrate before and after the transfer. The analysis is reported for the sample synthesized with both reduction and conversion at 750°C, but is observed in the entire set of samples. As reported in Fig. 3.8, a first evaluation is done on the intensity of the three samples: on the left, both the A_{1g} and E_{2g}^1 peaks are on the order of 2000 counts, whereas on the right, one can observe that the intensity drops to the order of 500 counts after the transfer. Also, the signal obtained from the TMDs on the TEM grids are significantly lower than those on the substrate due to the fact that part of the scattered light passes through the grid and is not reflected back towards the detector. As a consequence, the signal has a lower signal-to-noise ratio, but is still sufficient to provide quantitative information. From the fitting of the curves, the peak positions can be extracted and are summarized in Table 3.1. The original substrate shows the E_{2g}^1 peak at $356.91 \pm 0.10 \ cm^{-1}$ and the A_{1g} at $420.70 \pm 0.05 \ cm^{-1}$. If a negligible shift is observed for the substrate after the transfer, a small but noteworthy shift is registered for the TEM grid. Indeed, the E_{2g}^1 peak is detected at 354.08 \pm 0.14 cm^{-1} and the A_{1g} at 418.11 \pm 0.08 cm^{-1} . A similar behavior is observed in mono- and a few-layers of MoS_2 , where uniaxial strain has been applied. Therefore this effect can be attributed to steps in the transfer process that could have induced a strain in the material [46]. As previously mentioned, the mechanical manipulation could be one cause, but also the heating of the grid to improve the adhesion as well as the forces between the polymer and the substrate acting after the spin coating.

	$E_{2g}^1(cm^{-1})$	$A_{1g}(cm^{-1})$
Pre-Transfer	356.91 ± 0.10	420.70 ± 0.05
TEM Grid	354.08 ± 0.14	418.11 ± 0.08
Post-Transfer	356.57 ± 0.12	420.01 ± 0.06

Table 3.1: Summary of Raman peak positions in the substrate pre and posttransfer and the TEM grid. Overall, a redshift is observed for both the grid and the substrate after the flake delamination



Figure 3.8: Raman spectra showing strain-induced peak shifts of the TMD: on the left, the spectrum on the substrate before transfer; in the middle, the spectrum on the TEM grid; and on the right, the spectrum on the substrate after transfer. Notice the intensity difference between the spectra, especially between the original sample and the TEM grid.

3.3 Characterization Results

3.3.1 Grain Size Analysis

The transfer method described above enables further investigation of the material, taking advantage of the electron transparency achieved. A study of the influence of the synthetic parameters on the growth conditions can thus be carried out by analyzing the resulting morphology, microstructure and crystallinity of the resulting material. Grain size analysis is conducted in a systematic manner in order to better understand the effect of different temperatures of reduction and conversion in the lateral conversion synthesis approach. It is important to conduct a study of the growth temperatures since one of the objectives of the project is to develop a synthesis method that could be integrated with CMOS technology. In the CMOS industry, high temperatures are not suitable for integration since they would lead to the failure of the different materials in the chip. Therefore, the BCPtemplated TMD samples were synthesized with different combinations of reduction and conversion temperatures. A set of three different reduction temperatures, namely 750°C, 650°C and 550°C and the same set for conversion temperatures are combined, resulting in 9 combinations. In the RTA furnace described in section 2, samples are annealed in a reducing environment, with 450 sccm Ar flow and 50 sccm of H_2 for 10 minutes, then the furnace is pumped and refilled with the same gases, plus an additional 25 sccm of H_2S , for another 10 minutes of chalcogenation. Both processes are conducted at a pressure of 100 Torr. The short time of the

reaction can be explained by the fact that the extent of conversion to be reached is very small, on the order of < 10nm - around half the width of the line features defined by the BCPs. The following graph (Fig. 3.9) shows a schematic of the temperature ramp-up and hold over the entire process, for reduction at 750°C and conversion at 650°C.



Figure 3.9: Temperature ramp ups and downs for the RTA synthesis process. t_1 is the time needed to reach the set point temperature for reduction, t_2 is the reduction temperature, t_3 is the time to reach the conversion set point and t_4 is the hold time for conversion. Set point temperatures are changed in every reaction.

As a first overview, some interesting results are obtained from FE-STEM images captured at 30 kV, pointing out some differences in the synthesized samples, in particular providing an overall picture of the grain size and distribution in the BCP framework. This first analysis is performed to provide an initial screening of the output and to potentially optimize the transfer method. A deeper understanding of the growth dynamics is offered by the dark field STEM, once the transfer method has been validated.

From Fig. 3.10, a first statement can be that higher temperatures result in larger grains. It is hard to quantitatively determine the actual grain size, but one can notice that the sample obtained from both reduction and conversion at $750^{\circ}C$ shows remarkably larger particles than those obtained for $650^{\circ}C$ and $550^{\circ}C$. Notice that the three images are taken at a magnification of 100 kX, and the scale bar is 100 nm. By lowering the temperature, the particle size reduces, producing a more homogeneous material. Lower temperatures provide indeed a uniform distribution of the small particles, with a polycrystalline nature suggested. As can be observed in the figure, samples synthesized at $750^{\circ}C$ and $550^{\circ}C$ present some darker areas that are associated with the chalcogenated metal, whereas some other areas appear



Figure 3.10: Comparison between three different combinations of reduction and conversion temperatures: in 3.10a the highest temperatures provide the largest grains, whereas the smallest are identified in 3.10c. In 3.10b an intermediate is shown, also with the best uniformity of distribution. Images are taken in FE-STEM mode at 30 kV with 100 kX magnification and 100 nm scale bar. R = Reduction and C = Conversion.

as gray, which is associated with the SiO_2/Al_2O_3 top layer. As a result, these images are also insightful to give an indication of the effectiveness of the TMD lift-off. It appears that at 650°C the surface energies favor the transfer of the majority of the TMD on the TEM grid, the image displaying dark regions over most of the area. It is clear that a uniform distribution of the grains is achieved for this sample, and this trend can be extended to other samples for which the conversion temperature is 650°C. In the other two cases, the structure does not look as dense, suggesting that a significant part of the material either has remained attached to the original substrate or has been lost in the transfer liquid. Also, from these images, it appears clear that the BCP features are slightly dislocated during the transfer, since the stripes are not equally spaced, with some larger gaps appearing randomly in some areas. Further evidence of this can be found in appendix A.2.

3.3.2 High-Angle Annular Dark Field STEM

A deeper understanding of the dependence of the TMD morphology on synthetic parameters can be found by analyzing the STEM images acquired in dark field mode of the JEOL 2100-F field emission TEM. A representative set of images is shown in Fig. 3.11, organized in a tabular way to point out the overall differences between the different reaction conditions. As with the FE-STEM images, we see here that the samples reduced at higher temperatures have larger grains, as well as that those converted at 650°C present a good uniformity. Notice that in the filamentous regions, some of the structure appears to be brighter than others. This is explained by the fact that STEM is a technique sensitive to the thickness and mass of the material under analysis, therefore the higher effective atomic number Z of a material results in increased scattering of electrons, producing bright areas. The brightest spots are associated with unconverted W metal, as will become clearer in the next section.

A quantitative analysis of the dimensions of particles can be done for the set of samples reduced at 750°C. Indeed, this is the only set for which the dimensions and distribution of particles allow a calculation, being more sparsely distributed and bigger in dimensions. The other sets show particles for which the dimensions cannot be resolved singularly. Therefore, for the set of samples with 750°C reduction and 750°C conversion, the particle can be approximated with a rod-like structure, hence the measurements are done by calculating the longitudinal dimension. The 750°C reduction and 650°C conversion set is calculated in a similar way, even if in this case the particles appear to be more spherical. In both cases, 100 particles are measured, and the relative distributions are calculated. The results show an average length for the former to be 15.06 ± 1.50 nm, whereas the latter shows an average length of 9.89 ± 2.11 nm. The size distribution is graphed in Fig.3.12.



Figure 3.11: HA-ADF STEM set of images showing the grain formation inside the structure at different temperatures, recurring trends seen in FE-STEM for uniformity and grain dimensions can be seen.



Figure 3.12: Particle size distribution for the set of samples reduced at 750°C. Particles appear different in shape when reducing the conversion temperature, with a difference in the longitudinal dimension of 5 nm.

3.3.3 HR-TEM insights

To provide a more in-depth analysis of the quality of the material, high-resolution TEM images as well as electron diffraction patterns are collected using the JEOL 2100-F field emission TEM. Indeed, with this technique one is able to gather information on crystallography, adding to the contrast and texture information observed with STEM. In this case, crystallographic alignment closer to major zone axes result in more coherent diffraction, providing more phase contrast, and the ability to resolve crystalline structure with atomic resolution. The most basic information observed in the TEM images is that there are three main shades of gray with the dark and light corresponding to more or less electrons being transmitted through the sample. This can be seen in Fig. 3.13a and 3.13b. The amount of transmitted electrons is dependent on several factors: sample thickness, atomic number of the element - or Z contrast, and interference contrast. We have identified the lightest gray as the underlying carbon support membrane, the medium gray as the SiO_2/Al_xO_y hard mask layer, and the darkest color as the transferred WS_2 . Within the darker regions, further differences are associated with contrast due to crystallographic alignment, and incompletely converted tungsten metal. Highresolution images provide a great visualization of the crystallographic structure. In particular, in every sample, it is possible to identify two main crystalline features. In Fig. 3.13b we can observe the (100) lattice, which appears with the hexagonally symmetric lattice of the basal plane from a top view, which stands out from



Figure 3.13: HR-TEM of 750°C Reduction and 750°C Conversion: on the left 50 nm resolution image showing big dark grains sparsely distributed; on the right magnification reporting (002) crystal fringes largely present, with some (100) lattices appearing in some areas.

the amorphous substrate. We can also clearly observe the (002) crystal fringes, appearing as light and dark stripes. Some of the crystalline lattices are notated in yellow. A quantitative measure of the interlayer distances was performed,



Figure 3.14: HR-TEM set of samples reporting the grain distribution and additional insights on the polycrystalline nature of the features.

showing the interlayer distance of the (002) fringes to be 6.3 ± 0.5 Å, and the (100) orientation to be 2.7 ± 0.4 Å, matching closely with the reported literature values for the c and a lattice parameters, respectively [47]. The measurement was carried out on more than 50 crystal fringes amongst the entire number of samples by extracting a line profile through the lattice and measuring the distance between peaks. Representative measurements of the lattice spacings are shown in Fig. 3.15, where these grains can be clearly observed. From this evidence, we can speculate about the process of grain growth. With H_2S coming from the edge of the lithographically defined structure, we observe a kind of onion-skin-like morphology. Most of the grains show (002) crystal fringes at the edges, and a more basal (100) crystallographic orientation towards the center, with unconverted W metal in the center, appearing darker. The layered structure likely nucleates on the outer edges of the lithographically defined lines with the (002) surface facing outward, perpendicular to the substrate plane. As the growth continues, the

planes grow along the top and bottom surface of the SiO_2 layers sandwiching the center tungsten layer. This process likely continues from the surface toward the center, sometimes resulting in an unconverted tungsten center. We notice that the prevalence of unconverted W metal cores increases for samples reduced at higher temperatures. This could be a result of larger initial W grain sizes limiting the sulfur diffusion and resulting in incomplete conversion.



Figure 3.15: High resolution TEM image of a single grain showing the (002) fringes, (100) lattice and the unconverted metal in the centre. Evidence is supported by the electron diffraction pattern.

The reduction temperature has a clear effect on the size of the grains. As appears evident in Fig. 3.14, larger but more discontinuous particles are observed as the reduction temperature is increased. This is likely due to coarsening of the metal during the reduction step. We also notice the prevalence of unconverted W metal cores increases for samples reduced at higher temperatures, which could be a result of larger initial W grains that limit sulfur diffusion. At lower reduction temperatures, we observe more continuous and homogeneous material, however, the grain sizes are smaller. This can be seen in Fig. 3.16a, where the polycrystalline nature of the structures is evident. This is supported by bright rings of the electron diffraction image. Indeed, the disorganized distribution of the crystal fringes can clearly be seen in Fig. 3.16b.

Moreover, an observation from images taken at higher magnification (Fig. A.3), is that especially for lower reduction temperatures, as the conversion temperature is increased, the number of (002) crystal fringes is reduced, whereas an opposite trend is observed for the (100) lattice. Indeed, in Fig. 3.17, two images for a sample reduced at 550°C are provided, with the number of white circled areas (corresponding to (002)) reduced when passing from the image on the left (conversion



Figure 3.16: HR-TEM of 650°C Reduction and 650°C Conversion: on the left 20 nm resolution image showing good filling of the features, with the associated diffraction pattern suggesting poly crystallinity; on the right magnification reporting many crystalline lattices closed to each other.

at 650° C) to the one on the right (conversion at 750° C). Also, in the image on the right, large areas of basal plane crystals are observed. Additionally, an overall conclusion that can be made is that as the conversion temperature is increased, the number of layers in the set of (002) crystal fringes increases on average. Statistics were collected for 40 instances in different sample areas and reported in appendix A.1.

In many samples, a bright line can be observed running through the center of the converted TMD (see Fig.3.18). A speculation on this observation can be that as the diffusion reaction proceeds laterally from the external edges towards the middle, the W metal is consumed leaving a gap at the center. As a side note, at the end of the project, some tests have been performed using a slightly different transfer method. During the polymer's lift-off, applying a few droplets of diluted HF on top of the sample substituted the water immersion of the chip. This is interesting because in some cases the flakes delaminated from the substrate with some difficulties, due to the high surface-to-volume ratio of the pattern. By using a more powerful chemical to attack the surface, one could expect a more effective removal of the flake. This is indeed verified: HF intercalates at the interface between the Si substrate and the SiO_2 , dissolving the latter and lifting off the stack without leaving material on the original substrate but successfully transferring it entirely to the TEM grid. This is evidenced both by Raman after the transfer, showing no remaining signal on the substrate, and by electron imaging. Indeed, the HF-transferred flake appears uniform and homogeneous, without any area characterized by dislocated feature as it is evident is some random spot in the case of water-based transfer.



Figure 3.17: 10 nm resolution TEM images showing that as the conversion T is increased, the recurrence of (002) planes are reduced, and area of the (100) planes appear larger.



Figure 3.18: HR-TEM of 550°C Reduction and 550°C Conversion: notice the bright stripe in the middle of the BCP patterns.

3.3.4 Preliminary conclusions

The first part of the project provides some interesting insights into the prospects of integrating two-dimensional materials in a large-scale production. We demonstrated that the lateral conversion method can be successfully applied while shrinking the lithographic resolution. Indeed, by taking advantage of a combination of bottomup and top-down approaches, a BCP pattern can be treated in a way to create sub-20 nm features. The self-assembly and selective removal of polymers enabled the patterning of WO_x sandwiched between two SiO_2 layers, protecting it from environmental exposure. After the chemical transformation was performed in a rapid thermal annealing furnace, the material was converted to WS_2 , resulting in 7-8 layers of crystalline TMD remaining in the stack. To optimize the process, it was necessary to visualize the crystalline structure of the material to get more insight into the grain formation process. We achieved this by the transfer of the material onto a TEM grid using a wet transfer process. Raman spectroscopy confirmed the success of the transfer and provided information on the induced strain during the different steps. As a result, HA-ADF STEM and HR-TEM provided good information about the effects of the synthesis conditions on the materials physical properties. A further analysis that can be conducted in this context is the extension of this method to other types of TMDs, thus providing broader content in the field. Also, in order to test their applicability, a new set of samples could be created to have linear patterned BCP features so that electrical measurement can be conducted, possibly opening interesting possibilities in the context of electrical devices and sensing applications. Indeed, similar work has been presented by [48], where a gas sensor has been tested with a BCP assembly and MoS_2 as the active material.

Chapter 4

Design and Simulation of Optical Device

4.1 Overview of optical devices

In the previous sections, the quality of the synthesized material has been analyzed. The following sections will be dedicated to demonstrating the applicability of the lateral conversion synthesis of these materials, in particular WS_2 , to optical devices and how they can contribute to obtaining advantages over other more standard materials. First, simulations of the devices are performed using Finite-difference time-domain (FDTD) theory on Lumerical and fabricated accordingly.

4.1.1 DBR

Distributed Bragg Reflectors (DBR) are a type of high-quality reflectors, which can be integrated into different devices such as waveguides and optical fibers. The structure configuration is straightforward: it is made of a periodic alternation of multiple layers of different materials, having different refractive indices. The physical principle behind this structure is the partial reflection of the incoming optical wave at the interface between the different layers. If the central wavelength for which DBR is designed is close to four times the optical thickness of the active layer, the multiple reflections from boundaries produce constructive interference. As a result of these interactions, a certain range of wavelengths, called photonic stopband, can be reflected. Therefore, the interest in engineering such systems comes from the possibility of controlling the full reflection of a specific wavelength range by tuning the DBR geometry. The reflectivity of the DBR can be expressed by the following relation:

$$R = \left(\frac{n_0 n_2^{2N} - n_s n_1^{2N}}{n_0 n_2^{2N} + n_s n_1^{2N}}\right)^2 \tag{4.1}$$

where n_0 and n_s are the refractive indices of the surrounding medium and substrate, respectively, whereas n_1 and n_2 are those of the active materials and N is the number of repeating layers. Also, the stopband $\Delta \nu_0$, which is the one defined by the incoming light, can be defined from the central frequency ν_0 as

$$\Delta\nu_0 = \frac{4\nu_0}{\pi} \arcsin\left(\frac{n_2 - n_1}{n_2 + n_1}\right) \tag{4.2}$$

As it appears evident from equations 4.1 and 4.2, a larger number of pairs in the DBR produces a larger reflectivity whereas by increasing the difference in the refractive index of the materials both the reflectivity and stopband will increase. The optimal thickness of each layer is expressed as

$$t_i = \frac{\lambda_0}{4n_i} \tag{4.3}$$

with λ_0 being the central wavelength and n_i the refractive index of the material in the *i*-th layer [49].

4.2 FDTD simulations Lumerical

The Finite-Difference Time-Domain method is a rigorous model that solves Maxwell equations by a discretization of both time and space, including a reciprocal influence of the two field components and taking into account the effects of transmission, reflection, absorption, and scattering. The computation is based on a grid-like differential numerical solver, for which the partial differential form of Maxwell's equations are discretized using a so-called central difference approximation to the partial derivatives of space and time. Then electric and magnetic field components in a certain point of space are solved at consecutive instants of time. These points form a grid cell called Yee lattice and electric field components are aligned along the edges of the cell whereas the magnetic ones are normal to the faces of the cube. A complex system is composed of multiple Yee cells and the interaction is created by an electromagnetic wave that is distributed in space. Lumerical is a tool that helps solve nanophotonics problems using this method. Simulation starts by defining the geometry and creating a corresponding mesh. Then, material properties are assigned from a database or manually to the components. Fig. 4.1 shows one of the structures used for simulation as an example: 8 alternating layers of SiN (light blue) and SiO_2 (grey) on top of a substrate. Lumerical's materials library was used in all simulations to assign refractive indices of 1.46, 2.07 and 4.05 (at 700 nm) for silicon oxide [50], silicon nitride [49], and WS_2 [51], respectively. Correctly defining these values is important to calculate the exact thickness of each layer following the equation 4.3. Next, a physical region is assigned as the computational domain, where Maxwell equations are solved. A source is created to define the electromagnetic excitation of the system (purple arrow, corresponding to a plane wave coming from the top of the DBR) and a monitor is positioned to collect the output response.



Figure 4.1: Layered structure as built on in Lumerical

In this work, we simulate and compare the performance of two mirrors: (1) a traditional DBR based on SiN_x and (2) a high refractive index DBR based on WS2. The comparison is made to illustrate how the refractive index impacts on the reflective properties of DBRs. Both mirrors are designed for a central wavelength of 700 nm.

4.2.1 Silicon Nitride based DBR

To accommodate for difference in refractive indices of SiN_x and WS_2 and obtain reflection of both mirrors close to unity, it is necessary to increase the number of layer in the SiN_x DBR. Indeed, if one would have tried to keep the same number of layers for both structures, SiN_x DBR will have a 80% efficiency. Therefore, a sweep to calculate the minimum number of $SiN_x - SiO_2$ pairs was performed to obtain an almost perfect reflectivity. As can be noticed in Fig. 4.2a, as the number of pairs increases the red color intensity corresponding to a certain stopband wavelength range increases, reporting a value close to 1 when the number of pairs corresponds to 8. The DBR response for 8 pairs is shown in figure 4.2b, where a reflectivity





(a) Refractive index sweep and resulting associated stopband

(b) Reflectivy spectrum of the silicon nitride DBR for $\lambda_0 = 700 nm$

Figure 4.2: Parametric sweeps for stopband definition and number of layers in WS_2 DBR.

close to the maximum is displayed in the wavelength range between 600 nm and 850 nm. The lateral ripples are a consequence of the constructive and destructive interference of light waves as they interact with the periodic layers. When light encounters the interface between two layers, a portion of it is reflected back and a portion is transmitted forward. At each interface, both reflected and transmitted waves interact with the next set of layers, leading to interference effects.

4.2.2 TMD based DBR

As discussed previously, the advantage of engineering an optical reflector using WS_2 comes from the fact that it has a high refractive index. To illustrate this we performed a parametric sweep where the refractive index is incrementally increased, demonstrating a broadening of the stopband while maintaining an almost perfect reflectivity. The simulation results are shown in Fig. 4.3a, where a significant improvement is achieved when a material with a refractive index close to 4 is used, such as WS_2 . Also, considering the great difference in refractive index between SiO_2 and WS_2 , a lower number of pairs is required to show maximum reflectivity. To demonstrate this we performed another simulation (Fig. 4.3b). The results revealed that only 4 layers are enough to provide a near-unity reflection unlike SiN_x based DBR, for which we established that 8 pairs of bilayers are needed. This demonstrates that using TMDs can be advantageous to design thinner optical

components.



(a) Refractive index sweep and resulting associated stopband

(b) Optimization of the number of pairs sweep in WS_2 DBR

Figure 4.3: Parametric sweeps for stopband definition and number of layers in WS_2 DBR.

The geometry of the structure in Fig. 4.4a is then straightforward and similar to the one of the silicon nitride one. Indeed, the only difference is the active material used, for which the WS_2 (in light blue) is simulated with a refractive index of 4.05 as reported in [51]. The resulting reflectivity is shown in Fig. 4.4b, where one can notice a significant improvement in stopband range, therefore explaining the advantage of this configuration.



(a) XY view of the WS_2 DBR structure made of 4 pairs of layers



(b) Reflectivity plot of the WS_2 DBR, with notable increase of stopband

Figure 4.4: Geometry and simulation of the WS_2 DBR.

4.2.3 Losses estimation

So far the simulations have been proposed with the built-in materials of Lumerical and a fixed value of refractive index for each material. However, in order to provide a more complete and realistic prediction of the actual behavior of the structures, it is important to include in the analysis a loss estimation. In particular, for the SiN_x DBR one could perform spectroscopic ellipsometry after the material deposition to extract the actual refractive index and extinction coefficient as a function of wavelength. Fig. 4.5 shows the SiN_x DBR simulation results that take the losses into account. The difference between two curves in Fig 4.5b is not very large, but nevertheless one can observe a slight reduction of the stopband, proving a discrepancy between the simulations if losses are not accommodated for.

For the WS_2 case, instead, the information on the losses is extracted from [52], where the refractive index as a function of wavelength is reported and the extinction coefficient was calculated from the absorption spectrum using the following equation: $\alpha = \frac{4\pi k}{\lambda}$, where α represents the absorption coefficient, λ the corresponding wavelength and k the extinction coefficient. Fig. 4.6 shows the simulation results. The difference between the two reflectivity plots is more evident (see Fig. 4.6b).





(a) Perspective view of the Si_xN_y based DBR with losses inserted

(b) Comparison of reflectivity between simulation without losses (blue) and with losses (red).

Figure 4.5: Geometry and reflectivity of the structure accounting for losses in SiN_x DBR.

At smaller wavelengths, one can observe that the lateral ripples do not reach up to zero and this could be due to absorbance of the material in this range. Moreover, as can be observed in the magnified image in Fig. 4.7, inside the stopband the reflectivity shows a decreasing trend while increasing wavelength with respect to the simulation without losses. This can be explained by the fact that the refractive index is not constant for the entire range, producing this effect.





(a) Perspective view of the four layers WS_2 DBR

(b) Comparison of reflectivities with evident discrepancies especially at smaller wavelengths.

Figure 4.6: Geometry and reflectivity of the structure accounting for losses in WS_2 DBR.



Figure 4.7: Magnified view of the reflectivity inside the stopband, where a decreasing trend is observed for the structure with losses (red).

Chapter 5 Fabrication of Optical Device

5.1 Introduction on the methods - Substrates

As it has been validated by the simulations, this section provides a thorough description of the deposition of the different layers of the devices as well as the fabrication procedures to be adopted. The study proposes a first description of the substrates and their subsequent patterning process, including optimization of some crucial steps. Following the investigation of the synthetic parameters, the optimized conditions were used to integrate TMDs into a distributed Bragg reflector mirror (DBR), with the aim to demonstrate the performance advantages of TMDs. Once the fabrication is validated, a study on the lateral conversion of the original substrates is presented to determine the best combination of conditions to create the final device.

5.1.1 WS₂-based DBR substrates

The DBR stacking is created starting from a prime Si substrate and the alternating deposition of SiO_2 and WO_3 . The recipes for deposition have been previously validated, therefore the structure is a result of SiO_2 deposited by PECVD at 300°C producing a thickness of 120 nm and sputtered WO_3 at 100 W, 10 mTorr with 20% O_2 for a nominal thickness of 41 nm. Notice that these nominal values are hardly reproduced in each layer, therefore some variabilities appear. The total stack is made of 4 pairs plus an additional passivating silicon oxide layer. In Fig. 5.1 one can distinguish the four layers of the structure: on the left SEM image is taken with an in-lens detector whereas for the vertically oriented on the right it is uses the EsB detector, which takes advantage of the Z-atomic number contrast

producing a very neat definition of the boundaries between the layers; the bright layers represent the WO_3 whereas the darker ones the interlayers of SiO_2 and the passivating oxide layer.



Figure 5.1: DBR layered structure: In-lens SEM image showing the four layers (left) and vertically oriented EsB detector image (right).

5.1.2 $Si_x N_y / SiO_2$ DBR Fabrication Methods

The substrate for this sample is a transparent double-side polished silica with quadratic dimensions of 22 x 22 mm and a thickness of 300 μ m. The depositions are performed in a PECVD chamber, to carefully control their growth, and the substrate is heated up to 350°C. $Si_x N_y$ is deposited starting from two different precursors: silane (SiH_4) as Si precursor and ammonia (NH_3) for nitrogen. The gas flow for silane is 1900 sccm and for ammonia is 37 sccm. These conditions are tested on a test substrate and measured with an ellipsometer to extract the growth rate and refractive index after fitting. The growth rate results in 18.6 nm/min and the refractive index is 2.05. From the simulation, the 8 layers of silicon nitride should be 84.54 nm thick, therefore this recipe is suitable and controllable. Rounding the thickness to 85 nm, in the final recipe the Si_xN_y step is set to last 4 min 34 s. The same approach is used for SiO_2 deposition and after a couple of tests it is evident the requirement to lower the silane flow to 600 sccm, coupled with N_2O 710 sccm for oxygen precursor. These conditions provide a growth rate of 56.67 nm/min and a refractive index of 1.46. In this case a thickness of 119.8 nm is required, therefore the step is set to last 2 min 7 s. It is evident from this description that the nitride growth is more controllable than the oxide one, hence slightly larger variability in thicknesses is expected for SiO_2 .

5.2 First patterning and etching attempts

The importance of running testing experiments arises from the fact that an etching recipe for WO_3 had never been tested so far. On a first attempt, the materials are treated like SiO_2 , hence recipes of the latter are re-adjusted. In the beginning, to pattern and test the structures, a positive photoresist (ma-P 1215) is spin-coated on the surface of the samples. The details of this process are not presented since it is not the final chosen technique and due to the trivial standard steps that are performed. The reason why this type of patterning is not suitable for the process is demonstrated by the poor results obtained after the etching. This step is performed by means of an inductively coupled plasma (ICP) etcher. This system is composed of two parts: the first is a non-capacitive couple source, where a minimal voltage difference between the plasma and the wafer allows to transfer the energy to the plasma; the inductive plasma created controls the plasma density and the ion flux that impinges on the wafer; the second source is a bias power capacitively coupled to the wafer chuck. This bias controls the voltage difference between the wafer and the plasma, hence defining the directionality of the bombardment by ions. The overall advantage of this tool is the ability to control independently the ion flux and its energy. As can be observed in Fig. 5.2, the image on the left shows the result of a 4 minutes etching trial using a CH_3 based recipe. Besides a significant damage to the surface with a portion of the resist removed during the process, one can notice the oblique characteristic of the sidewalls. It is suggested, therefore,





Figure 5.2: Cross section-tilted images showing the effect of etching with positive photoresist (left) that creates oblique sidewalls and the improvement introduced by the application of a hard mask (right), producing vertical features.

to change the patterning approach and possibly also the etching recipe to obtain a throughput improvement. The first solution to be tested is represented by the application of a hard mask on top of the patterns. Therefore a lithographic step based on the spin coating and exposure of a negative photoresist is conducted, so that a metal hard mask can be applied later through lift-off. In Fig. 5.2, a preliminary result of the etching using a metal hard mask is shown. The details of the process are presented in the next section, but one can determine that in this case a good verticality of the structure is achieved, maintaining the same type of recipe. In the image, the layers of interest appear indeed sharp, with a consistent over-etching of the substrate, which suggests the requirement for a lower process time.

5.3 Optimization: Lift-Off Method

The process flow requires the application of a negative photoresist that can be easily removed after the metal deposition so that the latter can be used as a hard mask in the etching process. The different steps can be summarized as follows:

- Spin Coat ma-N 1420 negative photoresist on the sample at 4000 rpm for 45 s with a ramp up of 1500 rpm/s.
- Bake at 100°C for 2 minutes using a carrier wafer to create the contact with the bake plate, since the sample is usually small.
- Expose with a dose of $90mJ/cm^2$, therefore adjusting the exposure time with respect to the measured power density of the tool
- Develop using ma-D 533 developer at room temperature for around 50 seconds, agitating the system and then rinsing the sample in H_2O for 1 minute.

This first patterning sequence is then followed by the metal deposition, in this case chromium. One of the deposition options is represented by thermal evaporation. In a thermal evaporator, 10 nm of Cr are deposited with a rate of 0.4 Å/s at a power percentage of 30.2%. After, the actual lift-off procedure is done, by immersing the sample in acetone as a first step. During the first two minutes of immersion, delaminated metal is removed from the bath with a pipette, to avoid their successive redeposition. To complete the removal, a sonication for 10 minutes is required, followed by immersion of the sample in IPA, to get rid of the organic residues left by the acetone. The improvement shown in the previous section in terms of sidewall verticality is not enough to validate the process. Indeed, as can be noticed in Fig. 5.2, it looks like the etching does not proceed exclusively horizontally but penetrates also in the stack. Also, Fig. 5.3 reveals that at the end of the process a damage to the surfacial layers is produced. The cross-section images show that the uppermost layer of WO_3 (top surface is on the left of the vertically oriented figure) is removed alongside the Cr hard mask. This could be due to a physical bombardment of the plasma component on the surface, leading to hard mask failure and subsequent consumption of the outermost layers. This evidence suggests the need for the introduction of a new recipe, besides the application of a hard mask, as well as the introduction of a new element during the etching.



Figure 5.3: Cross section of the stack after etching. The top-most layer of WO_3 is removed during the process (the left side is the top) and can be noticed a removal of the material at the edges of the stack due to a possible horizontal over-etching. The left image is EsB detector acquired and the right one is produced by In-lens detection.

5.3.1 SF_6/C_4F_8 based recipe

The new etching recipe is based on a combination of of SF_6 and C_4F_8 gas flows, where the former is the etching agent and the latter is the passivating one. Indeed, this method proceeds by alternating etching and passivation of the surface with a polymer, resulting in good aspect ratios and vertical sidewalls. Also, the passivation of the sidewalls is likely to prevent the horizontal over-etching of the WO_3 layers, at the expense of a potential reduction of the etching rate. Also, the adjustment introduced for the etching regards the application of Fomblin® oil on the sample holder of the ICP fluorine etcher in order to increase the adhesion of the sample with the base and limit the modification of etching rates during the process, which is believed to be the problem of the process. Fomblin® is indeed a synthetic lubricant with good thermal stability and excellent viscosity. At the end of the etching recipe, the oil is removed from the backside of the sample with ethanol. This element, combined with the innovative recipe, allows to successfully obtain the etching of the stack as desired, therefore a summary of the steps is presented in the following. In Fig. 5.4, an illustration summarizes the different steps of the



Figure 5.4: Optimized process flow for DBR patterning: figure (a) shows the initial substrate covered with the negative photoresist after lithography; figure (b) reports the surface after the e-beam evaporation of Cr; figure (c) shows the structure after lift-off with the hard mask left on the desired areas and figure (d) shows the final result after etching with the four pairs etched and the pattern reproduced.

recipe: In 5.4a. the substrate made of Si is covered by the alternating stack of SiO_2 (yellow) and WO_3 (green), with the surface patterned by the negative photoresist (red) and exposed by lithography. In particular, the Berkeley Lab pattern when exposed to UV light is removed by the developer because the polymer is made more soluble; 5.4b. shows the structure covered by the metal. As a hard mask, 30 nm of Cr are evaporated on the surface through electron beam (e-beam) evaporation, a technique where a target of the desired material is raster scanned by the e-beam and this will cover the surface inside a vacuum-controlled chamber. The reason behind using an e-beam with respect to the thermal evaporator is that with the

e-beam one is able to deposit a denser layer, which could act more efficiently as hard mask. Profilometer measurement confirmed a thickness of 36 nm of Cr on the DBR structure. The next step is the lift off of Cr in acetone and IPA, with the result reported in 5.4c., where the hard mask is covering the logo, which is what will be remaining after the etching of the rest of the structure. The final output is represented by 5.4d., where the logo composed of the different layers is remaining on the substrate after the etching. We noticed also that the Cr removal after the etching can be challenging and we managed a way to speed up the process. Indeed, if one tries to remove it right after the ICP etching using the acidic Chromium etchant 1020, it would take roughly 15 minutes to completely remove it. Instead, if one perform an O_2 plasma step for 1 minute after the etching, the removal is significantly faster, being reduced to 2 minutes. A full removal can be observed by the neat change in color of the sample surface. The reason why this improvement happens can be explained by the fact that during the normal etching process a polymeric layer on top of the sample is deposited, which acts as a barrier layer for the Cr etchant, requiring a lot of time for it to diffuse through. By bombarding the surface with the oxygen plasma, tough, the polymer is physically removed, successfully improving the next removal step.

A parameter affecting the etching angle is the percentage of C_4F_8 used, in this case 38%. By keeping the same parameters, etching for 2, 4 and 7 minutes are performed and etching rates are extracted from SEM imaging in cross-section. A similar way to estimate the rates could be represented by profilometer investigation, but the SEM imaging resulted to be more precise. For each sample the etched thickness is calculated taking into account the Cr present on top and by averaging the results over 10 different spots. Therefore, 2 minutes etching shows 115.75 nm/min rate, the 4 minutes sample a 99.17 nm/min and the 7 minutes one 111.27 nm/min. Overall, performing a linear extrapolation of the etching rate on Matlab, the resulting etch rate is 114.2 nm/min. Fig. 5.5 reports the linear characteristic with the etch rate being the angular coefficient of the line.

Moreover, by changing the percentage of the passivating gas (i.e., C_4F_8) it is possible to notice a change in the horizontal over-etching extent. In particular in Fig. 5.6, the left image is obtained after etching with 38% of C_4F_8 whereas on the right it is shown the result by using 43% of the gas. It is hard to notice but the latter seems to have a lower extent of the etching in the interlayers: indeed, if one considers as removed materials the dark spots shown in the layers, one can conclude that the right image presents a lower number of these holes, the layers appearing overall brighter, suggesting also a granularity proper of the material. This may be explained by a stronger passivating effect of the gas, which affects also the SiO_2 layers, resulting in fewer vertical sidewalls. Also, it can be noticed that the bright substrate of the sample appears to have small hills randomly distributed on the surface. This is the product of the Cr bombardment on top of the mask.



Figure 5.5: Linear extrapolation of the etch rate for DBR structure, with an overall etch rate of 114.2 nm/min represented by the line slope.

Indeed, when some Cr atoms of the mask are bombarded, they can eventually be dislocated from the surface and they deposited on the substrate. There, they act as masks thus producing these hills and valleys in the material, creating a significant roughness on the surface.



Figure 5.6: SEM images reporting results of etching using different amounf of C_4F_8 gas: on the left, etching with 38% of C_4F_8 and on the right 43% of C_4F_8 . The slight difference tells that a higher percentage of passivating gas reduces the horizontal over-etching.

5.3.2 Energy dispersive X-ray measurement

To prove that the conversion from WO_3 to WS_2 has occurred, the energy dispersive X-ray spectroscopy technique can be employed, since it is possible to provide a unique elemental mapping of a sample. It relies on the excitation from an electron beam of X-rays in a sample. Indeed, when a sample is not excited the electrons are in the ground state in discrete energetic levels associated with the nucleus of the atom. The incoming beam excited the atoms producing their ejection and the creation of an electron hole. At this point, an electron from a higher energy level will fill the lower energy hole, and the difference in energy between the two levels is released in the form of an X-ray. Therefore, an electromagnetic emission spectrum is created with unique peaks associated with atoms when the X-rays are collected by a spectrometer. In Fig. 5.7a one can notice the slightly tilted SEM image with the yellow line indicating the line where the scan is performed along the cross-section of the sample. The spectrum in Fig. 5.8 shows the atoms of interest and their characteristic peaks. Being the beam excitation of 5 kV, it is possible to observe as well distinct the oxygen peak at 0.5249 keV and the sulfur one, at 2.3075 keV, both arising from X-rays associated with the K-shell, which is the innermost electronic level in the atoms. On the contrary, the Si peak at 1.7398 keV and the W peak at 1.7744 keV cannot be ultimately resolved and the peaks appear to be overlapping. This comes from the fact that both are showing signals coming from the M-shell even if W would be in principle able to provide information from the L-shell at higher energy. However, the excitation energy is not enough to excite this transition. Nevertheless, the focus is not on Si and W, which come from the original substrate, but it is instead on the identification of the presence of S in the prescribed layers. In this perspective, Fig. 5.7b reports the presence of S in the four different layers, which correspond to the brighter regions in the SEM image and the red curve shows four identifying peaks. The same applies to oxygen, which has peaks corresponding to the regions where the oxide should be present and valleys in the WS_2 regions. The other two lines, namely in green and light blue, cannot be resolved and do not provide meaningful information for the analysis.



Figure 5.7: EDX analysis of the DBR sample through line scan. Fig. 5.7a reports an SEM image taken at 5 kV with scale bar 400 nm: in yellow is the line where the scan is performed. Fig. 5.7b is a line scan and resulting intensity plot of the elemental mapping: in red S line shows the presence of the element in the brighter regions of the DBR, corresponding to the active layers; in blue O_2 present peaks in the oxide regions and valleys in the layers where S is predominant. The other lines cannot provide information on Si and W since their peaks overlap in the spectrum.



Figure 5.8: EDX spectrum of associated to the line scan. Relevant peaks are associated with S (2.3075 keV K-shell), O_2 (0.5249 keV K-shell). The Si and W peaks, at 1.7398 keV and 1.7744 keV respectively, cannot be resolved.

5.4 Study on reduction and conversion temperatures

5.4.1 DBR Lateral Extent

The aim of this study is to assess the optimal combination of temperatures and length of reaction for the DBR samples. Indeed, since in this case, the WO_x layers are thick, a good lateral extension is expected. Therefore, three different temperatures are tested, as well as different reaction times. In particular for both 650°C and 750°C 30, 45 minutes and 1 hour are tested. For 550°C, instead, longer times are tested, namely 1 hour, 1 hour and 30 min and 2 hours, since at lower temperatures the lateral extension is harder to observe, molecules taking more time to diffuse in the material. The gas flows are kept constant for each experiment: reduction is done with 1000 sccm of Ar and 50 of H_2 at 100 Torr and for the conversion, after pumping and refilling of the gas, 25 sccm of H_2S are added in the stream. The output of these tests is reported in Fig.5.9, where one can notice that the lateral extent is relatively low. Specifically, after 1h the extension is $0.98 \pm 0.09 \ \mu$ m, after 1h and 30 min is $1.80 \pm 0.15 \ \mu$ m and $2.45 \pm 0.15 \ \mu$ m after 2h.



Figure 5.9: Extent of conversion trend for 550°C DBR. Data points correspond to optical microscope images. After 1h the extension is $0.98 \pm 0.09 \ \mu m$ (a), after 1h and 30 min is $1.80 \pm 0.15 \ \mu m$ (b) and $2.45 \pm 0.15 \ \mu m$ after 2h (c).

As can be noted by Fig.5.10, tests on higher temperatures give important information on the output of the reaction. Indeed, at 750°C one can observe an overall non uniformity of the converted material, with a lack of sharp separation at the interfaces, but most importantly by increasing the reaction time an optical microscope top view of the structure suggests that the four different layers are converting at different rates, thus producing different colors when observed. In particular, the sample converted at 750°C for 1 hour shows a great lateral extension, namely $12.36 \pm 0.15 \ \mu$ m, but also a very pronounced effect of the different reaction rates for each layer, emphasized by the ring-like showcase of the sample.



Figure 5.10: Extent of conversion trend for DBR synthesized at 750°C. To data point in the graph corresponds to an optical microscope image. After 30 min the extension is $5.01 \pm 0.17 \ \mu m$ (a), after 45 min is $8.75 \pm 0.16 \ \mu m$ (b) and $12.36 \pm 0.15 \ \mu m$ after 1h (c).

In contrast, samples reacted at 650°C shows a neat interface even for longer times, demonstrated by the 1 hour-long process, which appears to have a lateral extension of $6.35 \pm 0.10 \ \mu\text{m}$ and a good uniformity in color. For this reason, it is suggested that the optimal growth conditions are represented by the 650°C reactions, for which one can tune the reaction time and obtain the desired extension, following an approximately linear trend. This output confirms the results observed for the BCP structures, where the best uniformity is observable for the 650°C based reactions.



Figure 5.11: Extent of conversion trend for DBR synthesized at 650°C. To data point in the graph corresponds to an optical microscope image. After 30 min the extension is $2.81\pm0.21 \ \mu m$ (a), after 45 min is $4.39\pm0.18 \ \mu m$ (b) and $6.35\pm0.10 \ \mu m$ after 1h (c).

Chapter 6

Results and Discussion Optical Device

6.1 Silicon Nitride based DBR performance

After the fabrication of SiN-based DBR, the optical response was measured using UV-Vis spectroscopy, where the sample is illuminated with a light of different wavelength and the intensity of transmitted light is registered. To minimize the substrate contribution to reflection and absorption, a transparent double-side polished silica substrate was used for the fabrication of SiN DBR. The design of the structure is made to have the λ_0 centered around 700 nm, therefore the region of interest was the visible range. Fig. 6.1 compares simulated and experimental results. The red curve is the signal coming from the actual sample, while the blue curve is the simulated response. First, an overall blueshift of the reflected band is registered. The measured optical response clearly demonstrates DBR behavior with the central wavelength around 675 nm and a stopband of 100 nm. As suggested in [53], a simultaneous modulation by absorption and by refractive index is generally verified in DBRs. Indeed, the spectrum is produced by the combination of phase and coupling mismatch of the incoming wave. The phase mismatch is null at the central Bragg wavelength and tends to increase as one deviates from it, producing also a reduction in reflectivity. On the other hand, the coupling is maximum on the blue side of the Bragg wavelength and this effect tends to predominate over the phase mismatch. Being the latter produced by interference, it is practically independent of the DBR length whereas the coupling increases as the number of pairs in the structure arises. Therefore, as the number of layers increases the general observation is a blue shift of the reflectivity peak, as well as of the entire spectrum. Although we accommodated for the wavelength-dependent refractive index and extinction coefficient, obtained with the ellipsometer, a slight discrepancy between the experimental and simulated curves can be noticed. One reason for that could be the variability in the thickness of the layers, as the actual thickness might be lower than the expected one. Moreover, the real sample shows a narrower stopband range. This can be attributed to the interfacial roughness between the DBR layers and the creation of Si - O - N transition layers at the boundaries between the oxide and the nitride, as observed also in [54]. Another aspect to notice is that at lower wavelengths the spectrum minima do not fully return back to 0 as in the simulation. This effect is characteristic of losses in the material, mainly associated with absorption.



Figure 6.1: Comparison between the simulated spectrum (in blue) and the reflectivity measurement performed by UV-Vis spectroscopy (in red). The sample replicates the expected behavior, although the spectrum is shifted and absorbance appears at smaller wavelengths.

6.2 WS₂-based DBR performance

Unlike SiN_x , WS_2 -based DBRs were fabricated on a non-transparent substrate and as a result, were measured in a backscattering geometry on a Montana Instruments confocal microscope at room temperature. White light is focused on a diffractionlimited spot with a dimension of 1μ m through an objective lens. The reflection contrast (RC) defined as $RC = \frac{\Delta R}{R}$ with $\frac{\Delta R}{R} = \frac{R_{sample} - R_{ref}}{R_{ref}}$ is measured. The reflectivity of the sample is compared to a reference spectrum (thick Au film), which is subtracted from R_{sample} , and normalized to the reference sample. A description of how to implement the transfer matrix method is proposed by Byrnes [55], with a strategy based on analyzing Fresnel equations at the interfaces of the multilayered stack. For the optical measurement analysis, a Python code inspired by Byrnes' work is modified and compared with the experimental findings. In particular, dielectric functions for different materials are accessible and define the real and imaginary parts of the refractive index. The measurements are performed on the set of samples synthesized at 650°C with 1 hour-long reduction and conversion steps, and showed good conversion uniformity. Multiple small-range measurements were performed and stitched together due to the limited spectral range of the setup. In particular, measurements with λ_0 is centered around 600, 700, 800, and 900 nm were obtained. These multiple measurements slightly overlap with each other, which is necessary to validate the measurements and correctly stitch them. The results are shown in Fig. 6.2, where red and blue curves correspond to measured and simulated reflectivity responses of the DBR stack. It is noticed that for the spectrum collected at $\lambda_0 = 900$ nm, the data is unreliable, since the detector count is lower compared to other regions and the final reflection contrast appears to be distorted. While the fabricated stack shows a DBR-like behavior, it is apparent that the measured signal deviates from what was expected. The spectrum also reproduces a lateral ripple from the simulations at smaller wavelengths. The boundaries of the photonic stopband are not as sharp as the simulation and appear broader. There are multiple reasons that can explain the differences. First, similar to the SiN DBR, ripples at lower wavelengths do not reach the minimum that can be explained by light absorption. Fig. 6.2 shows the dependence of WS_2 extinction coefficient (k) on the wavelength [56]. The curve exhibits an absorption peak between 600 and 700 nm.

Another reason for the low DBR performance could be the difference between designed and fabricated WS_2 thickness. This can be due to non-uniform deposition of WO_3 using sputtering or underestimated volume shrinkage after WO_3 conversion into WS_2 , which was observed also in the BCP samples. Another mechanism of voids creation can be the ICP etching that was shown to isotropically etch WO_3 . So, defects and voids introduced during the TMD synthesis reduce the effective refractive index. As a result, the interference patterns responsible for the creation


Figure 6.2: White light reflectivity measurement results: image on the right shows in blue the simulated spectrum as calculated by the transfer matrix method whereas in red is reported the actual measurement by confocal microscopy on the DBR converted at 650°C. Even if the spectrum is centered around 700 nm, the curve significantly deviates from the expected behavior, mainly due to synthesis issues. On the left, the purple curve shows the imaginary part of the refractive index of a multilayer WS_2 structure as support of the augmented absorbance observed for wavelengths below 600 nm.

of the photonic stopband are influenced by these changes, changing the reflectivity spectrum.

6.3 Preliminary conclusions DBR

While the fabricated WS_2 -based DBR does not fully replicate the simulated behavior, it still demonstrates DBR-like behavior and serves as a proof of concept, but has to be further improved. For example, the voids formation can be suppressed by converting from metallic W instead of WO_3 . This will solve the volume shrinkage problem. Another important aspect to address is the ability to have a better control over the DBR layers thickness uniformity within the stack that can be achieved by optimizing deposition conditions, such as sample-to-target distance, rotation, lower deposition rates, etc. Also, a better control over the conversion step would be advantageous, for example by using a more gradual ramp up of temperatures during the reduction and conversion steps. In conclusion, we were able to integrate TMDs grown using lateral conversion into an optical device for the first time. For this multiple nanofabrication process flows were designed and simulation routines created.

6.4 Future prospects DBR: BSW simulations

An interesting phenomenon that can be experimentally verified in such optical structures is the generation of Bloch Surface Waves (BSW). Optical surface modes can appear inside the photonic bandgap of a dielectric multilayered structure when the regular periodicity is interrupted by a so-called defect layer. The electromagnetic surface modes are called BSW and are sensitive to both a TE and TM polarization of the excitation field. One of the modes can propagate along the surface with wavevector \mathbf{k}_{BSW} and a defined propagation constant [57]. An exponential decay in the direction with normal incidence to the interface is registered. Therefore, the optical field is confined to a portion of the surface of the stack, which is suitable for its application in integrated optics based on in-plane 2D systems and biosensing. As a matter of fact, other types of surface waves already exist, namely represented by plasmons, therefore the advantage of using BSW has to be analyzed. Plasmons are generated at the interface between metals, whereas BSW arises in the presence of dielectrics. It is demonstrated that the propagation of the electric field of plasmons at the interface is in the order of a few micrometers, due to their high absorbance, whereas the propagation of the BSW on the surface of dielectrics is demonstrated to be in the order of millimeters at telecom wavelengths, but can be enhanced by using grating couplers. This is evident from the sharp, narrow lines in the angular spectrum of reflected light intensity of BSW. Moreover, the tunability of the multilayers makes the BSW scalable for a broad range of wavelengths and its amplitude can be changed by modifying the thickness of the additional top layer [58]. If one considers that some experiments require coupling of modes at the surface, the possibility of having surface waves expanding for such lengths is of crucial importance. This section provides a description of additional elements to the original DBR design to elucidate the BSW effect on the surface of the stack. A Python code is modified in order to extrapolate the simulation results. Parameters to be set are related to the conditions that can be replicated by the experiment: in particular, the half angle in the dispersion is defined, corresponding to the angle of illumination that can be measured once the critical angle is overcome; also, the number of points in that angle range and the number of wavelengths in a certain range are defined for the simulation. The materials definition is also important: this replicates what is set in the FDTD simulation, with the central wavelength centered around 700 nm with the thicknesses of the layers defined subsequently, taking into account a reference value for the refractive index. It is worth noticing the introduction of absorption elements, represented by the imaginary part of

the permittivity of WS_2 . This replicates the losses of the material, which are responsible for the visualization of the BSW. At the same time, the absorption should not be excessively high, otherwise the BSW intensity would be low resulting in a difficult visualization. The geometry definition recalls the four layers of the DBR, with additional layers at the bottom, which simulate the oil immersive objective lens, with a refractive index comparable to the one of SiO_2 . An additional top layer is also required, for which PMMA was chosen. The PMMA layer breaks the regularity of the repetition of layers and allows to visualize the BSW. The thickness of this layer can be tuned in order to shift the the BSW, so that it can move from the border of the stopband, where it is hardly visualized, to the center of it, becoming easily observable, since the BSW cut-off is overcome. The advantage of using the DBR with WS_2 in the stack allows to have a larger tunability of the thickness of PMMA to shift the curve because it can move inside a broader range of reflected wavelengths. In Fig. 6.3, one can visualize the simulation of an angle-resolved reflected light intensity when the DBR is illuminated from the bottom with an immersive objective lens at angles higher than the critical one. The critical angle is defined by the effective refractive index of the structure and the signal is monitored at the bottom of the structure. The y-axis on the



Figure 6.3: Angle-resolved reflected light intensity for DBR structure with two different PMMA thicknesses on top: left image shows the BSW characteristic curve for PMMA thickness of 150 nm whereas the one on the right reports the shift of the BSW when the PMMA is 100 nm thick.

figure is the wavelengths expressed in nm whereas the x-axis is the illumination angles θ , with respect to the normal to the bottom surface of the DBR. The

simulation demonstrates the reflectivity, with the stopband vertically oriented and the maximum value in the range between 400 nm and 1100 nm, approximately. The yellow of the color bar represents the maximum reachable value whereas the purple color is evident in the lateral ripples, corresponding to low reflectivity. This is true for angles of incidence up to the critical one, around 42° . Beyond this critical value, the BSW is actually observable, as it appears inside the stopband of the DBR. Below the critical angle, this effect would be masked by the ripples and not shown inside the stopband range. Moreover, notice that the maximum of reflectivity does not reach the unity, and this can explained by the fact that in the simulation two additional bottom layers to simulate the immersive lens are added, thus reducing the maximum achievable reflectivity values. Also, it is worth noticing the narrow aspect of the resonances, which is an indirect result of the interactions happening at the surface, where, in contrast to the metal plasmons, the intensity of the decaying signal is not quenched in a short range. The difference between the two figures arises from the thickness of the topmost layer on top of the structure. On the left, a PMMA thickness of 150 nm is reported, whereas the right image shows the effect for a PMMA thickness of 100 nm. Although the difference in PMMA thickness is only 50 nm, the difference in terms of BSW curve position at the critical angle position is about 200 nm. Indeed, a reduced PMMA thickness results in a shift of the BSW curve towards lower wavelengths. The advantage of using a WS_2 -based DBR is evident: such a large difference in terms of wavelengths shift is observable only if the photonic stopband is large enough to accommodate for such a measurement, which is not the case for a traditional DBR, for which a shift of 200 nm would be out of range.

Chapter 7 Conclusion

The dissertation has explored a novel synthetic method aimed at advancing the prospects for enabling large-scale integration of TMDs. The method is a lithographyfirst approach that aims to precisely pattern few-layer TMDs. In this perspective, the research arises from the need to provide a reliable method to precisely control the synthesis of these innovative materials, taking advantage of their properties and tunability. By combining a top-down and bottom-up approaches, we implemented the self-assembly of polymers on top of a substrate (i.e., BCPs) as a lithographic template to enhance the resolution of the features, down to sub-20 nm, which is appealing for the next generation of electronics. The main purpose of the work was to provide a quality assessment of the converted TMD material, to optimize the process steps, and highlight the most critical points for improvement. In particular, the synthesis method is based on the lateral conversion of a metal oxide to a TMD through diffusion of a vapor-phase precursor in a lithographically defined structure. Metal oxides were chosen as the TMD precursor due to the high conformality and thickness control that can be achieved using the atomic layer deposition. With the metal oxide layer deposited and patterned, the chemical conversion was performed in two steps; reduction to metal, and conversion to TMD. Raman spectroscopy was performed to identify the TMD, however TEM was necessary to characterize crystallographic microstructure. To enable TEM measurements, ultra-thin electron transparent samples needed to be prepared. For this reason, a polymer assisted, wet lift-off method was used to transfer the patterned 2D TMDs onto TEM grids. The transfer process was optimized, enabling a repeatable process, providing a reliable way to make samples suitable for TEM characterization. Raman spectroscopy was used to confirm the success of the method, providing some additional information on the strain induced during transfer. This achievement enabled the systematic study of the growth process, and characterization of the grain structure with atomic resolution. The investigation of the TMD synthesis with such high-resolution, enabled us to tease out the effects of temperature on the reduction and conversion

steps of the process, and gave valuable insights into potential methods to optimize the quality of the TMDs. The systematic study on reduction and conversion temperature highlighted that as the reduction temperature was increased the grains became larger but more discontinuous due to a coarsening of the metal, whereas lower reduction temperatures generated smaller but more continuous grains. The optimal conditions appear to correspond with lower reduction temperature and higher conversion temperature. Once the growth quality was optimized, the second part of the project was dedicated to designing and fabricating an optical DBR device using the lateral conversion method. Since we could not find existing literature on multilayer WS_2 -based DBRs, it was necessary to design our own device structure and develop a synthetic strategy. Simulations performed by FDTD on Lumerical demonstrated the advantage of integrating such a device with WS_2 , paving the way to obtain a larger range of reflected wavelengths and a more compact structure compared to more traditional materials. During the device fabrication, the etching recipe for layered WO_x stack had to be developed, requiring many rounds of optimization. The final result produced a reliable method to process the stack by means of dry etching. EDS measurements confirmed the success of the synthesis of the TMD, which was optimized in terms of the uniformity of the extent of lateral conversion. In the final stage, some preliminary measurements were performed in order to compare the fabricated samples with the simulated ones. Although the reflectivity spectrum of the WS_2 -based DBR deviates from the simulated structure, one could obtain valuable information to further improve the synthesis.

In conclusion, the work constitutes a solid starting point for future investigations. The synthesis of sub-20 nm features lays the groundwork to extend this synthesis and characterization methodology to other types of TMDs. It could also be extended to study linearly patterned BCP features, enabling electrical conductivity measurements, paving the way to develop sensors. On the other hand, the optical device findings can be important in the context of setting the basis for an investigation to optimize the layer thickness, the etching recipe, and improved material quality responsible for the effective index modification. Also, the last part of the dissertation has shown a possible application in the generation of BSW, which may find application in many fields taking advantage of the novel properties of TMDs.

Appendix A



Figure A.1: Statistics reporting an increase of the number of (002) crystal fringes with the increasing conversion temperature, for the set of samples reduced at 550°C.



Figure A.2: Low-magnification HR-TEM set of images showing the coverage of the transferred flakes onto the TEM grid.

Appendix



Figure A.3: High-magnification HR-TEM images showing the distribution of crystallographic orientations in the features.

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