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NWO Graduate Program in Advanced Materials

Valley Optoelectronics based on Semiconducting Transition Metal Dichalcogenides

PhD. Proposal submitted to
 Zernike Institute for Advanced Materials
 Faculty of Mathematics and Natural Sciences
 University of Groningen

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 Topmaster Nanoscience Program

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1. Project Title

Valley Optoelectronics based on Semiconducting Transition Metal Dichalcogenides

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4. Abstract

Layered Transition Metal Dichalcogenides (TMDs) have long been studied [1a], and used traditionally in applications like catalysis, lubrication *etc.* However, only recently have their potential as versatile two-dimensional (2-D) materials beyond Graphene been recognised. Several studies have demonstrated interesting and technologically relevant electronic (direct-indirect band gap transition), optical (valley polarized luminescence), magnetic (strong spin-orbit interaction) and superconducting properties of ultra-thin TMD layers. The future development of this class of materials has to meet the challenge of growing high quality TMDs in a scalable way, a crucial step beyond the most of the present studies using mechanical exfoliation.

This proposal aims to highlight the further investigation of fundamental properties of thin films of TMDs. It begins with a brief review of the state-of-the-art in 2-D TMD research with emphasis on the growth of single and few layer sheets as well as their performance in devices. Afterwards, new methodology for the growth of high quality, large-area ultrathin TMDs is discussed. Strategies are then proposed for fabricating electric double layer (EDL) and light-emitting (LE) transistors to allow investigation of the effects of breaking inversion and time-reversal symmetry using electric fields and current direction respectively for the electrical control of polarized photoluminescence for application in optoelectronic devices.

5. Project Duration

The project will begin in September 2014 and last for a period of 4 years.

6. Personnel

This is a multidisciplinary project, combining input from the Laboratory for Device Physics of Complex Materials and the Photophysics and Optoelectronics group. Below are the personnel and their functions.

6.1 Senior Scientists

Name	Task	Time
Prof. Maria Antoinetta Loi	Supervision and Management	10%
Prof. Jianting Ye	Supervision and Analysis	10%

6.2 Junior Scientists and Technicians

Name	Task	Time
Dr. Satria Z. Bisri	Supervision and Analysis	10%
Dr. Jie Yang	Supervision and Analysis	10%
Mustapha Abdu-Aguye*	Experiments and Analysis	100%
Jan Harkema	Technical Support	5%
Arjen Kamp	Technical Support	5%

* *Onderzoeker in Opleiding*

7 Cost Estimate

7.1 Personnel Costs

Funding is requested for one “*Onderzoeker in Opleiding*” position to be filled by the applicant.

7.2 Running Costs

Towards covering expenses for chemicals, other reagents and consumables. Conferences, summer schools and general maintenance.

7.3 Equipment

All the equipment required for this project is already installed in the laboratories of the research groups within the Zernike Institute and associated research groups. Therefore, no additional budgetary allocation is requested for this purpose.

7.4 Other Support

This project will be supported by infrastructure of the Zernike Institute and Rijkuniversiteit Groningen; with contribution from senior scientists and technicians (more in section 9).

7.5 Budget Summary

	2014	2015	2016	2017	2018	Total
PhD Students	4/12	1	1	1	8/12	4
Senior scientists	-	-	-	-	-	-
Technicians	-	-	-	-	-	-
Guests	-	-	-	-	-	-
Personnel costs	13.000	38.000	43.000	46.000	32.000	172.000
Running budget	7.500	15.000	15.000	15.000	7.500	60.000
Equipment						
Total (k€)	20.5	53	58	61	39.5	232

8 Research Program

8.1 Introduction

Since the ground-breaking work of isolating a single layer atomic sheet, Graphene, from bulk layered graphite by Novoselov *et al.* in 2004 [3a], great interest has gone into investigating its exotic properties with many exciting discoveries associated with its Dirac band structure [3b]. This interest also led to the discovery of the multilayers of these 2-D materials, with several contrasting properties such as semiconductor (bilayer under bias) [1b] and metal (trilayer) [1c] as a function of number layers. Taking a broader view from materials science, the existence of many layered compounds provides new choices if thin films of one or multilayers could be prepared [28]. This development could enrich the choice of the existing properties of Graphene by adding a clear defined band gap since the semi-metal band structure in pristine Graphene [7-9] can be only altered by tedious engineering (for instance by etching into nanoribbons). Another important advantage is that many inherent properties in other layered compounds could be re-investigated when ultrathin films are prepared. The properties include conductivity change of metal-insulator transition, superconductivity, charge density wave and ferromagnetism after magnetic doping. Similar to Graphene research, to harness any of these properties for device applications, scalable growth of high quality crystalline films is highly demanded. Large area, high quality thin films are the basis for any device technology; in addition to seamless amalgamation with current manufacturing technologies.

For this reason, layered van-der-Waal solids such as transition metal dichalcogenides have becoming increasingly promising candidates; If prepared into ultrathin films, their 2-D structure leads to a wide range of desirable electronic properties: such as the emergence of an indirect-direct band gap transition as their thickness decreases to a monolayer (for the semiconducting members of the family). They also show other technologically relevant properties such as the presence of topologically conducting states [10], thermoelectric effect

[11] and the presence of so-called “valleys” in their band structures which represent an additional internal ‘degree of freedom’ other than electronic spin for the encoding and processing of information [12].

Structure and Properties of TMDs

Transition metal dichalcogenides (TMDs) have stoichiometry MX_2 (M = metal atom such as Ni, V, Re, Nb, Mo, W *etc.* and X = chalcogen, i.e. S, Se or Te) and generally consist of a hexagonal lattice of metal atoms (M) sandwiched between an upper and lower layer of chalcogen atoms (X) in an X-M-X geometry. Depending on the number layers per cell and metal atom coordination, TMDs can be designated either $2H$, with trigonal prismatic (D_{3h}) symmetry, $1T$ with octahedral (C_{3v}) symmetry or $3R$, that is rhombohedral stacking but with trigonal prismatic symmetry [4, 13]. Another important fact to note is that these materials have bulk crystals which consist of stacked layers with strong intra-layer interactions and weak van der Waal interactions between different layers.

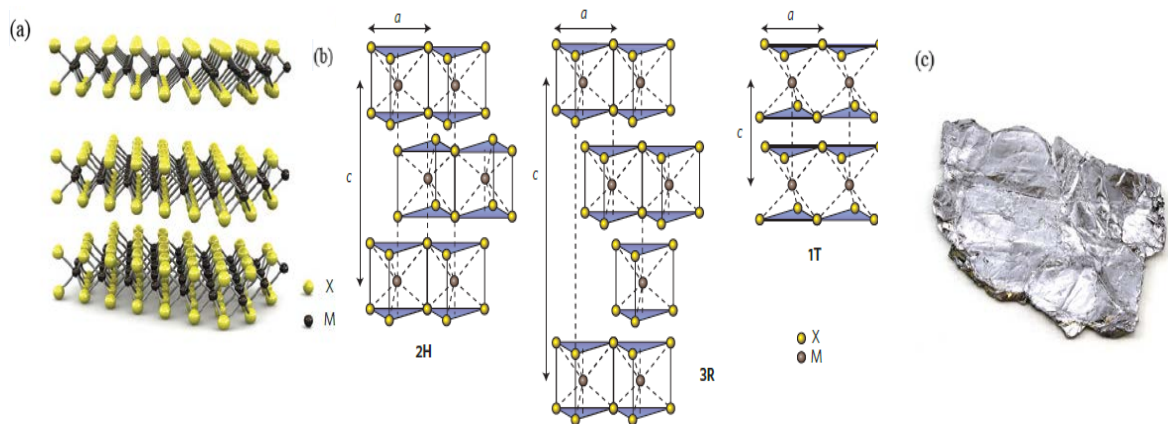


Figure 1: (a) Schematic representation of the bulk layered MX_2 structure (b) crystal structure of $1T$, $2H$ and $3R$ Polymorphs; they consist of respectively one, two and three layers as structural repeat unit (c) Photograph of bulk (cm-sized) MoS_2 crystal [4]

An interesting feature outlined in several studies [14, 15, 45] of semiconducting ($\text{M} = \text{Mo}, \text{W}$) 2-D TMDs of which MoS_2 is a prototypical member has shown that as the number of layers decreases from the bulk toward a monolayer, there is a crossover from an indirect (1.29 eV between energy minimum at the middle of Γ - K direction and Γ point) to a direct band gap (1.90eV at the K point). The evolution of this band gap is strongly dependent on the metal M for different splitting at K point of the valence band which is important for device applications since desired large spin splitting could be engineered by choosing different metal elements [5]. The evolution of the band-gap can be explained by considering TMD monolayers as consisting of two inequivalent sub-lattices composed of the metal atom and chalcogen respectively in contrast to the two carbon atoms for the same sub-lattice in Graphene. A clear defined band gap is formed in monolayer TMDs at the two inequivalent valleys at the K and K' points of their Brillouin zone resulting from broken spatial inversion symmetry; implying different optical

selection rules for each valley. This gives rise to the possibility to apply them in “valleytronics”. This is in addition to the strong spin-orbit interaction, which induces the spin splitting as a function of the metal atom, which implies a longer spin-lifetime and thus makes them attractive candidates for keeping the spin information during the transport if transport from a specific valley could be selected [46].

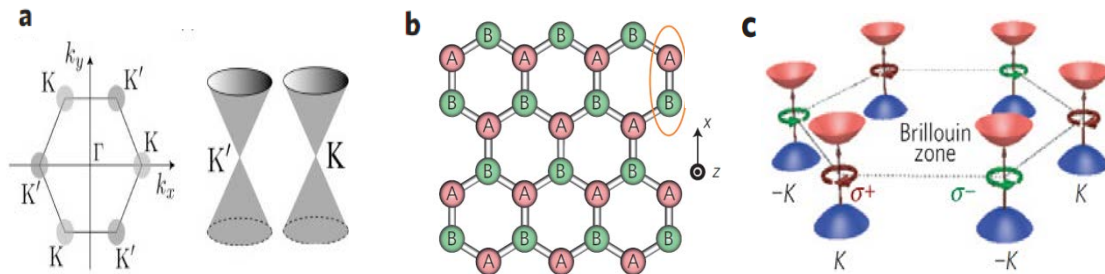


Figure 2: (a) The Brillouin zone of Graphene, showing the two equivalent Dirac points (b) Top view of the honeycomb lattice, for Graphene A & B are both C-atoms while for TMDs they are a transition metal and chalcogen (c) the resulting inequivalence at K and K' points in the Brillouin zone, with different optical selection rules for each valley [6, 22]

As shown in figure 2, monolayer semiconducting TMDs possess two inequivalent minima in their conduction bands (or maxima in their valence bands) making them attractive candidates for valley-optoelectronics, the lifted spin degeneracy resulting from broken inversion symmetry in monolayers and the fact that the valleys are well-separated in K-space implies reduced inter-valley scattering. Recently, Mak *et al* [23] and Zeng *et al* [20] both demonstrated controlling valley-response in monolayer MoS₂ via optical pumping, their results indicate that it is possible to achieve selective valley population leading to the polarized photo-luminescence as a result of differing optical selection rules for the K and K' valleys, a spin polarization retention time of about 1ns was observed [23], which is consistent with theoretical predictions [5]. While it is also possible to achieve this with a magnetic field which is another common way able to break time reversal symmetry; neither of these two methods allows easy electronic control which can be embedded into modern electronics.

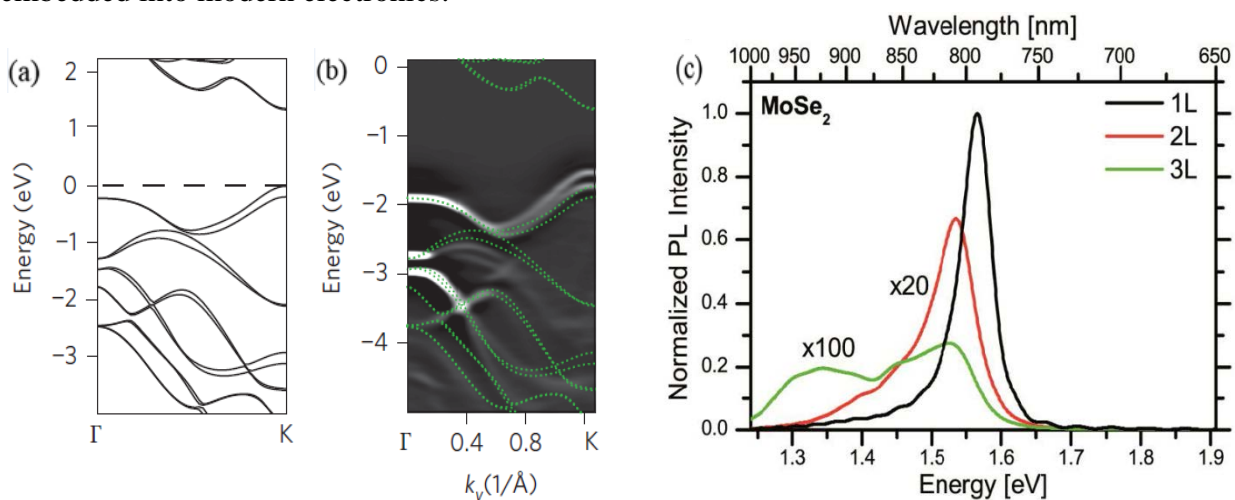


Figure 3: (a) DFT calculations by Zhang *et al* [19] showing the band structure of monolayer MoSe₂; VBM is set to 0 eV (b) Angle-resolved Photoemission data for (a) shown as a second derivative for clarity, green lines show calculations in (a) renormalized in energy (c) Thickness dependence of PL intensity in MoSe₂ mono and bi and tri-layers [45]

As we will elaborate in section 8.2, changing the current direction will be an important method to achieve valley-distinctive responses.

This valley-sensitive optical response is not only found in monolayer MoS₂, but a property shared by other semiconducting TMDs (M = Mo, W; X= S, Se, Te) [16]. Recent calculations and experiments also suggest that the indirect band gaps of bilayer TMDs can be almost continuously modulated by external bias applied perpendicular to the layers [17,18]. This important finding indicates that the essential spatial reversal symmetry, which leads to the valley-distinctive band structure, could be alternatively realized by applying an external electric field, a method directly connected to device applications.

In addition, there have been a number of theoretical studies on 2-D TMDs regarding the effect of adsorbed atoms such as Fe and V [24], H, B, C, N, O and F [25] and even transition metal vacancy sites [26]; the results of which all suggest that interesting new magnetic and electronic properties arise. More specifically, [26] reports a study of semiconducting TMDs such as MoSe₂, MoTe₂ and WS₂, their results indicate that Mo vacancy sites in MoSe₂ exhibit spin-polarization and long range anti-ferromagnetic coupling. Thus, growing the TMD single crystals with proper doping and vacancy engineering could expand a broad horizon in addition to the valley properties.

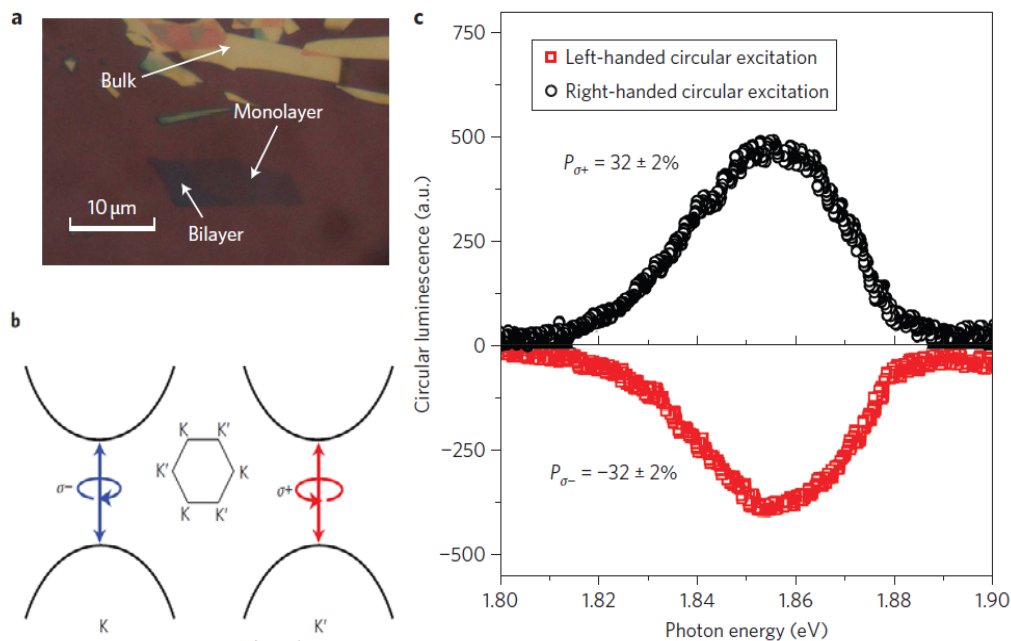


Figure 4:(a) Optical micrograph of MoS₂ flakes prepared by mechanical exfoliation (b) Simplified band diagram showing optical selection rules at K and K' in reciprocal space and (c) valley polarization dependent luminescence as a function of photon energy – from reference [20]

Synthesis of Ultrathin TMD Sheets

Similar to Graphene, there have been methods to prepare TMDs beside mechanical exfoliation (the so-called “scotch tape” method) widely used in preparing monolayers. Chemical vapour deposition (CVD) has already proven to be an effective method to grow high quality Graphene. However, because TMDs are not composed of a single element like Graphene, it is unclear

whether the direct transplant of Graphene CVD technology could apply trivially to the growth of 2-D TMD monolayers.

For instance, for solution phase synthesis, one has to take into consideration factors such as ensuring that the chalcogenide anions (S^{2-} , Se^{2-} and Te^{2-}) are in the right oxidation state by finding precursors that display favourable decomposition dynamics such as H_2S , which decomposes when heated with the metal. Similarly, for vapor phase growth, it is extremely important to find the right balance of growth parameters such as temperature, pressure, choice of carrier gas *etc.* Interestingly, reports of ultrathin TMD sheet growth in literature [34, 35, 36] have hitherto been uncatalysed.

Mechanical exfoliation seems to be the method of choice in many reported studies; however, the reduced dimensionality of TMD sheets evidenced by an extremely high surface area to volume ratio implies high sensitivity to topological effects, the substrate and presence of impurities or adsorbates. Studies in literature [2, 34, 37] have demonstrated other methods such as chemical exfoliation involving ion intercalation to break the weak van der Waals bonds between layers followed by dispersion in organic solvents or surfactants; vapor phase growth by methods such as sputtering, physical vapor transport, thermal evaporation, chemical vapor deposition (CVD), pulsed laser deposition *et cetera*. Additionally, chemical reactions, thermolysis of single-source precursors and van der Waal Epitaxy have been recently reported with varying degrees of success.

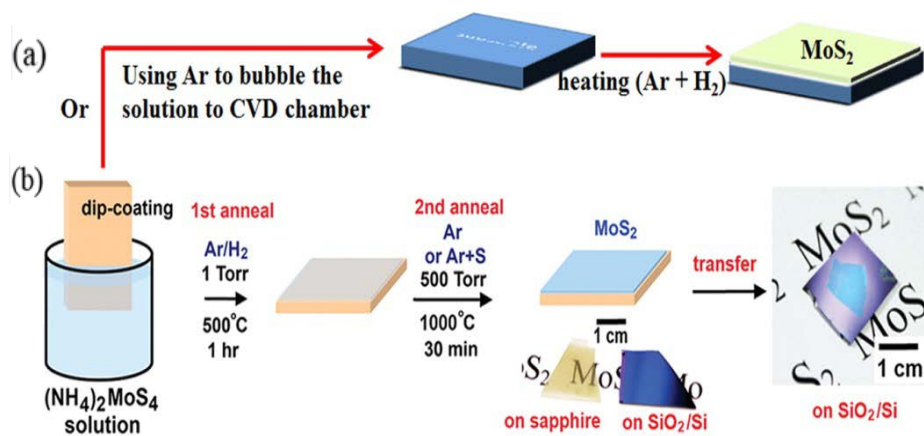


Figure 5: (a) CVD method and (b) two-step thermolysis methods for making MoS₂ thin sheets (bilayers, trilayers) from a solution precursor, reported in [40]

Device Performance

Ultrathin TMD field effect transistors were investigated just slightly later than Graphene [28]. The early results suffered from very low mobility in the order of $1 \text{ cm}^2/\text{Vs}$, far below the performance of Graphene. With the introduction of strong dielectric gate of high- k HfO_2 , the mobility of devices was significantly improved. The n -type field effect mobility in single-layer MoS₂ is in the order of $200 \text{ cm}^2/\text{Vs}$ with a 10^8 current on/off ratio [26]. While this value is comparable with those in bulk MoS₂ with a mobility ranging between $200\text{-}500 \text{ cm}^2/\text{Vs}$ [27], other reports [27,28] with conventional FETs have given rather low mobilities; more than two

orders of magnitude lower than the bulk value to be precise. Despite studies and calculations [29,30] regarding whether the reduced mobility in few or single layer MoS_2 is as a result of decrease in carrier concentration, or localization of carriers due to trapped charges between the semiconductor and dielectric; an exact picture of electronic transport in such devices has not been firmly established.

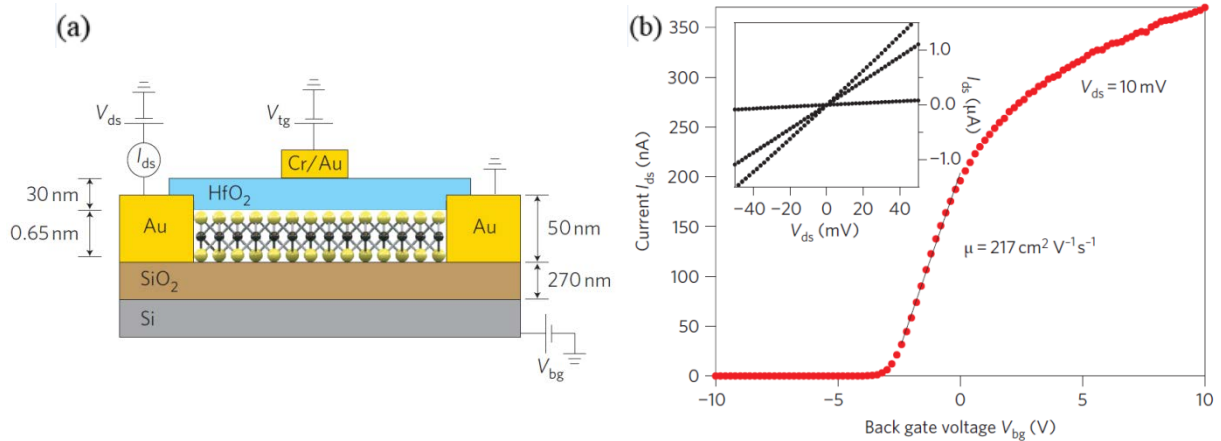


Figure 6: (a) Schematic diagram of the monolayer MoS_2 transistor from Reference [26] (b) Transfer characteristic of the transistor at room temperature, with $V_{ds} = 10\text{mV}$, inset shows I-V curves for V_{bg} values of **0, 1 and 5V**

At a different polarity, monolayer WSe_2 FETs displayed *p*-type mobility at around $250\text{ cm}^2/\text{Vs}$ and on/off ratio greater than 10^6 [31]. In this case, another dielectric (ZrO_2) was used; together with a strategy to reduce the Schottky barrier (contact doping with NO_2 and high-work function Pd electrodes), this device while having mobility only about half of the reported value in the bulk, exceeded the bulk on/off ratio by 5 orders of magnitude [32].

Interestingly, in another report [33], there are claims that the existence of a Schottky barrier between the TMD layer and metal contacts can result in ambipolar behaviour; this particular study utilized chemically synthesized WS_2 deposited on an Al_2O_3 substrate with Ti/Au as the source and drain electrodes respectively. This device recorded 10^5 current modulation at room temperature.

8.2 Goals of the Project

The specific goals of this project are to achieve a versatile method for growth of large-area, high quality semiconducting ($M = \text{Mo}, \text{W}; X = \text{S}, \text{Se}, \text{Te}$) ultrathin TMD sheets on a range of substrates, the structural and electronic transport of the sheets will be characterized by optical microscopy, AFM, Raman spectroscopy and electric double layer transistors (EDLTs) using either an ionic liquid or ion-gel gating technique. Our expertise with ultrafast laser spectroscopy will enable us carry out polarization-resolved studies of valley dependent photoluminescence. Finally, light emitting transistors (LETs) will be fabricated to investigate the effects of breaking time reversal symmetry using current (momentum) and to enable the achievement of dynamic control of current driven polarized-luminescence.

Synthesis of TMDs

Notably, not every method reported in literature has been successful in synthesizing good amounts (large-area) of single layer TMDs with high quality – evidenced by reduced carrier mobility, high resistivities, and structural inhomogeneity shown by Raman spectroscopic studies. Thus, a major challenge towards future research in this emerging field is the reproducible preparation of high quality material, in large enough amounts to enable further device characterization. Also, depending on the particular application, a versatile method that enables growth on various different substrates (conducting, non-conducting) and controllable number of layers while remaining compatible with existing device fabrication methods is highly required.

Recently, there was one report [38] of successful synthesis, by a facile vapor-solid method of MoS₂ flakes of sizes around 400 μm² with high optical quality as evidenced by near unity valley polarization at 30K, which remained as high as 35% even at room temperature. Despite this, since no devices were reportedly fabricated with these samples, it is unclear whether the high optical quality would also imply equally high electronic transport performance.

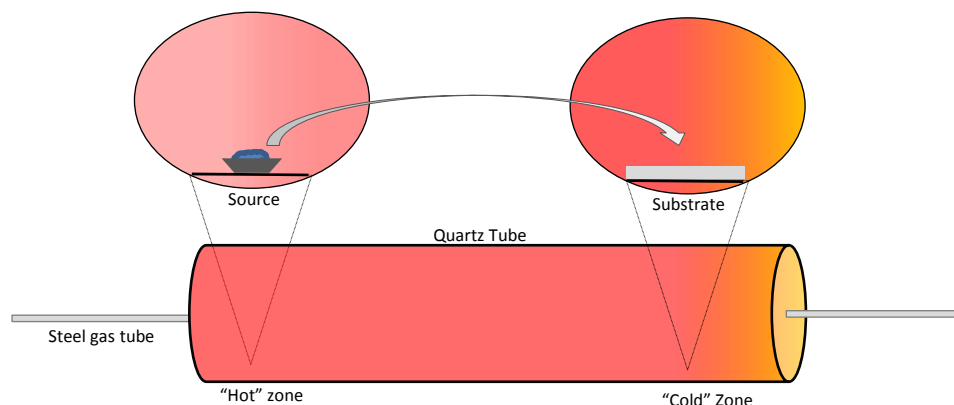


Figure 7: Schematic representation of the vapor-solid deposition process for the growth of high quality crystalline MoS₂ sheets; an unreactive carrier gas enters from one side as carries the source material from a zone at a high temperature to the substrate in a zone at a lower temperature.

Electric Double Layer Transistors (EDLTs)

Making TMD monolayers is only one way of breaking spatial inversion symmetry; another way is by the application of a large electric field as done by Ye *et al* and more recently by Yuan *et al*. This is achieved by using an electric double layer transistor (EDLT) with a liquid-gating technique that has recently been applied to various other materials including carbon nanotubes [42] and colloidal nanocrystals [41].

As shown in Figure 8, the large interfacial electric-field in an EDLT breaks the spatial inversion symmetry in TMD layers while leaving them time-reversal invariant; it also provides extremely high charge carrier accumulation. This technique has proven to be a valuable tool towards obtaining ambipolar characteristics in MoS₂ [43] and investigating spin orbit interactions in WSe₂ [21].

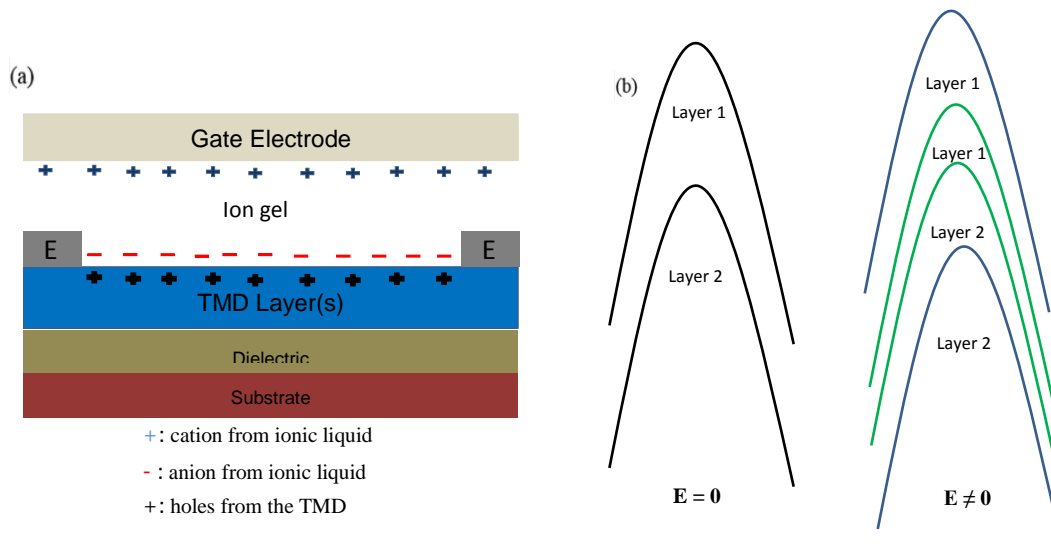


Figure 8: (a) Schematic of EDLT, a negative bias applied to the gate electrode induces a build-up of anions at the interface of the TMD layers forming an electric double layer (b) Simplified band diagram showing the valence band maxima for a TMD bilayer, and the effect of an electric field as in an EDLT, blue and green lines represent spin up and down polarizations respectively.

The significance of the former study will be discussed in the next section; the latter work revealed that SOI in WSe_2 thin layers resulted in gate-modulated out-of-plane Zeeman-like spin polarization at the high symmetry K points, which suggest longer spin lifetimes in such systems and might be important for the design valley selective transport devices. EDLTs are thus a facile, proven method to investigate several fundamental properties of TMDs without specifically using monolayer samples, which are ordinarily inaccessible due to spatial symmetry in even numbered and thick multilayers; also the technique will be extremely useful for further investigating the physics of CVD grown mono- or multi-layered TMD sheets.

Light Emitting Transistors (LETs)

Recently, the emergence of the possibility to make light emitting transistors (LETs); which combine the advantage of LEDs (electroluminescence) together with the functionality of a transistor (switching ability and gate tunable properties) has led to several groups demonstrating LET operation with various materials ranging from organic single crystals to polymers [44]. The significance of the study by Ye *et al* (highlighted above) [43] lies in the fact that in general every ambipolar FET can be operated as a LET. Many studies on LETs have reported that they are capable of operation at higher current densities, higher efficiencies and with lower excitonic losses than LEDs based on similar materials.

Another advantage of LETs is that the recombination (and therefore, light emission) zone can be controlled by the gate electrode; thus, using imaging techniques, information about material (recombination processes, presence of defects *etc.*); and device properties (charge injection efficiency) can be obtained. Monolayer TMDs are excellent candidates for LETs owing to their direct band-gap, ambipolar characteristics, high carrier mobility, and high ON/OFF ratios. Furthermore, electrical control of their valley-dependent luminescent properties is an interesting possibility especially since there has been no report of successful LET operation with TMDs till date.

In addition to the more “mainstream” applications of ultrathin TMD LETs in flexible and low cost displays, lighting technologies, and the highly desirable electrically driven laser; gate-control of polarized electroluminescence would be extremely valuable for device applications.

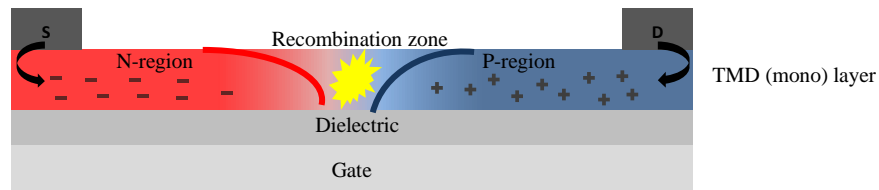


Figure 9: Schematic of a bottom-gated LET, there are several options for gate and dielectric materials; electrons and holes are injected from the source and drain electrodes respectively and recombine in the gate-controlled channel. It is also possible to try several geometries such as multilayer structures, and different gating techniques

List of tasks (not exhaustive) related to the general realization of this project

1. Establishment of a CVD growth method for the reproducible synthesis of high quality semiconducting TMD thin films.
2. Understanding and optimization of growth processes and parameters for different substrates, desired film thicknesses and atomically flat surface morphology.
3. Precise characterization of grown TMD sheets by atomic force microscopy, Raman spectroscopy, transmission electron microscopy, photoluminescence spectroscopy *etc.*
4. Assessment of possibilities for upscaling synthetic methods for large area synthesis.
5. Fabrication of electric double layer transistors (EDLTs) to investigate SOI and ambipolar operation under high carrier densities in mono and few-layer TMDs.
6. Optical characterization of valley sensitive response from ultrathin TMD thin films.
7. Fabrication of LETs for the realization of electric current induced luminescence, establishing electrical control with gate bias and current bias direction for the control of circular polarization in luminescence for valley-sensitive devices.

8.3 Work Schedule

Below is a summary of the intended plan for the project, but deviations from this plan might occur depending on findings that open further opportunities to discover newer and more exciting physics from these systems.

Time	Activity
1 st Year	<ul style="list-style-type: none"> • Growth of TMD Nanosheets • Characterization of TMD Nanosheets
2 nd Year	<ul style="list-style-type: none"> • Optimisation of growth parameters • Further characterization and fabrication of Transistors
3 rd Year	<ul style="list-style-type: none"> • Assessment of possibility to upscale established synthetic method(s) • Exploration of further applications such as valley-control and PVs
4 th Year	<ul style="list-style-type: none"> • Follow up of research • Thesis Writing

8.4 Collaborations

The multidisciplinary nature of this project will require input from several other research groups within Zernike institute such as Solid State Materials for electronics (SSME), Nanostructured Materials and Interfaces, the Zernike Nanolab, and the Surfaces and Thin Films group.

9 Infrastructure

The Zernike institute within its research groups houses a large number of equipment we shall require for growth and characterization of our Ultrathin TMD sheets – specifically, the SSME group has equipment for growth via physical vapor transport, a SQUID and PPMS. The Photophysics and Optoelectronics group has access to AFM, clean rooms and facilities for transistor measurement, as well as a laboratory for laser spectroscopy. In addition, Atomic layer deposition would be an interesting method to attempt for large area synthesis if the Nanolab acquires one, as planned.

10 Project Outlook and Application perspective

As the search for greener and more environmentally friendly technologies continues with the ever more stringent demands for high speed and low power consumption. Novel functionalities that were hitherto thought unachievable have quickly gained credence and new materials systems are constantly being investigated for application in new technologies. The rapidly approaching end of the Silicon roadmap and success with Graphene have fuelled interest in the growing field of 2D nanomaterials as viable alternatives to traditional Silicon-based technologies. However, limitations inherent in the use of pristine Graphene have invariably led scientists to other (structurally) similar materials such as TMDs.

This project aims to position the Zernike institute as a hub of research in TMDs, by leveraging the expertise of several research groups in the synthesis, characterization and application of nanomaterials towards next generation technologies. From a scientific point of view, we are just starting to gain a full understanding of the unusual and remarkable new properties that arise as the dimensionality of materials is confined to a plane. In the decade since Graphene has been (re)discovered, a widely diverse range of applications have been shown to be possible – we can only imagine that a whole new family of 2D materials will only shed more light on this relatively new direction of research at worst, or at best even lead to the discovery of more fascinating science.

From an application perspective, the use of TMDs in (opto) electronics seems to be a possibility in the near future especially since several proof-of-concept devices have already been demonstrated. Ultrathin TMD sheets possess several desirable properties for applications in logic, lightweight and flexible (opto) electronics, spin and valley-tronics and

even molecular sensing; in addition achieving electric current driven light emission would take us a step further to achieving the highly sought after electrically pumped laser and would represent another important milestone for technology.

However, these will depend on the establishment of an easily upscaleable, reliable method for the preparation of mono and few layer TMDs with precise control, in the high quality limit required for such applications, which is compatible with current manufacturing techniques. Also crucial is further research into the fundamental properties of various TMDs and device systems.

11 References

1. (a) Frindt, R.F. *Single Crystals of MoS₂ several molecular layers thick*. J. Appl. Phys. 1966, 37, 1928 (b) Oostinga, J. B.; Heersche, J. B. *et al. Gate-induced insulating state in bilayer Graphene devices*. Nat. Mater. 2007, 7, 151 (c) Craciun, M. F.; Russo, S. *et al. Trilayer Graphene is a semimetal with a gate-tunable band overlap*. Nat. Nanotech. 2009, 4, 383.
2. Butler, S. Z.; Hollen, S. M. *et al. Progress, Challenges and Opportunities in two-Dimensional Materials beyond Graphene*. ACS Nano 2013 7(4), 2898.
3. (a) Novoselov, K. S.; Geim, A. K. *et al. Electric Field Effect in Atomically Thin Carbon Films*. Science 2004, 306, 666 (b) Novoselov, K. S.; Geim, A. K. *et al. Two-Dimensional Gas of Massless Dirac Fermions in Graphene*. Nature 2005, 438, 197
4. Wang, Q. H.; Kalantar-Zadeh, K. *et al. Electronics and optoelectronics of two-dimensional transition metal Dichalcogenides*. Nat. Nanotech 7(2010), 699
5. Zhu, Z. Y.; Cheng, Y. C.; Schwingenschlogl, U. *Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors*. Phys. Rev. B 2011, 84, 153402.
6. Wu, S.; Ross, J. S. *et al. Electrical tuning of valley magnetic moment through symmetry control in bilayer MoS₂*. Nat. Phys. 2013, 9, 149.
7. Chernozatonskii L. A.; Kvashnin, D. G. *et al. Similarity in Band Gap Behaviour of Modified Graphene with Different Types of Functionalization*. J. Phys. Chem. C, 2014, 118 (2), 1318–1321
8. Giovannetti, G.; Khomyakov, P. A. *et al. Substrate-induced band gap in Graphene on hexagonal boron nitride: Ab-initio density functional calculations*. Phys. Rev. B 2007, 76, 079902.
9. Zhang, H.J.; Liu, C. X. *et al. Topological Insulators in Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ with a Single Dirac Cone on the Surface*. Nat Phys. 2009, 5, 398.
10. Ghaemi, P.; Mong, R. S. K. *et al. In-Plane Transport and Enhanced Thermoelectric Performance in Thin Films of the Topological Insulators Bi₂Se₃ and Bi₂Te₃*. Phys. Rev. Lett. 2010, 105, 166603.
11. Gunawan. O.; Shkolnikov, Y. P. *et al. Valley Susceptibility of an Interacting Two-Dimensional Electron System*. Phys. Rev. Lett. 2006, 97, 186404.
12. Podberezskaya, N.; Magarill, S. *et al. Crystal Chemistry of Dichalcogenides MX₂*. Struct. Chem 2001, 42(4), 654.
13. Mak, K. F.; Lee, C. *Atomically Thin MoS₂: A New Direct-Gap Semiconductor*. Phys. Rev. Lett. 2010, 105, 136805.
14. Splendiani, A.; Sun, L. *et al. Emerging Photoluminescence in Monolayer MoS₂*. Nano Lett. 2010, 10, 1271.
15. Ramasubramaniam, A. *Large Excitonic Effects in Monolayers of Molybdenum and Tungsten Dichalcogenides*. Phys. Rev B 2012, 86, 115409
16. Boker, Th.; Severin, R. *et al. Band structure of MoS₂, MoSe₂, and α -MoTe₂: Angle-Resolved Photoelectron Spectroscopy and Ab-Initio Calculations*. Phys. Rev. B 2001, 64, 235305.

17. Klein, A.; Tiefenbacher, S. *et al.* *Electronic Band Structure of Single-Crystal and Single-Layer WS₂: Influence of interlayer van der Waals interactions.* Phys. Rev. B 2001, 64, 205416.
18. Pereira, V. M.; Castro Neto, A. H. *Strain Engineering of Graphene's Electronic Structure.* Phys. Rev. Lett. 2009, 103, 46801.
19. Zhang, Y.; Chang, T-R. *et al.* *Direct observation of the transition from indirect to direct band gap in atomically thin epitaxial MoSe₂.* Nat. Nanotech (2013) doi:10.1038/nnano.2013.277
20. Zeng, H.; Dai, J. *et al* *Valley polarization in MoS₂ monolayers by optical pumping.* Nat. Nanotech 7(2012), 490
21. Yuan, H.; Bahrami, M. S. *et al.* *Zeeman-type spin splitting controlled by an electric field.* Nat. Physics 2013, 9, 563
22. Enoki, T. *Role of edges in the electronic and magnetic structures of nanographene.* Phys Scr. 2012. 014008.
23. Mak, K. F.; He, K. *et al.* *Control of valley polarization in monolayer MoS₂ by optical helicity.* Nat. Nanotech 7(2012), 494
24. He, J. G.; Wu, K. C. *et al.* *Magnetic Properties of Non-Metal Atoms Adsorbed MoS₂ Monolayers.* Appl. Phys. Lett. 2010, 96, 082504.
25. Ma, Y. D.; Dai, Y. *et al.* *Electronic and Magnetic Properties of Perfect, Vacancy-Doped, and Non-Metal Adsorbed MoSe₂, MoTe₂ and WS₂ monolayers.* Phys. Chem. Chem. Phys. 2011, 13, 15546.
26. Radislavljevic, B.; Radenovic, A. *et al.* *Single-layer MoS₂ transistors.* Nat. Nanotechnol. 2011, 6, 147.
27. Fivaz, R.; Mooser, E. *Mobility of Charge Carriers in Semiconducting Layer Structures.* Phys. Rev. 1967, 163, 743.
28. Novoselov, K. S.; Jiang, D. *et al.* *Two-dimensional atomic crystals.* Proc. Natl. Aca. Sci. U.S.A. 2005, 102, 10451.
29. Ghatak, S.; Pal, A. N. *et al.* *Nature of Electronic States in Atomically Thin MoS₂ Field-Effect Transistors.* ACS Nano 2011, 5 (10), 7707.
30. Kaasjberg, K.; Thygesen, K. S. *et al.* *Phonon-Limited Mobility in n-Type Single-Layer MoS₂ from First Principles.* Phys. Rev. B 2012, 85, 115317.
31. Fang, H.; Chuang, S. *et al.* *High-Performance Single Layered WSe₂ p-FETs with Chemically Doped Contacts.* Nano Lett 2012, 12(7), 3788.
32. Podzorov, V.; Gershenson, M. E. *et al.* *High-Mobility Field-Effect Transistors Based on Transition Metal Dichalcogenides.* Appl. Phys. Lett. 2004, 84(17), 3301.
33. Hwang, W. S.; Remskar, M. *et al.* *Transistors with Chemically Synthesized Layered Semiconductor WS₂ Exhibiting 10⁵ Room Temperature Modulation and Ambipolar Behaviour.* Appl. Phys. Lett. 2012, 101(1), 013107
34. Li, C.; Huang, L. *et al.* *Role of Boundary Layer Diffusion in Vapor Deposition Growth of Chalcogenide Nanosheets: The Case of GeS.* ACS Nano 2012, 6, 8868.
35. Shi, Y.; Zhou, W. *et al.* *van der Waals Epitaxy of MoS₂ Layers Using Graphene as Growth Templates.* Nano Lett. 2012, 12, 2784.
36. Xu, M.; Liang, T. *et al.* *Graphene-Like Two-Dimensional Materials.* Chem. Rev. 2013, 113, 3766.

37. Wu, S.; Huang, C. *et al.* Vapor–Solid Growth of High Optical Quality MoS₂ Monolayers with Near-Unity Valley Polarization. *ACS Nano* 2013, 7 (3), 2768.
38. Ramasubramaniam, A.; Naveh, D.; Towe, E. Tunable band gaps in bilayer transition-metal Dichalcogenides. *Phys. Rev. B* 2011, 84, 205325.
39. Gutierrez, H. R.; Perea-Lopez, N. *et al.* Extraordinary Room-Temperature Photoluminescence in Triangular WS₂ Monolayers. *Nano Lett.* 2013, 13(8), 3447
40. Liu, K. K.; Zhang, W. *et al.* Growth of Large-Area and Highly Crystalline MoS₂ Thin Layers on Insulating Substrates. *Nano Lett.* 2012, 12, 1538.
41. Bisri, S. Z.; Piliago, C. *et al.* Low Driving Voltage and High Mobility Ambipolar Field-Effect Transistors with PbS Colloidal Nanocrystals. *Adv. Mater.* 2013, 25, 4309
42. Gomulya, W.; Costanzo, G. D. *et al.* Semiconducting Single-Walled Carbon Nanotubes on Demand by Polymer Wrapping. *Adv. Mater.* 2013, 25, 2948.
43. Zhang, Y.; Ye, J. *et al.* Ambipolar MoS₂ Thin Flake Transistors. *Nano Lett.* 2012, 12, 1136.
44. Bisri, S. Z.; Piliago, C. *et al.* Outlook and Emerging Semiconducting materials for Ambipolar Transistors. *Adv. Mater.* 2013. doi: 10.1002/adma.201304280
45. Tonndorf, P.; Schmidt, R. *et al.* Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂. *Optics Express*, Vol. 21, Issue 4, 4908 (2013)

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PERSONAL INFORMATION

- Date of Birth: 30th August, 1988
- Sex: Male
- Nationality: Nigerian
- Contact Address: Photophysics and Optoelectronics Group, Zernike Institute for Advanced Materials, University of Groningen; the Netherlands

EDUCATION

2012-present	University of Groningen, Groningen, The Netherlands <i>Master of Science in Nanoscience (Topmaster Nanoscience Program)</i>
2010-2011	African University Of Science and Technology (AUST), Abuja Nigeria <i>Master Of Science in Theoretical Physics</i>
2005-2009	Ahmadu Bello University (ABU), Zaria Nigeria <i>Bachelor of Science in Physics (Upper Second Class)</i>
1999-2005	Federal Government College, Kaduna. Nigeria <i>West African Secondary School Leaving Certificate (WASSCE)</i>
1994-1999	Ahmadu Bello University Staff School, Zaria, Nigeria <i>Primary School Leaving Testimonial</i>

RESEARCH INTERESTS

- Photophysics and spectroscopy of nanomaterials.
- Super-resolution imaging and photophysics of nanoscale light emitters.
- Molecular machines and Responsive materials.

RECENT RESEARCH

Masters Project
(In progress)

Photophysics & Optoelectronics Group
Zernike Institute for Advanced Materials
University of Groningen

Supervisor

Prof.dr. M.A. Loi
Zernike Institute for Advanced Materials, University of Groningen

Short Project
(Mar 2013 – Jun 2013)

A self-assembled, unidirectional walker molecule

Supervisor

Prof.dr. Sijbren Otto
Stratingh Institute for Chemistry, University Of Groningen

SELECTED AWARDS AND ACHEIVEMENTS

Sep 2013 – Aug 2014 Eric Bleumink Scholarship, University of Groningen

Sep 2013 – Aug 2014 Board Member, African Students Community, Groningen

Sep 2012 – Aug 2013 Zernike Institute Grant for the Topmaster program in Nanoscience

July 2010 – Dec 2011 Ngozi Okonjo-Iweala Full Scholarship to study for a Masters in Theoretical physics at AUST Abuja

Nov 2010 – July 2011 Volunteer: Science, Technology, Engineering and Mathematics (STEM) outreach program; AUST Abuja

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Declaration of hospitality and financial support for research costs

Appendix to the Proposal for a PhD research position
 in the NWO Graduate Programme Advanced Materials, deadline 2 Feb. 2014

Name of the applicant: ABDU - AGUYE, Mustapha Tisan

Title of the proposal: Valley Optoelectronics based on Semiconducting
 Transition Metal Dichalcogenides.

By signing this document the staff member declares that she/he is willing to host and supervise the PhD research project that is mentioned above. In addition, the staff member declares that she/he has and makes available the materials, infrastructure and the funding that is needed for covering the research costs (the costs in addition to the salary of the PhD student some funding for travel and training), as described in the proposal.

The signing staff members must be affiliated with the Zernike Institute for Advanced Materials (including the associate members).

Signatures

Applicant (the student applying for the PhD grant)

Date:	Name:	Signature:
30/01/14	M. T. ABDO - Aguye	

Daily PhD supervisor (only needed if applicable, in case of supervision by an assistant professor or UD/UHD without ius promovendi)

Date:	Name:	Signature:
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1st Promotor (staff member with ius promovendi)

Date:	Name:	Signature:
30/01/14	M. A. Loi	
30/01/14	J. Ye	