### Thesis subject 2017

**Laboratories:** Group of Electrical Engineering – Paris in collaboration with Department of Materials Science and Engineering, National University of Singapore

**University:** University Pierre and Marie Curie / National University Singapore

**Title of the thesis:**

LOW DIMENSIONAL HETEROSTRUCTURES FOR HYBRID ENERGY HARVESTERS

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**Collaborations within the thesis:**
This project is within the framework of joint collaborations with Tokyo Institute of Technology and KEK accelerator (Japan), Chang Gung University (Taiwan – JRC CNRS-MOST 2017-2018).

**Program affiliation:**
Cotutelle: under discussion with NUS

**University:** National University Singapore

This subject can be published on the doctoral school’s web site: yes
Thesis’s summary (abstract):

Energy-harvesting technologies for powering portable devices to improve the longevity of batteries and power consumption are being extensively investigated. This approach becomes particularly appealing in dedicated applications such as wireless sensor nodes. Therefore, multi physics or hybrid energy harvesters coupling e.g. photovoltaic, mechanical, thermoelectric among others sources are considered to address this challenge. The recent advances in material sciences and the worldwide energy concern have triggered a large research effort to develop high-performance harvesters’ materials and devices for energy conversion using the integration capabilities of nanotechnology. In that regard our research focuses on the layered transition metal dichalcogenides (TMDCs) that have attracted considerable interest for their unique electronic and optical properties. The TMDCs such as MoS₂ and WS₂ are usually indirect semiconductors and not proper for luminescence devices in their bulk and multilayer form. These systems become interesting partly because their band gaps can be adjusted by changing their thickness or by functionalization. When approaching the monolayer the semiconductor shifts from indirect-to-direct and enhances light-intensity by quantum confinement. For example, owing to the strong light-matter interactions in TMDCs, graphene/TMDCs/graphene solar cells could reach an extrinsic quantum efficiency of 30% potentially enabling the next generation photovoltaic. Nevertheless unabsorbed photons generates heat that reduces the efficiency of the solar device. To address this issue Hybrid Thermo Photovoltaic (HTPV) systems are proposed to convert the excess heat in exploitable energy. Moreover as the temperature of the photovoltaic cell will decrease, the conversion efficiency increases again. Interestingly, the low dimensionality possibly allows to decouple the thermal and the electronic transport suggesting that these new materials could be suitable for thermoelectric conversion. The goal of this proposal is to demonstrate the feasibility of such a coupled device exploiting the peculiar electronic properties of low dimensional materials for photo detection and thermoelectric generation. For that purpose material synthesis, characterization and nanofabrication techniques will be utilized.

Candidates with Physics or EEng master’s degree are encouraged to apply and must have the willingness to involve in a strong experimental and multidisciplinary study.

Subject

1. INTRODUCTION- POSITION OF THE PROPOSAL

Energy-harvesting technologies for powering wireless devices to improve the longevity of batteries and power consumption are being extensively investigated. This approach becomes particularly appealing in dedicated applications such as wireless sensor nodes. Therefore, multi physics or hybrid energy harvesters coupling e.g. photovoltaic, mechanical, thermoelectric among others sources are considered to address this challenge. The recent advances in material sciences and the worldwide energy concern have triggered a large research effort to develop high-performance harvesters’ materials and devices for energy conversion using the integration capabilities of nanotechnology. In that regard our research focuses on the layered transition metal dichalcogenides (TMDCs) that have attracted considerable interest for their unique layer-number-dependent
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electronic and optical properties\(^2\). The TMDCs such as MoS\(_2\) and WS\(_2\) are usually indirect semiconductors and not proper for luminescence devices in their bulk and multilayer form. These systems become interesting partly because their band gaps can be adjusted by changing their thickness or by functionalization\(^3,4\). When approaching the monolayer the semiconductor shifts from indirect-to-direct and enhances light-intensity by quantum confinement effect\(^5\). For example, owing to the strong light-matter interactions in TMDCs, graphene/TMDCs/graphene solar cells could reach an extrinsic quantum efficiency of 30\% potentially enabling the next generation photovoltaic\(^6\). Yet there is still room to improve the conversion efficiency: considering the Shockley-Queisser (SQ) limit the solar spectrum is continuous over a wide range of energies and a photovoltaic (PV) cell efficiently converts only photons at the energy corresponding to the energy gap of its absorbing component: photons with energy lower than \(E_g\) are not absorbed while photons with energy larger than \(E_g\) are partially convert their energy into heat, setting the cell temperature \(T_{Cell}\). Furthermore, multijunctions composed of a gradient of tandem p-n junction with band gap decreasing from top electrode to bottom each junction being separated by a tunnel junction to allow the current flow could be engineer to improve the conversion efficiency. Nevertheless all these configurations inherently transform part of the absorbed photons into heat. In order to collect the heat dissipated one can assemble a Hybrid Thermo Photovoltaic (HTPV) systems\(^7\), figure 1.

![Figure 1: schematic of a hybrid PV thermoelectric harvesting system. A realistic device will be composed of multiple junction for both the PV cell and the thermoelectric generator\(^8\).](image)

Recent theoretical and limited experimental works demonstrated that thermoelectric devices could benefit as well from the peculiar band structures of low dimensional materials\(^9,10\). Interestingly, the optimization of the figure of merit \(ZT\) relies on a contradictory trend: materials must exhibit a very low thermal conductivity while both electrical conductivity and Seebeck coefficient must be large, Eq.1.

\[
ZT = \frac{S^2 \sigma T}{\kappa_l + \kappa_e} \quad \text{Eq. 1}
\]
S is the thermoelectric power or Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the lattice thermal conductivity and $\kappa_e$ is the thermal conductivity of the electronic carriers. In bulk materials, these transport coefficients are interrelated. Large values of $ZT$ require high $S$, high $\sigma$, and low $\kappa$. Increasing the carrier density, $n$ increases the electrical conductivity which is detrimental to the Seebeck coefficient that decreases. The term $S^2\sigma$ i.e. the power factor is optimized for degenerated narrow gap semiconductors with $n \approx 10^{19} \text{cm}^{-3}$. On the other hand, the thermal conductivity $\kappa$ is dominated by the phonons contribution to the heat conduction. In that regard, low dimensional materials could potentially change the picture, the inherent quantum confinement (2D or topological insulators) sharply change the density of states improving $S$ as well as the phonon scattering reducing the lattice contribution to the thermal conductivity. The low dimensionality particularly enhances the density of states near the Fermi level $E_F$, leading to an enhancement of the Seebeck coefficient. Besides scattering, potential barriers in 2D heterostructures can be engineered in super lattices. For sufficiently thick barriers where tunneling is prevented, the electron transport occurs owing to hot electrons that possess sufficiently high energy for thermionic emission over the barrier. In this type of band gap engineered structures, figure 2, it is possible to substantially increase the Seebeck coefficient with a relatively low impact on the electrical conductivity as the interfacial thermal conductance would be suppressed. In 2015, Hippalgaonkar et al., demonstrated in single and few layer MoS$_2$ a record high power factor as large as 8.5 mW/mK$^2$ at room temperature. This is twice higher than commercially used bulk Bi$_2$Te$_3$ therefore showing the potential of TMDCs for thermoelectric applications. The enhanced power factor is assigned to a unique combination of high mobility and high effective mass. The successful design of a hybrid harvester depends not only on the conversion efficiency of the two independent mechanisms involved but also on the technology that assembles them on one chip or system. Here we believe that it will be conceivable to design using a same set of low dimensional materials assembled in p-n van der Waals heterostructures a photovoltaic device (PV) and a thermoelectric generator (TEG). As the p-n junction is a key building block for both devices devising a full 2D materials stack will be a major step toward their integration in functional system. The bidimensional nature of these materials, allows fabricating either a lateral junction with a one-dimensional interface or a vertically stacked structure with a 2D interface. The photo-response from the lateral junctions of mono- or few-layer TMDs has been recently reported and is typically limited to the local area across the one-dimensional interface, because the full depletion of the

Figure 2: schematic of a 2D based heterostructure including TMDC, graphene and a tunnel barrier such as MX/h-BN
monolayer limit the carrier injection throughout the entire monolayer. To obtain a broad optical area device, vertically stacked structures with 2D junction interfaces are usually preferred. However the carrier leakage across the atomically thin layer in the vertical junctions could prevent the efficient recombination of the injected carriers.

NUS has pioneered large area direct deposition of graphene and 2D TMDs at low temperature and has successfully implemented fabrication of graphene coated electron emitters\textsuperscript{14,15}. The precise control of the PLD process will help to stack a finite number of layers and also facilitate the doping of 2D materials, figure 3. This first stage will permit fabrication of the required 2D heterostructures, figure 3.

Figure 3: MoS\textsubscript{2} deposited using PLD at 400 °C with (a) cross sectional TEM confirmation of a triple layered film and (b) plan view microscope image confirming a large uniform area of deposition\textsuperscript{14}.

2. FRAMEWORK

For the last 5 years GeePs and NUS labs have focused on graphene based heterostructures for field effect devices\textsuperscript{4,3}, energy storage\textsuperscript{16}. This work has recently been extended to h-BN and MoS\textsubscript{2} materials through national and international collaborations\textsuperscript{17}. GeePs has extended its characterization facilities with various equipment coupling spectroscopy techniques to electrical measurements to investigate various types of heterojunctions. Moreover, GeePs and INSP are discussing the upgrade of the PPMS measurement system to include measurement of the thermoelectric properties such as the Seebeck coefficient. The purpose of this proposal is to develop a collaboration on hybrid or coupled energy harvesters exploiting the peculiar electronic properties of low dimensional materials e.g. decoupling the thermal and the electronic transport.

**National collaborations:**
Centre de Nanosciences et de nanotechnologies (C2N)
Institute des Nanosciences de Paris (INSP)

**International collaborations:**
Tokyo Institute of Technology (Japan)
Chang Gung University (Taiwan) – JRC CNRS/MOST

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3. TENTATIVE WORK PLAN AND EXPECTED RESULTS

This research proposal is structured around 3 axes: materials synthesis, electronic properties of materials and interfaces, nanofabrication and electrical characterization of the heterostructures. The candidate will focus on evaluating and modulating the electronic properties to suit photovoltaic and thermoelectric purposes and attempt to prototype standalone microsystems.

3.1. TASK 1: MATERIAL SYNTHESIS:

The precise control of the PLD process will help to stack a finite number of layers and also facilitate the doping of 2D materials to fabricate a 2D heterostructure. The same material systems will be further utilized in order to measure the structural and the electronic transport properties to benchmark the materials for our purpose. The challenge here will be to synthetize 2D heterostructures for PV and thermoelectric purpose. The major asset of this technique is that it potentially allow considering the low temperature process to stack the junctions making the hybrid system monolithic. Various test structures will be designed and patterned using dedicated nanotechnology processes.

3.2. TASK 2: ELECTRONIC AND THERMEOLECTRIC PROPERTIES

Photoelectron spectroscopies are valuable tools to study electronic properties of hetero-junctions and determine the interfacial energy band diagram by measuring several parameter values such as work function, valence and conduction band offsets, figure 4. These properties are key to select the appropriate 2D materials system. These measurements will be carried out with and without functionalization to evaluate the shifts in band offsets. Moreover detailed knowledge of the band offsets could serve as precise inputs for TCAD simulations. In-situ XPS/UPS will be employed to measure the bandgap and work function. In addition, with the ability to anneal to 600 °C in ultrahigh vacuum, in-situ XPS/UPS will be used to study band shift temperature effects on the multi-material 2D stacks. Furthermore the measurement of the dopants/concentration and its related interatomic bond distance using XANES and NEXAFS will take place at the Singapore Synchrotron Light Source (SSLS). This allows to study the fundamental properties and effectiveness when

![Figure 4](image-url)
Few atomic layered 2D materials are modified through doping. A shift in the Fermi level with respect to its location in pristine MX2 and MX would be the signature of a charge transfer between the 2D materials composing the heterojunction. The charge transfer mechanism will be also be probed using transport measurements in a field effect transistor (FET) configuration. This way, we will be able to probe the variation of MX2 or MX conductivity under illumination and determine the photo generation regimes. We will investigate monolayer and multilayer samples to tune the band gap of the material for multijunctions purpose. The transport properties will be carried out using low temperature Hall effect measurement under a PPMS system in order to assess the material properties such as carriers’ density, resistivity and mobility. The PPMS system is being upgraded at INSP to extend the capabilities to thermoelectric properties. These measurements will help to benchmark the thermoelectric properties for various growth processes and materials and establish a design rule for an efficient thermopile.

3.3. TASK 3: FABRICATION OF HETEROJUNCTIONS FOR HYBRID HARVESTING DEVICES

The ultimate objective of our project will be the development of p-n junctions with photovoltaic photo response on one hand and sufficient thermoelectric figure of merit ZT on the other hand to convert the excess heat in exploitable energy. Regarding the photo detection, recent work by C2N lab have shown very promising results concerning the performance of graphene/MoS2 devices with high photo response (107 A/W). Other studies have reported the realization of Graphene-MX2 photodetectors, but also heterojunctions based on MX2 layers. In this task, the photo response of the systems will be investigated through the modulation of the electronic properties of the interface. We believe that a breakthrough in device performance can be obtained by correctly engineering the band structure of the MX2 and MX. The photo response is strongly affected by the position of the Fermi level at the heterojunction. We will investigate the device made of different thickness of MX2 or MX with a transparent top electrode and contacts such as graphene demonstrated by GeePs and C2N in a recent work. The challenge here will be to devise a stack of heterojunctions separated by a tunnel barrier to allow the current flow for the multijunction configuration. The device electrodes could possibly be graphene which workfunction and transport properties can judiciously be tuned by functionalization through chemical molecules or by interfacing a semiconductor. The carrier lifetime and the recombination mechanisms will be determined using temperature dependent modulated photoluminescence developed at GeePs that is particularly important for the PV cell. On the other hand, the thermoelectric device will be composed of large density of pn junctions showing sufficient ZT (~ 2) patterned in a thermopile, achieving a ZT close to 2 would be a major step forward for such systems. The larger the density of thermoelement the larger the voltage generated hence the importance of nanopatterning. The key design rule will be to thermally isolate the cold and hot junctions in order to maintain a temperature gradient.

4. RISKS ASSESSMENT

This work will involve an important aspect of technology development as well as material characterization. There is limited risk for task 1 and medium risk for tasks 2, respectively, since the growth protocols of chalcogenides materials are being developed by NUS and the characterization platforms are available at both labs. Moreover, we may benefit...
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from existing collaboration between the C2N team and INSP lab (UPMC) where newly installed reactors will be able to
grow various low dimensional materials of interest. Our
goal for the PV device is to achieve a tandem cell
Graphene/MoS2 with efficiency superior to 30%.
Developing a 2D heterostructures (task 3) for
thermoelectric purpose is more challenging fr om a
technological and characterization perspective; there is
little experimental work to date. The research on the
thermoelectric properties of 2D heterostructures and their
engineering is a growing field and limited results are
available rendering this proposal ambitious. Possible
strategies consist of phonon scattering to reduce the
thermal conductivity using materials assembled in super
lattices or doping regimes. Although a complete hybrid
harvester device may be challenging to achieve within the scope of this PhD, the characterization and the technology
developed will pave the way toward the assembly of a hybrid harvesting system exploiting the two conversion
mechanisms as well as strengthen the NUS/UPMC collaboration on energy harvesting materials and devices.

5. REFERENCES