International Doctoral Program 2024
Strategic Partnership

THERMOELECTRIC TRANSPORT IN TRANSITION METAL DICHALCOGENIDES

Supervisors/Advisors :

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Labs and platforms :

. Sorbonne University : GEEPS (UMR 8507) & IMPMC (UMR 7590)

. NTU College of Engineering : Nanoelectronic lab (School of Electronic and Electrical Engineering)

Context and framework

The heat waste is an under-exploited source of energy that could be harvested directly and reversibly through thermoelectric (TE) transducers thus providing a cleaner form of useable energy. The efficiency for the energy conversion i.e., the TE figure of merit of a material is defined by the dimensionless $ZT = S^2\sigma/(\kappa_e + \kappa_l)$ where S is the Seebeck coefficient, σ is the electrical conductivity T is the absolute temperature, κ_e is the electronic thermal conductivity and κ_l is the lattice thermal conductivity. High performance TE materials should ideally exhibit : a high S, a high σ and a low κ. However, these transports factors (S, σ, κ) are strongly entangled to each other through charge carrier concentration (n) and mobility (µ), thus, it is still a great challenge to enhance the ZT of TE materials. Therefore, there is an urgent need to develop a portfolio of thermoelectric materials offering thermal stability, especially for the temperature range 300-400 K, where a large amount of heat is wasted into the environment, but no standalone harvesting methods are suitable to effectively generate electrical power. Several routes have been proposed to achieve high ZT materials e.g., band convergence, low dimensionality, and energy filtering. Low-dimensional materials such as transition metal dichalcogenides (TMDs) are particularly interesting as they encompass the alternative routes owing to quantum confinement and their peculiar band structures. They typically present higher S values than 3D bulk materials and are prone to energy filtering (EF) whereby the energy dependence of the density of states (DOS) presents singularities, substantially enhancing S and σ. The goal of current TE research is to disentangle S and σ. Low dimensionality increases the DOS near the Fermi level E_F, leading to an enhancement of S. These improvements are mainly observed in chalcogenides such as Bi_2Te_3, $PbTe$, and Sb_2Te_3 that exhibit a ZT close to unity and have been widely integrated into TE generators. Recently, Yang *et al*[1]. have measured a PF of 0.150 $mWm^{-1}K^{-2}$ on 8 nm Bi_2O_2Se at 300 K. They observed a high mobility which independently enhances σ without compromising S. Similarly, GEEPS and NTU also measured a high value, *i.e.* $S \approx$ -250 $\mu V/K$ for a 14 nm film at 300 K. However, their PF $\approx$ 0.9 $mWm^{-1}K^{-2}$, figure 1, is 6-fold higher and presents a stable temperature window centered on 280 K, in striking contrast with the observation of Yang *et al.* While the mobility decreases, it remains high (350 $cm^{-2}V^{-1}s^{-1}$ at 400 K) with a transition at 120 K from acoustic phonon to piezoelectric scattering regime below which we observe the decoupling of S and σ, departing from the Mott equation, figure 2.

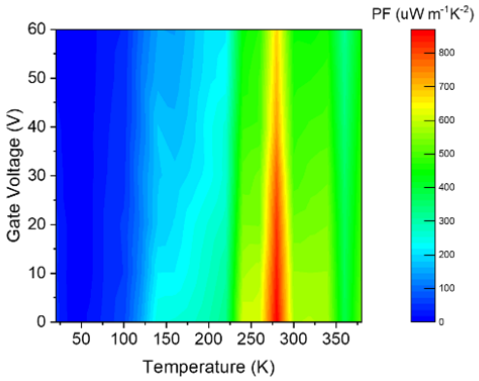

Figure 1 – PF contour map of 14 nm thick Bi_2O_2Se (under review)

Objectives of the research project

Our work on 2D TMDs and the large PF of Bi_2O_2Se observed is very encouraging and, at the same time, raises fundamental questions on the underlying mechanisms that led to such an enhancement. Understanding

these factors could, eventually, lead to the design of new TE systems outperforming current high ZT materials. Our recent experimental observations revealed a substantial enhancement of the power factor ($S^2\sigma$) on 2D TMDs and highlight the importance to investigate transport mechanisms at low dimensions, particularly 1D nanowires (NW). These later could be formed with nano inclusions whereby, lower energy electrons scattered by the potential barrier of the interface, may also induce a significant improvement. In this PhD project, we propose to benchmark the TE properties of 3D, 2D and 1D configurations of the same selected material grown by chemical vapor transport (CVT), using the same measurement techniques. While 1D nanowires (NW) are the most promising candidates for TE due to their sharp DOS near E_F, their growth and processing are challenging. One innovative aspect of the project relies on the original nano-jackhammer technology developed by Prof Li Hong at NTU-Singapore[2].

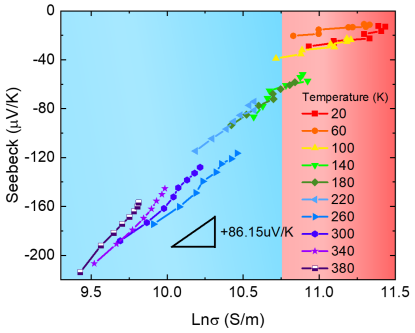

Figure 2 – Jonker plot of 14 nm thick Bi_2O_2Se where Seebeck coefficient is plotted against $S.vsLn\sigma$, the decoupling occurs at the transition blue to red region.(under review)

This method allows fast throughput and low-cost fabrication of NWs or any substrate and permit the direct fabrication of NWs in homo or heterostructure phase particularly interesting to induce energy filtering, figure 3. As a result, we will be able to investigate the impact of dimensionality and carrier scattering mechanisms under the same configuration over a wide range of temperature and magnetic field. Our methodology to achieve our goals is complementary as it covers material sciences and technology as well as dedicated instrumentation. Bulk crystals (*e.g.* titanium disulfide TiS_2) will be grown at IMPMC[3] and transferred to NTU for patterning by nano jackhammer. IMPMC and GEEPS will carry out structural and photo emission electron microscopy (PEEM) experiments to determine the band structure of the material with and without nano inclusions as well as the carrier relaxation time[4,5]. Theoreticians at IMPMC will support these experiments with *ab-initio* calculations and provide insight to tailor the experiments related to the transport coefficient *i.e.* S, σ, κ and fitting models. Upon completion of this first phase, the candidate will then focus on the study of scattering mechanisms under different stressors such as temperature and magnetic field (spin Seebeck) as well as interfaces (substrates) to determine the ZT figure of merit and extend her/his study to promising TE materials grown at Sorbonne University.

Risks management

The partners are already working together, and a lot of efforts (with the support of NTU and CNRS) have already been dedicated to assemble a robust characterization instrumentation offering a unique opportunity to investigate the TE properties. Yet the implementation of the nanojackhammer fabrication method on TMDs is exploratory and we may face technological obstacles such as the efficiency of imprinting dichalcogenides NWs at room temperature. To mitigate this issue NTU will upgrade its platform with temperature control to anneal the sample upon ultra sound patterning. In the worst case scenario, we will keep investigating 3D and 2D materials while developing the growth of NWs with alternative techniques available at IMPMC.

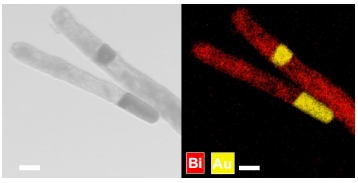

Figure 3 – TEM and EDS of Bi NW with Au nano inclusions, scale bar is 100 nm[2]

Applicant profile

This topic requires a candidate willing to involve in various technological as well as characterization aspects with a focus on transport measurements. Hands on and dedicated applicants with excellent physics and/or EEng background are encouraged to apply. Python programming skills appreciated.

1. F. Yang et al., Adv. Mater. 33, 2004786 (2021)
2. J. Ge et al., Nat. Commun. 12, 3146 (2021)
3. H. Moutaabbid et al., Inorg. Chem. 55, 6481–6486 (2016)
4. C. Euaruksakul et al, Journal of Electronic Materials, 1543-186X (2020)
5. K. Fukumoto et al., J. Phys. Appl. Phys. 53, 405106 (2020)