Solid State Thermionic Devices: Effects of asymmetry, defects, and electron-phonon coupling on thermionic transport

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To my family

Abstract

The miniaturization of electronic devices leads to the rapid increase of heat power densities. The management of high heat power densities in nanoscale devices is a significant scientific and engineering challenge. In microelectronics and nanoelectronics, the self-heating effects significantly reduce both transistor efficiency and lifetime, and in a very large-scale integrated circuit (VLSI), the heat generation and thermal management become one of the bottlenecks to further improve clock speed and make smaller feature sizes. Moreover, the recent development of embedded systems in an internet of things viewpoint will require local and on-chip thermal management abilities. Solid-state thermionic (SSTI) coolers integrated with these devices are among the few viable options for addressing some of these issues. The same SSTI devices with the same design can also be used as heat to electrical power generators for applications such as wearable electronics. The primary objective of this dissertation is to theoretically design highly efficient SSTI devices based on two-dimensional (2D) van der Waals (vdW) heterostructures. This work also theoretically investigates the effect of asymmetry of the electrode, electron-phonon interaction, and defects on the SSTI device performance. The size effect and the significance of electron-phonon interaction in nanoscale thermionic devices are evaluated by knowing the mean-free path of electrons in the bulk version of the 2D semiconductor material used as the channel in the SSTI device. To evaluate the effect of electron-phonon interaction, the highly accurate electron-phonon scattering rates

of the bulk form of the 2D semiconductor channel are computed from the first-principles. The calculated electron-phonon scattering rates are then utilized to investigate the effect of electron-phonon interaction on electron transport of the same bulk semiconductor from full first-principles calculations. In addition, in this work, the first SSTI device based on 2D vdW heterostructures is fabricated and characterized in collaboration with experimental groups. The figure of merit of the fabricated device is measured using a hybrid technique that combines thermoreflectance and cooling curve measurements. Finally, as a separate route, this work theoretically and experimentally investigates how polymorphism in Bi₂Se₃ allows it to be tuned for unique thermoelectric properties.

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Chapter 1: Introduction

1.1 Thermionic Energy Conversion

Thermionic energy conversion is the process of converting heat directly into electricity using heat as the source of energy and electrons as the working fluid. A thermionic converter essentially is a heat engine converting thermal energy directly to electricity. Similar to most other heat engines, thermionic devices can operate in different operational modes. In its power generation mode, heat is used to 'boil off' electrons in the cathode (emitter). These electrons are then collected by a colder anode (collector). A part of the thermal energy is thus converted directly to electricity and the rest is rejected as heat to the cold side. The very same devices can also operate in the refrigeration mode where the current is passed through the device to pump heat from the cold side to the hot side. The most common operational mode of these devices is however their rectifying mode. Vacuum thermionic diodes were once the heart of the electronic industry. They have been mostly replaced by solid-state devices nowadays, but still have a reasonable market and are the basis for cathode-ray tubes, radio tubes, and broadcast transmitters. Thermionic devices are simple in construction and, having no moving parts, are quiet in operation. They are environmentally friendly as no emissions of greenhouse gases are involved and are highly reliable. Thermionic devices have attracted a lot of interest for several decades due to these excellent features.

There are two main types of thermionic converters: vacuum state thermionic converters (VSTIC) and solid-state thermionic converters (SSTIC). VSTICs operate at very high temperatures (above 1500°K), produce high power, yet occupy a very small volume. They

are suitable for applications such as solar concentrated power generators, waste heat conversion from nuclear reactors, and fossil fuel combustion. SSTICs work at much lower temperatures and under smaller temperature differences and are more suitable for power generation applications involving less amount of heat such as residential and industrial waste heat recovery (less than 600°K). Both VSTICs and SSTICs can be used in power generation as well as refrigeration mode as the parameters affecting their performances in both modes are similar. Hence, if a VSTIC or an SSTIC exhibits good performance in power generation mode, a similar level of performance can be expected in its refrigeration mode. It is also possible to use TICs as thermal switches [1,2] and/or active coolers [3] that are actively pumping heat from the hot side to the cold side. However, in these last two modes of operation, the design parameters are different. Finally, the Photon-enhanced Thermionic Converter (PETIC), recently proposed, is essentially a hybrid version of the VSTIC. It utilizes both light and heat as its energy source and could be viewed as a hybrid photoelectric-thermionic device. PETIC has been demonstrated in the power generation mode. [4]

1.2 History of Thermionic Converter

The discovery of thermionic emission by Edison in 1885 paved the way for developing a new method of energy conversion using the thermal emission of electrons. Thermionic diodes (also called thermionic valves or thermionic tubes) were invented by Fleming in 1904. They have been widely used in radio and telephone communications. A thermionic converter is very similar in operation to a thermionic diode. Even though, the idea of thermionic energy conversion was first suggested by Schlicter [5] in 1915, extensive theoretical and experimental investigations for practical level power generation using this concept were not carried out until the 1950s. In 1956, Murphy and Good published a rigorous study of thermionic and field-emission theory. [6] Hatsopoulos studied vacuum thermionic and vapor thermionic converters during his Ph.D. work on the thermoelectron engine. There, he discussed the single and the multiple emitter-collector configurations for power generation. [7] In 1957, Ioffe briefly discussed vacuum thermoelements in his book [8] on thermoelectric conversion. H. Moss [9] evaluated the importance of many of the device parameters in her calculations on thermionic devices. Hernqvist *et al* demonstrated a practical thermionic converter with an efficiency of several percent in 1957. [10] In 1958, Webster evaluated the performance of a high-vacuum thermionic converter using Langmuir's work on thermionic diodes. [11] Hatsopoulos et al used cylindrical emitter and collector with 0.125-inch diameter in their preliminary experiment on thermionic diode model. With an interelectrode separation of 10 µm to minimize the so-called space charge effect, and an emitter temperature of 1540 °K, a 13% energy conversion efficiency was obtained. [12] Wilson used positively charged cesium ion gas (plasma diode) to cancel the negative inter-electrode space charge effect and has demonstrated 9.2% conversion efficiency and output power of 3.1 W cm^{-2} . [13]

In 1959, the first thermionic converter exhibiting promising results was installed into the water-moderated core of the Omega West Reactor. A short circuit current of 35 A and an open-circuit voltage of 3.5 V was produced by this converter although it had a fairly large interelectrode space of about 6 mm. [14] Initial development of thermionic converter in the United States took place using the solar energy and the radioisotopes as the thermal source. In the 1960s, the Jet Propulsion Laboratory Solar Energy Technology Thermionic

Program started a solar thermionic converter evaluation and generation program, where they developed and tested several converters. The majority of the converters were operated at an emitter temperature of about 1900°K with a lifetime of 11,000 hours including one particular converter with a lifetime of 20,000 hours. The converters generated 150watts power exhibiting an energy conversion efficiency of 7 to 11 percent. However, the program was discontinued in the 1970s as the thermionic converters could no longer compete with the evolving solid-state-based photovoltaic and thermoelectric energy conversion techniques. [14,15]

Later the focus shifted to space power generation systems using nuclear heat sources. NASA and the Atomic Energy Commission (AEC) started to fund the development of incore and out-of-core thermionic fuel elements. Experimental testing of a prototype of an in-core thermionic converter advanced to multi-cell TI fuel element design using tungsten-clad UO₂ emitters started in 1970, which operated at an emitter temperature of 1900°K with a lifetime of 10,000 hours. In 1970, General Atomics (GA) developed a Mark III reactor that could operate at 1900°K with a lifetime of 12,500 hours. The thermionic space reactor development program was canceled in 1973 as congress and the executive branch shifted funding out of the space power field. In the 1970s, there was no major development in thermionic research except for the USSR's TOPAZ (Russian acronym for Thermionic Experiment with Conversion in Active Zone) project. The TOPAZ reactor system generated 5 to 10 kW of power with a lifetime of 3,000 to 5,000 hours. TOPAZ-II, a 6 kW converter with an energy conversion efficiency of 10 percent and an interelectrode gap of 100 μ m was flown by the Soviet space program in 1987. This project was then terminated due to budget restrictions. [14–16]

In 1973, thermionic application in the area of fossil-fueled terrestrial power systems attracted the attention of researchers. A significant development in this time includes a new type of converter designed applying advanced electrode and plasma technologies to improve the thermionic cell lifetime and performance. During this time, a flame-fired thermionic conversion unit was developed to generate electricity using the waste heat produced from an environment where high temperature is attained by combustion. [17]

In 1979, a rebirth of the space program was brought about by the joint initiative of NASA, the Department of Energy (DOE), and the Department of Defense (DoD). Together they launched the space power advanced reactor (SPAR) program focusing exclusively on heat pipe technology. In 1982, the SPAR program was extended and renamed as SP-100 program. The main focus of the SP-100 program was to design a 100-kW nuclear power system suitable for outer space applications. Research from 1984 to 1986 was primarily focused on a better understanding of the system design, but no major reactor was demonstrated. [14,15,18]

A number of government programs as well as many individual researchers continued research in the field of thermionic converters over the next decade. In 2001, a report published by the National Research Council projected a negative perspective on the viability of thermionic energy conversion. [15] However, increasing demand for clean energy and advancement in nanotechnology helped create a renewed interest in thermionic conversion in recent years.

In 1997, Shakouri and Bowers [19] proposed a single-layer solid-state thermionic diode in which the vacuum is replaced by a semiconducting material. In this structure, the semiconductor layer is the energy barrier that an electron experiences. In the following year, Mahan proposed the idea of using multi-layer barriers in which each layer maintains a small temperature difference. [20,21] These proposed structures created a sudden surge in SSTIC research. Over the next several years, extensive studies were carried out in search of suitable materials which would enhance the performance of SSTICs in both power generation and refrigeration modes. As these structures can be grown directly on a chip. Scientists soon realized the potential of SSTICs as integrated coolers for hotspots in electronic and optical devices. [22–25] A large number of thin-film coolers lattice-matched to Si, GaAs, or InP were fabricated and characterized. InGaAsP/InP¹⁸, [26–28] and InGaAs/InP [29] lattice-matched to InP and AlGaAs/GaAs [30] lattice-matched to GaAs, all grown by metal-organic chemical vapor deposition (MOCVD) and InGaAs/InAlAs [31], InGaAsSb/InGaAs [32], SiGe/Si [33–35] and SiGeC/Si [36] deposited by molecular beam epitaxy (MBE) were all reported around this period. In 2015, for the first time, Cronin used a 2D van der Waals heterostructure, a stack of atomic layers, to build an SSTIC. [37] The unstable nature of the van der Waals heterostructures and the difficulty in providing a proper metallic contact to these structures were identified as the main stumbling blocks preventing the experimental demonstration of highly efficient van der Waals heterostructure-based SSTICs. Recent indepth theoretical calculations indicate the potential these structures hold in thermionic energy research. [38,39]

1.3 Theory of Thermionic Converters

1.3.1 Basic Working Principle

The simplest form of a thermionic converter consists of two electrodes, an emitter (cathode) and a collector (anode). A general schematic diagram of a VSTIC is shown in *Figure 1.1(a)* and that of an SSTIC is shown in *Figure 1.1(b)*. In the case of VSTICs, the emitter and the collector electrodes are enclosed in a vacuum container. The electrodes are separated from one another by an inter-electrode vacuum gap. The emitter is in thermal contact with a heat source and the collector is in thermal contact with a cold heat sink. The heat source supplies thermal energy to the emitter raising the emitter's temperature. Thus, the high-energy electrons in the tail of the Fermi-Dirac distribution function acquire a sufficient amount of energy to overcome the work function energy barrier and escape the emitter. These electrons enter the vacuum gap and are then absorbed by the collector. Once in the collector, they reject their extra energy to the heat sink. Finally, the electrons flow back from the collector to the emitter through an external load. This flow of electrons delivers useful electrical work to the external load.



Figure 1.1: A general schematic diagram of a (a) VSTIC, an (b) SSTIC, and a (c) heat engine.

SSTICs operate in a similar manner. The vacuum gap is replaced by a semiconductor giving rise to several consequences. First, the energy barrier is smaller, so the SSTICs can operate at lower temperatures. The energy barrier in the case of VSTICs is the work function of the emitter (φ_E), but for the SSTICs, it is the difference between the emitter work function and the electron affinity of the semiconducting layer ($\varphi_E - \chi_S$). Second, the vacuum gap is micron to millimeter size while the semiconducting layer thickness is much smaller (<100nm) to ensure ballistic transport. Third, radiation, the only heat transfer mechanism in a vacuum, for VSTICs is replaced by conduction in SSTICs. As a consequence, SSTICs suffer from large heat leaks compared to VSTICs and in comparison, they can only operate at much smaller temperature differences. Fourth, lack of background positive charges, create a space charge effect in VSTICs which to an extent is absent in SSTICs when the proper level of doping is provided in the semiconducting layer. The absence of the space charge effect is an advantage for SSTICs as the presence of space charges would otherwise lower the performance of the thermionic converters. Finally, connection to a heat source and heat sink is much easier in SSTICs due to the absence of a vacuum.

A thermionic converter can be viewed as a heat engine as shown in *Figure 1.1(c)* in which the emitter receives heat from a high-temperature source, the collector rejects heat to a cold sink, and some part of the input thermal energy converts to electrical energy as useful work. The energy conversion efficiency of a heat engine is limited by the Carnot efficiency, which is defined as

$$\eta_C = 1 - \frac{T_C}{T_H}$$

where, η_c is the Carnot efficiency, Tc is the temperature of the cold side (collector in this case), and T_H is the temperature of the hot side (emitter). The upper bound of emitter temperature is limited by the melting point and the chemical and mechanical stability of the emitter material. The emitter and the collector, in VSTICs, are separated by a vacuum gap. This gap allows only a very small amount of radiative heat to be transferred through it. Consequently, it is possible to maintain a very high-temperature difference between the emitter and the collector and achieve a higher Carnot efficiency compared to other heat engines. For instance, a typical VSTIC operating with a collector temperature of 1100°K, and an emitter temperature of 2000°K will reach a Carnot efficiency of 45%. On the other hand, SSTICs operate at lower temperatures and with smaller temperature differences. As a result, they are more suitable for applications such as waste heat recovery wherein the available temperature is in the 400-600°K range. As the temperature difference is smaller the Carnot efficiency of SSTIC is also relatively smaller compared to VSTIC.

1.3.2 Ideal Output Current, Voltage, and Power

Consider the simplest type of thermionic converters, a single barrier structure. *Figure 1.2* shows the energy diagram of it. The energy barrier is represented by Φ_E which is equal to φ_E for VSTICs and is equal to $\varphi_E - \chi_S$ for SSTICs. Similarly, we named the barrier height (the energy offset) at the collector side as Φ_C which is equal to φ_c for VSTICs and

 $\varphi_c - \chi_s$ for SSTICs. In *Figure 1.2*, it is assumed that the emitter energy barrier Φ_E is larger than the collector energy barrier, Φ_C , plus the total voltage *V* (*V* = *IR* + *IR*_{*l*}, *R*_{*l*} is the load resistance and R is the internal resistance of the thermionic converter).

In order to overcome the potential energy barrier, electrons inside the emitter must be energized above the energy barrier. When thermal energy from the heat source is supplied to the electrons inside the emitter, they obtain enough energy to escape the emitter surface. The net current density of the electron flux from the emitter to the collector is given by the Richardson-Dushman equation [40,41] which can be written as

$$J = A_R T_H^2 \exp\left(-\frac{q\phi_E}{k_B T_H}\right) - A_R T_C^2 \exp\left(-\frac{q(\phi_E - V)}{k_B T_C}\right)$$
(1)

where T_H is the emitter temperature, T_c is the collector temperature, Φ_E is the work function of the emitter material, k_B is the Boltzmann constant, q is the electron charge constant, V is the total voltage and A_R is the Richardson constant. The theoretical value



Figure 1.2: Potential energy diagram of a (a) VSTIC and an (b) SSTIC

of $A_R = \frac{4\pi q m^* K_B^2}{h^3}$ is calculated assuming parabolic band structure. Assuming effective mass to be the same as the mass of a free electron, $A_R = 120 \frac{A}{cm^2 K^2}$. However, the experimental values of A_R vary with materials arising from the complex Fermi surface of the metals. As current depends on the energy barrier exponentially (Eq. 1), a small change in the value of the energy barrier results in a significant change in the current density. The first term in Eq. 1 is the flux of electrons from emitter to collector and the second term is the leak current flux going backward from the collector to the emitter. The power density delivered to the load is

$$p_{load} = (V - IR)J.$$
⁽²⁾

Similarly, the thermal current of the thermionic converters can be written as:

$$J_{Qc} = A_R T_H^2 \exp\left(-\frac{q\phi_E}{k_B T_H}\right) \left(\phi_E + 2k_B T_H/q\right) - A_R T_C^2 \exp\left(-\frac{q(\phi_E - V)}{k_B T_C}\right) \left(\phi_E + \frac{2k_B T_C}{q}\right) + J_{Q-leak}$$
(3)

$$J_{Q-leak} = \begin{cases} \frac{T_H - T_C}{R_t} & \text{for SSTICs} \\ \sigma \epsilon (T_H^4 - T_C^4) & \text{for VSTICs} \end{cases}$$

Here, $\phi_E + \frac{2k_B T_H}{q}$ is the average energy of the electrons passing above the energy barrier. The $2k_B T$ factor comes from Fermi Dirac statistics and is considered as the excess energy factor that lowers the efficiency. J_{Q-leak} is the thermal leak current which is mainly due to radiation in VSTICs and conduction in SSTICs. In the case of VSTICs, it is proportional to the effective emissivity of the cathode and anode, ϵ . To minimize the radiation, one can use cathode and anode materials with low emissivity at the operating temperature of VSTICs. In the end, radiation is much weaker compared to other channels of heat transport. In this context, in most VSTICs, plasma gas is used to minimize the space charge effect. When used, plasma gas creates a convective channel of heat transport which increases the heat leak significantly. In the case of SSTICs, the leak problem is even more serious. J_{Q-leak} in this case, is due to conduction and is inversely proportional to the thermal resistance, R_t . To minimize J_{Q-leak} , we need to maximize R_t which is a very difficult task considering the small required size of the semiconducting layer (<100nm).

Finally, the conversion efficiency of a thermionic converter is defined as the ratio of the output electrical power to the heating power supplied to the emitter and can be calculated as

$$\eta = \frac{p_{load}}{J_{Oc}} \tag{4}$$

where p_{load} is the power density delivered to the load and J_{QC} is the thermal current. To optimize the efficiency, instead of matching resistance conditions, the resistance of the load (R_l) should be adjusted according to the internal resistance of the thermionic diode (R) and the Richardson current to satisfy: [42]

$$R_l = \frac{k_B}{A_R T_C A q} \exp\left(q \frac{\phi_E - V}{k_B T_a}\right) + R \tag{5}$$

The barrier height can also be optimized, and it is shown that the optimum barrier height to maximize the efficiency is on the order of $2-5 k_B T$. The theoretical analysis demonstrated that the total energy conversion efficiency of a VSTIC can exceed 30% but cannot be greater than 90% of the Carnot efficiency. [43] Mahan theoretically showed that the efficiency of a SSTI refrigerator can be greater than 80% of the Carnot value. [44]

1.4 Limitation of VSTICs and the emergence of SSTICs

There are several non-ideal effects that lower the efficiency and need to be considered in the design of highly efficient VSTICs. Radiation leak from the hot cathode to the anode lowers the efficiency as shown in the theory section (Eq. 3 and 4). We note that radiation is weak at low temperatures, however, the VSTICs work at high temperatures and as a result, the radiation leak plays a role in lowering the efficiency. This leak could be minimized if the cathode and the anode are made out of materials with low emissivity. Unoxidized tungsten for example is a material with low emissivity (0.15 at 1000 °K and 0.28 at 2000 °K) [45] and is suitable for highly efficient VSTICs. Any internal electrical resistance including the resistances of the leads further lowers the efficiency as the RI² generated as a result of internal resistance is subtracted from the total power generated (see Eq. 2). Another problem is the inaccessibility of the cathode and anode for the purpose of cooling and heating. The electrodes are inside a vacuum, and it is not possible to put their surface in direct contact with the external heat source and the heat sink. The space charge effect also has a significant effect on the performance of a VSTIC. Considering that VSTICs are only operating at very high temperatures, it is desirable to extend their operation to lower temperatures where the heat sources are more abundant. The biggest challenge in lowering the operating temperature comes from the high energy barrier developed due to the large work function of the electrodes which the electrons cannot overcome at lower temperatures. The difficulty in finding low work function electrodes restricts the performance of the VSTICs at very high temperatures. The need for a vacuum restricts direct access to the electrodes. These and many other challenges aspired to the design of a solid-state replacement.

1.4.1 SSTICs Design considerations

SSTICs were introduced to resolve many of the challenges of VSTICs but they also posed some new difficulties. In particular, the high work function of the metals and the space charge effect are not relevant to SSTICs. Instead, SSTICs suffer from conduction heat leakage due to the small thickness of the semiconducting layer. Thermionic conditions impose the requirement of ballistic transport in the semiconducting layer. Note that if the transport is diffusive in the semiconducting layer, then the device should be described as a thermoelectric device working based on the Seebeck effect. In that case, within the bulk semiconducting layer, electrons will lose their memory and reach near equilibrium with lattice. To maintain ballistic transport of the hot electrons, the semiconducting layer thickness, L, should be equal to or less than the mean free path, λ , of the electrons inside the barrier: $L \leq \lambda$. On the other hand, too thin of a barrier results in tunneling of electrons, which is undesirable since low-energy electrons (with energies smaller than the chemical potential, μ) will act as holes and lower the efficiency of the electron transmitting device (similar to the bipolar effect in the case of thermoelectric transport). If the height of a square-shaped barrier of length L_t is $e\phi$, the probability of electron tunneling through is proportional to $\exp\left(2L_t\sqrt{\frac{2m^*e\phi}{\hbar^2}}\right)$ while the probability of thermionic emission is proportional to $\exp\left(\frac{e\phi}{k_BT}\right)$. [21] Thus, the minimum thickness L_t which makes the thermionic emission dominant while suppressing the tunneling part is $L_t = \frac{\hbar}{2k_BT}\sqrt{\frac{e\phi}{2m^*}}$. [21] So, the semiconducting layer thickness should satisfy the condition: $L_t < L \leq \lambda$.

It is known that for an ideal SSTIC, internal electrical resistance, *R*, is zero. Non-zero values of *R* lower the performance. [9] Therefore, having a small thickness and ballistic transport is beneficial since it will result in smaller values of *R*. Effect of non-zero value of *R* could be considered negligible for $R \ll 0.5(k_BT_C/eJA)$, where J is the Richardson current, A is the electrode area, and T_c is the temperature of the cold side. [42] For example, the output power of an SSTIC operating with a barrier height of $5k_BT$, anode and cathode area of 1 cm^2 , T_H at 400*K* and T_c at 360*K*, would be close to that of the ideal TICs if the value of is *R* smaller than $10^{-7}\Omega$. Therefore, any internal resistance below the limit could be neglected and the SSTIC, in that case, could be approximated by an ideal diode. In SSTICs, *R* represents the total electrical resistance that has a contribution from the semiconductor layer, the electrodes, and the semiconductor-electrode interfaces. The electrical resistance of the semiconductor layer is very small as its thickness is less than

100 *nm*. Typical electrodes with 1 mm thickness and 1 cm^2 area have very small electrical resistances on the order of $10^{-7}\Omega$. Therefore, the interfacial electrical resistance plays the most important role among the three components of *R*. To minimize the internal resistance, the work function of the barrier and the cathode should be aligned to prevent the formation of a Schottky barrier and to form Ohmic contacts with low interfacial resistance. [42]

Small thickness is inherently useful for maintaining low electrical resistances but is also the cause of a decrease in the thermal resistance which increases the heat leak of SSTICs. The low thermal resistance prevents a large temperature difference between the electrodes to develop and sustain. While there are no optimum thermal resistance values, it is desirable to have thermal resistance, R_t , larger than $(e/k_B J)$. This criterion essentially reduces the conduction loss to a minimum value that arises due to the use of a solid barrier. If R_t is much larger than $(e/k_B J)$, then the thermal leak is negligible. If it is only larger, the thermal leak is not negligible but low and the device can still work with high efficiency. To be highly efficient, an SSTIC operating with the same parameter as described above would need $R_t > 9 \times 10^{-6} m^2 K W^{-1}$ or $G_t < 0.1 M W m^{-2} K^{-1}$, which is a very small number to attain practically considering the size of the device. R_t represents the total thermal resistance contribution from the semiconductor layer and the semiconductor-electrode interface. In the diffusive limit, a way of increasing R_t is by increasing the thickness of the barrier. But thermionic devices are working in the ballistic limit where resistance is independent of length. Therefore, a good design should address the issue of making the semiconductor-electrode interfacial thermal resistance to be as large as possible and find a suitable semiconductor layer that will have very high thermal resistance within a thickness less than the electron mean free path. An SSTIC with all the optimization discussed above is estimated to achieve efficiency higher than that of the state-of-the-art thermoelectric modules. [42]

1.4.2 Single vs. Multi-barrier SSTI Structures

So far, both single-layer and multilayer SSTICs have been investigated. In 1997, it was predicted that an optimized single-layer SSTIC, operating in refrigeration mode, will result in 20-30 °K of cooling with cooling power density exceeding kW/cm². [19] High barrier height at the anode side was suggested as a means to reduce the backflow of the reverse current in this configuration [19]. Shakouri *et al* introduced the idea of using high barriers in superlattices and theoretically demonstrated an order of magnitude improvement in efficiency with respect to the bulk materials. [46] Increased Seebeck coefficient and reduced thermal conductivity in the superlattice compared to the bulk were cited as the main reason behind this improvement. Though ballistic transport was not taken into account during the calculation, it was suggested that the addition of this transport will improve the efficiency further. Later on, it was found that non-ideal effects like contact resistance, the finite thermal resistance of the substrate, and the heat sink limit the actual cooling to 1 to 4 degrees experimentally. [47] Monte Carlo simulation of a single-barrier InGaAs/GaAs/InGaAs thermionic cooler indicated that most of the heating and cooling happens at the contact region. [48] At low temperatures and low carrier concentrations, the linear Peltier coefficient reduces remarkably but the non-linear part of the Peltier coefficient (that is nonlinear with respect to current) survives and dominates the transport. This dominant behavior can be achieved at a current in the order

of 10⁵Acm⁻². A single barrier device operated in this condition could achieve a sevenorder increase in maximum cooling efficiency. [49]

Mahan and Woods, in 1998, argued that the optimum temperature drop which gives the maximum efficiency for an SSTIC is only about 20°K. To obtain larger temperature differences they proposed the multilayer structure. [21] The idea is to maintain a small temperature difference in each layer, the sum of which results in a large temperature difference and high efficiency. This device was estimated to have a performance twice that of conventional thermoelectric devices. A suitable superlattice that facilitates the flow of hot electrons but blocks that of the cold electron was used for this purpose. Later on, the reduction in thermal conductivity was identified as the only benefit of using a multilayer geometry. [50,51] Superlattices, including metallic ones, with very low thermal conductivity, were studied extensively. Regular metals have a low Seebeck coefficient because of the symmetric distribution of conduction electrons around the Fermi energy. The symmetry can break when tall energy barriers are inserted, filtering only high-energy electrons (electrons with energies above the Fermi energy) to enhance the Seebeck coefficient. [52] HfN/ScN and ZrN/ScN metal/semiconductor superlattice were studied theoretically and found to exhibit low thermal conductivity in cross-plane directions. [22,23]. Thermoelectric properties of mercury cadmium telluride (HgCdTe) based superlattices have also been studied which is the primary material for highperformance infrared imaging systems. Bulk HgCdTe has a low Seebeck coefficient because of its low effective mass and non-degenerate single conduction band. Tall barriers were found to create asymmetric differential conductivity near the Fermi energy and increase the Seebeck coefficient. Hg_{1-x}Cd_xTe at different compositions has also been studied for thermoelectric application.²¹ An increase in the Seebeck coefficient was predicted to be observed by increasing the carrier concentration. But, doping HgCdTe superlattices to as high as 10¹⁹ cm⁻³ has proven to be a difficult challenge to overcome. [53] Vining and Mahan did a comparative study between a thermoelectric and an SSTIC module using linearized Richardson's equation and showed that the efficiency of the thermoelectric module is always dominant if they both have similar parameters. [51] Their analysis is valid and reliable when transport is linear and most importantly when thermal interfacial resistances are small compared to the thermal conductance of the semiconducting layer. The latter can easily break into nanoscale devices. Later on, in a detailed study of SSTICs operating in a non-linear regime, it was found that thermionic power generators can achieve efficiencies higher than those of the state-of-the-art thermoelectric modules. [54]

1.4.3 2D Van-der-Waals Heterostructures based SSTIC

2D materials and in particular, the stack of 2D materials, are the latest class of lowdimensional materials studied for SSTI converters. We refer to such stacks as 2D van der Waals heterostructures (2DvdWH). In these structures, the in-plane atoms are covalently bonded to each other while the cross-plane atoms are weakly bonded by van-der Waals force. Due to weak interlayer bonding, it is possible to stack different 2D materials on top of each other without any strain that would otherwise develop because of lattice mismatch in presence of strong bonding. [55] The bandgap of 2D materials can be tuned by applying strain, electric field, and also by changing the number of stacked layers. For example, silicene and germanene are semimetals, but their bandgap opens up when a vertical field is applied and the gap size increases linearly with the electric field. [56] TiSe₂ gap opens up under the biaxial strain. [57]

Another important property of 2D van der Waals heterostructures is their low value of thermal conductance in the cross-plane direction developed due to the presence of the weak van der Waals bonding between each layer. Earlier it was discussed that the thermal conductance should be as small as possible and extremely small values of $0.1 MWm^{-2}K^{-1}$ are desirable for achieving high efficiency in SSTIC [42]. The super-low thermal conductance together with the other beneficial properties of the 2D van der Waals heterostructure mentioned above thus has grabbed the attention of researchers in this field. Several theoretical studies of SSTICs based on this structure have been reported to predict high ZT. [38,39,58] Chen et al experimentally measured a very low thermal conductance of 4.25×10^{-7} W/K for graphene/h-BN/graphene heterostructure. [37] Though this structure exhibited superior thermal properties suitable for thermionic devices, its electronic properties were poor. Insulating nature of hBN means too large of a barrier for the electrons to overcome and consequently they found a very small ZT of 1.05×10^{-6} . By using seven layers of MoS₂, Yuan *et al* experimentally obtained thermal conductance smaller than $1 MWm^{-2}K^{-1}$. [59] Afterwards, a cross-plane ZT of 2.8 has been calculated theoretically for a graphene/MoS₂/graphene heterostructure. [60] Massicotte et al experimentally reported a cross-plane thermal conductance of $0.5 MWm^{-2}K^{-1}$ in graphene/WSe₂/graphene heterostructure that was tested for photothermionic emission [61]. The cross-plane phonon thermal conductance of the Au/G/P/G/Au heterostructure was found to be as small as 4.1 MW m⁻² K⁻¹ from first-
principle calculation and an equivalent ZT of 0.13 was predicted for a thermionic device based on this structure. [38] Recently, a ZT of 1.2 at room temperature and 3 at 600K has been calculated theoretically using first principles calculations and Green's function formalism for a Sc/WSe₂/MoSe₂/WSe₂/Sc van der Waals heterostructure. [39] In 2DvdWH structures, it is crucial to have enough layers to block the tunneling current. Transmission function in Au/G/P/G/Au heterostructure with varying number of phosphorene layers is shown in *Figure 1.3*. [38] The averaged electron transmission of 2P and 5P structures was



Figure 1.3 (a) The averaged electron transmission of the heterostructures. 1P, 2P and 5P are short for the heterostructures with monolayer, bilayer and quintuple layer phosphorene, respectively. Inset shows the zoom-in of the 1P transmission around the Fermi level. (b) The band-resolved trans- mission of 1P by HSE. The black and magenta curves are the local band structures of phosphorene and graphene, respectively. The 1D q-resolved transmission of (c) 1P, (d) 2P and (e) 5P. The data of 2P and 5P are calculated by PBE.

theoretically studied by Wang *et al* and is shown in *Figure 1.3(a)*. In the case of 1P and 2P, phosphorene layers are still not thick enough to eliminate the quantum tunneling effect, which results in non-zero transmission within the band gap, as seen in *Figure 1.3(d)*. They observed no quantum tunneling for 5P, as indicated by the zero transmission right above the Fermi level shown in *Figure 1.3(a)* and the white region in *Figure 1.3(e)*. [38]

Achieving a good degree of chemical and thermal stability in 2D materials is very difficult. [62,63] Stacking them is the next challenging task. The interfaces between the layers need to be clean to obtain large electrical conductance. An ohmic contact is required between the metallic contact and the 2DvdWHs. At the same time, the thermal conductance needs to be extremely small. For these reasons, there has not been any experimental demonstration of SSTICs with a large equivalent figure of merit based on 2DvdWHs thus far.

1.5 Dissertation Organization

The main objective of this dissertation is to theoretically design highly efficient SSTI devices based on 2D vdW heterostructures. This work also theoretically investigates the effect of asymmetry of the electrode, electron-phonon interaction, and defects on the SSTI device performance. Knowing the mean-free path of electrons in bulk form of the 2D semiconducting channel, the size effect and the importance of electron-phonon interaction in nanoscale thermionic devices are evaluated. In doing so, the highly accurate electron-phonon scattering rates of the bulk form of the 2D channel are calculated from the first-principles. The computed electron-phonon scattering rates are then used to

investigate the effect of electron-phonon interaction on electron transport of the bulk form semiconductor material from full first-principles. In addition, the first SSTI device based on 2D vdW heterostructures is fabricated and characterized in collaboration with experimental groups. Finally, this study analyzes theoretically and experimentally how polymorphism in Bi2Se3 allows it to be tuned for unique thermoelectric properties.

The dissertation contains six main chapters. The history of thermionic converters is discussed in the first chapter, as was already presented, and is then followed by the theory of thermionic converters, which outlines the fundamental operating concept and provides the mathematical equations for the ideal output current, voltage, power, and efficiency of thermionic converters. The chapter then discusses the drawbacks of VSTICs and the need to develop SSTICs, a solid-state alternative. In addition, the design considerations of SSTI devices are discussed in this chapter. The next section of the chapter explains why 2D vdW materials are the best option for creating SSTICs that are highly efficient. The second chapter presents the study of the transport properties of MoSe₂-based SSTI devices. First, a systematic study of the contact between the MoSe₂ and various metals is conducted and the metal that forms the Ohmic contact is identified. Then the thickness-dependent thermionic performance of the MoSe₂-based SSTI devices is studied. Finally, the effect of asymmetric metallic contact, electron-phonon interaction, and defects is investigated theoretically. To investigate the effect of electron-phonon interaction on the performance of MoSe₂-based SSTI devices, highly accurate electronphonon scattering rates of bulk MoSe₂ are calculated from the full first principle. The third chapter uses the calculated electron-phonon scattering rates of bulk MoSe₂ to investigate their effect on electronic and thermoelectric transport properties. In this work, the effect

of electron-phonon scattering along with ionized impurity scattering on the electronic and thermoelectric properties of bulk MoSe₂ in the in-plane and cross-plane direction at room temperature without and with including the effect of vdW interaction is investigated theoretically. The calculated in-plane mobility and electrical conductivity are compared with experimentally obtained values. Finally, the developed method was used to optimize the in-plane power factor times temperature (PFT) of MoSe₂ with respect to carrier concentration and temperature. In the fourth chapter, thermionic transport across a gold-graphene-3 layer of WSe₂-graphene-gold (Au-Gr-3WSe₂-Gr-Au) structure is studied computationally and experimentally. In this work, the first 2D vdW-based SSTI device is fabricated and characterized. A new experimental technique that combines the thermoreflectance and cooling curve measurements are used to extract the equivalent figure merit of the SSTI converter. Finally, the theoretically obtained figure of merit is compared with the experimentally obtained value. As a separate route, the fifth chapter investigates how polymorphism in Bi₂Se₃ allows it to be tuned for unique thermoelectric properties. The commonly reported rhombohedral structure is a topological insulator, a narrow gap semiconductor with a bandgap of 0.2–0.3 eV, and has been widely studied for thermoelectric applications. The alternative orthorhombic structure is a semiconductor with a larger bandgap of 0.9–1.2 eV. The opportunity to fabricate a mixture of these orthorhombic and rhombohedral structures provides a chance for materials engineering to optimize its electrical and thermal properties. In this work, mixed-phase, Se-rich, n-type Bi₂Se₃ films are prepared by electrodeposition using an acidic bath and the Seebeck coefficient of the films is measured experimentally. Firstprinciples calculations are used to determine the Seebeck coefficient of the orthorhombic

and rhombohedral phases. Finally, the experimentally measured Seebeck coefficients are compared with the theoretically calculated ones. The sixth chapter summarizes the key outcomes of the research work.

Chapter 2: Low-resistance contact in MoSe2-based SSTICs: effect of asymmetry, electron-phonon interaction, and defects on the device performance

The advent of low-power portable and wearable electronics signifies the need for mesoscale power generators and coolers [19,20,64–66]. Mechanical generators cannot be miniaturized to such scales and hence currently we rely on batteries to power portable electronics. Thermionic power generators and coolers can be built with nanoscale thickness and provide a solid-state solution for energy scavenging and integrated cooling.

A thermionic converter essentially is a heat engine that converts thermal energy directly to electricity using electrons as the working fluid. Similar to most other heat engines, thermionic devices can operate either as power generators or coolers. There are two main types of thermionic converters: vacuum state thermionic (VSTI) converters and solid-state thermionic (SSTI) converters [19–21,42,67]. In the power generation mode, heat is used to increase the energy of electrons in the cathode. The hot electrons with energies higher than the energy barrier can pass above the barrier with a Richardson flux. These electrons are then collected by a colder anode. A part of the thermal energy is thus converted directly to electricity and the rest is rejected as heat to the cold side. The energy barrier in the case of VSTI is the cathode work function, which is on the order of a few electron volts in typical metals. Therefore, vacuum thermionic power generators can only

operate at very high temperatures. Also, the need for a vacuum in a VSTI restricts direct access to the electrodes. To overcome these difficulties, Shakouri and Bowers [19] proposed a single-layer solid-state thermionic in 1997 diodes in which the vacuum is replaced by a semiconducting material. In this structure, the semiconductor layer is the energy barrier that an electron experiences. In the following year, Mahan proposed the idea of using multi-layer barriers in which each layer maintains a small temperature difference [20,21]. Electrons in a solid-state thermionic device can face an effective energy barrier height on the order of meV as the energy barrier is the difference between the electron affinity of the semiconductor and the work function of the metal. This is compared to a few eVs barrier heights in a vacuum thermionic device. Hence, SSTICs can operate at much lower temperatures compared to VSTICs. Our previous theoretical work focusing on the mathematical optimization of solid-state thermionic devices concluded that for optimum performance the optimum barrier height should be on the order of a few K_BT [54].

The transport inside the semiconducting layer of an SSTIC has to be ballistic to avoid electron-phonon thermalization. To maintain ballistic transport in a solid-state thermionic device, the semiconducting layer thickness should be lower than the electron mean free path. At the same time, a minimum barrier thickness is needed to suppress the tunneling of electrons in the device. If electrons of energy lower than the semiconductor barrier height tunnel through, they carry less energy if their energy is above the Fermi level, and will carry negative heat (a rare event) if their energy is below the Fermi level. This leads to a lower Seebeck as our previous and present studies have shown. Hence, SSTICs are considered nanoscale devices appropriate for integrated circuits [67-69]. At such small scales, the main challenge of SSTICs, is their thermal leakage [44]. To maintain a noticeable temperature difference at such a small length scale, the thermal conductance of an SSTIC needs to be very small. Our recent work has shown that the thermal conductance of a solid-state thermionic device should be smaller than 0.1 MWm⁻²K⁻¹ to obtain reasonable efficiencies [54]. To our best knowledge, within ordered and nonporous systems, this very small thermal conductance is only possible in the van der Waals heterostructures [70,71] due to their weak van der Waals interactions compared to covalent bonding [72]. In one work, our group showed that five layers of black phosphorene sandwiched between gold and graphene have a thermal conductance value of 4-6 MWm⁻²K⁻¹ [73]. In another work, our group theoretically calculated a thermal conductance value of 16 MWm-2K-1 for the Sc-WSe2-MoSe2-WSe2-Sc structure [74]. Other weakly bonded structures also demonstrated extremely low thermal conductance values. It was shown that interfacial thermal conductance between seven layers of MoS₂ and crystalline silicon (c-Si) is smaller than 1MWm⁻²K⁻¹. [59] In another work, it was experimentally shown that 5-10 MWm⁻²K⁻¹ thermal conductance can be obtained in the van der Waals structure [75]. A theoretical work based on molecular dynamic simulation obtained a slightly higher thermal conductance value of 17 MWm-²K⁻¹ for both graphene-WSe₂-graphene and graphene-MoSe₂-graphene structures. In another experimental work, a very low thermal conductance value of 0.5 MWm⁻²K⁻¹ was estimated for a graphene-WSe₂-graphene structure [61]. In addition, in a van der Waals heterostructure, the barrier height, which plays a significant role in improving the device performance can be tuned by changing the number of layers in the heterostructure from 0 in the tunneling regime (one layer) to the bulk bandgap value for a large enough number of



Figure 2.1. Ball stick model of a metal-MoSe₂-metal device configuration.

layers (typically 10 layers) [73]. In recent years, these two important features of van der Waals heterostructure have renewed interest in solid-state thermionic devices [37,39,66,73,76,77].

In this chapter, we represent the study of thermionic transport properties of metal-MoSe₂metal structure as shown in *Figure 2.1* by using density functional theory (DFT)-based first-principles calculations combined with real-space Green's function (GF) transport formalism. MoSe₂, a layered two-dimensional (2D) transition metal dichalcogenides (TMDs) used as the semiconducting material in these calculations. An advantage of layered TMD materials such as MoSe₂ is that the saturated covalent bonds within one layer and noncovalent binding between the layers allow for atomically sharp and stressfree interfaces between similar or dissimilar materials [78]. Another important feature of MoSe₂ is that the electronic properties depend on the number of layers. For example, bulk MoSe₂ has an indirect bandgap of 0.85 eV while monolayer MoSe₂ has a direct bandgap of 1.55 eV [79,80]. Moreover, the thermal transport in MoSe₂ in the cross-plane direction is greatly reduced due to the lack of covalent bonding between layers. These electrical and thermal properties make MoSe₂ a suitable material for designing efficient solid-state thermionic devices. In nanoscale electronics contacts often play a more important role than the semiconducting material itself [81,82]. While contact in Si-based devices is no longer challenging after many years of engineering optimization, contact with nanoscale electronic devices based on 2D TMD materials has become a major challenge [83–86]. A strong interface bonding creating interface states that pin the Fermi level [87] or a weak bonding creating a potential step due to Pauli repulsion [88,89] at the interface can cause a high barrier height between the metal contact and the 2D TMDs. Therefore, for the applicability of novel 2D TMDs such as MoSe₂ as nanoscale devices, a comprehensive study of metal contacts to the 2D TMDs is very important. There are several ways to extract the metal-2D TMD barrier height [90]. In this work, we extract the barrier height between MoSe₂ and various metals (Au, Pt, Ni, Cu). We then study the thickness dependence of the contact and identify Ohmic contacts. We also study the thermionic performance of these structures.

Next, we investigate the effect of asymmetric metallic contact on the performance of SSTI devices. In a VSTI device, the output power is proportional to the work function difference between the cathode and the anode. Hence, it is desired to have asymmetric electrodes wherein the cathode has a larger work function compared to the anode [9,11,13]. The solid-state thermionic devices designed so far have similar metallic contact as cathode and anode [39,66,73]. Therefore, the effect of asymmetric metallic contact with different work functions on the device performance is unknown. In our work, we evaluate the performance of two sets of asymmetric structures (Au-MoSe₂-Pt and Cu-MoSe₂-Au) and compare their performance with their symmetric counterparts

(Au-MoSe₂-Au, Pt-MoSe₂-Pt, and Cu-MoSe₂-Cu). Finally, we investigate the effect of point defects, namely substitutional and vacancy defects, on the performance of the Au-3L MoSe₂-Au SSTI device.

2.1 Computational Method

2.1.1 DFT calculation details

To model the proposed device, we use open boundary conditions along the z-axis, while periodicity is imposed in the xy plane. To study the structural and electronic properties of the metal₁-MoSe₂-metal₂ van der Waals heterostructure, we used the state-of-the-art density functional theory (DFT) based first-principles calculations combined with real-space Green's function (GF) transport formalism, as implemented in the SIESTA package [91]. We used the exchange-correlation functional of Perdew-Burke-Ernzerhof [92] revised for solids [93] and standard basis set, namely, double zeta plus polarization (DZP). Real-space mesh cutoff energy was set to 300 Ry. A single k point in the cross-plane direction whereas a 5×5 k mesh in the basal plane was used for the Brillouin zone sampling.

2.1.2 Making and optimization of the SSTI structures

We first optimized the lattice parameters of Au, Pt, Cu, Ni, and MoSe₂ separately for the purpose of obtaining the optimized in-plane lattice parameters of the structures. The optimized in-plane lattice constants are 4.08 Å, 3.93 Å, 3.61 Å, 3.52 Å, and 3.31 Å respectively. Our calculated in-plane lattice parameter of MoSe₂ matches the reported

value in the literature [39,94–96]. Therefore, the in-plane lattice parameters of the relaxed <111> plane of the metallic contacts (Au, Pt, Cu, Ni) are 2.885 Å, 2.779 Å, 2.553 Å, and 2.489 Å respectively. In the structures, 3-6 layers of MoSe₂ are sandwiched between 6 layers of <111> plane of the metallic contacts. In the DFT-GF method, the electrodes are assumed to be semi-infinite and using 6 layers we achieved convergence in the results. The transport properties will not change when the number of layers of the metallic contact increased beyond 6. The in-plane lattice parameters of the structures are fixed to the optimized metal <111> plane for the symmetric structures while the average of relaxed metal₁ <111> plane and relaxed metal₂ <111> plane for asymmetric structures and in-plane MoSe₂ lattice parameters were adapted accordingly $(2\sqrt{3}a_{Au/Pt<111>}) =$ $4a_{Cu/Ni < 111>} = 3a_{MoSe_2}$, a is the lattice constant) to minimize the strain. Thus, the MoSe₂ in the Au-MoSe2-Au, Pt-MoSe2-Pt, Cu-MoSe2-Cu, Ni-MoSe2-Ni, Au-MoSe2-Pt, and Au-MoSe₂-Cu structures experience 0.65% tensile, 3% compressive, 2.8% tensile, 0.26% tensile, 1.24% compressive and 1.73% tensile strain respectively. It is known that the tensile strain increases the bandgap while the compressive strain decreases the bandgap [97,98]. After forming the devices, all the structures are optimized again. In the optimization process, the atomic positions of two inner layers of metal from each side along with all the MoSe₂ layers, called the channel region, are allowed to relax without any constraints along the cross-plane direction until the forces on all atoms are less than 0.01 eV/Å while the atomic positions of the outer four metallic layers from each side, considered as left and right contacts, are kept fixed. We use the non-local van der Waals DFT functional (vdW-DF-optb86) [99,100] to correctly take the van der Waals interaction into account during the structure optimization.

2.1.3 Electron transport calculations

The electronic transport properties of the SSTI devices are studied by using density functional theory (DFT)-based first-principles calculations combined with real-space Green's function (GF) transport formalism. The transport properties calculations of the optimized structures are performed using PBE functionals. Although the GGA functional such as PBE used in this work underestimate the bandgaps, due to the presence of two metallic electrodes which strongly screen the Coulomb interaction, the bandgap becomes small so that we have a cancellation of this underestimation error. This was confirmed in our previous work by comparing with the GW calculations on the same structure [39]. The electron transmission functions are calculated using real-space Green's function method as in the TranSIESTA implementation [101]. TranSIESTA deals fully with the atomistic structure of the whole system, treating both the contact and the electrodes on the same footing. After calculating the electron transmission function using TranSIESTA, the transport coefficients are obtained using the linear response approximation [102]:

Conductance, $G = q^2 L_0$

Seebeck coefficient, $S = L_1/qTL_0$

Electronic thermal conductance, $\kappa_{el} = (L_2 - L_1^2/L_0)/T$

where,
$$L_n = 2/h \int dET(E)(E - \mu)^n (-\frac{\delta f}{\delta E})$$

where q is the electron charge, and f is the Fermi-Dirac distribution function.

2.1.4 Electron-phonon scattering rate and mean free path (MFP)

calculation

We compute the electron-phonon scattering rate and the MFPs in bulk MoSe₂ using the first principles. The equilibrium properties of electrons and phonons are calculated using the density functional theory (DFT) and density functional perturbation theory (DFPT) as implemented in the QUANTUM ESPRESSO package [103]. The norm-conserving pseudopotentials [104] with the Perdew-Burke-Ernzerhof (PBE) [105] functional for the exchange-correlation are used. A 6×6×2 and a 12×12×4 Monkhorst-Pack k-point mesh are used for the self-consistent and non-self-consistent field calculations, respectively and the cutoff energy of the plane wave is chosen as 60 Ry. The convergence threshold of energy is set to be 10⁻¹² Ry. Lattice was relaxed with the force convergence threshold of 10⁻⁴ Ry/Bohr. The obtained relaxed lattice constant of bulk MoSe₂ in the hexagonal structure are a=b=3.31 Å and c=12.89 Å. The dynamical matrices and phonon perturbations are computed on a 6×6×2 q point mesh in the phonon calculations. To obtain the electronphonon scattering rates, the EPW package [106] is employed to interpolate the electronphonon coupling matrices as well as electron and phonon eigenvalues obtained by DFT and DFPT calculations from coarse to fine k and q point meshes (30×30×30) using the Wannier interpolation scheme [107]. Further details of the electron-phonon scattering rate calculations can be found in the method section of chapter 3. The electron group velocities are obtained from the BoltzTrap package [108]. Finally, the MFP is obtained by multiplying the electron-phonon scattering rates with the group velocities.

2.2 Results and Discussion

2.2.1 Metallic contact for MoSe₂ based electronics

Today, a large number of 2D layered materials are identified. Monolayers can be peeled off and stacked on top of each other to form a variety of desired thermal, optical, and electronic properties, opening the possibility of nanoscale electronic devices for a variety of medical, environmental, security, and sensing applications. A challenge to making the desired planar electronics out of these lego-type stacked layers is the formation of lowresistance metallic contacts. The contact resistance and in particular the potential barrier height are important parameters for thermionic transport as well as making metallic contact in a 2D planar device consisting of TMD materials. To form low-resistance contact between the metal and the 2D TMD materials, the potential barrier height needs to be very low (on the order of k_BT). We calculate the potential barrier height of metal-MoSe₂metal SSTI structure consisting of 5 layers of MoSe₂ for different metals (Au, Pt, Cu, Ni) as well as Au-MoSe₂-Au structure for 3-6 layers of MoSe₂. A simple way to estimate the potential barrier height is the Schottky-Mott (SM) rule, $E_b = I-W$ (for holes) or $E_b = W-\chi$ (for electrons), where E_b is the potential barrier height, W is the metal's work function, I is the ionization potential of the semiconductor, and χ is the electron affinity of the semiconductor. However, this simple and approximate method does not always predict the correct potential barrier height [73] and certainly does not work well for our studied structures. Here, we use a more accurate first-principles-based method to extract the potential barrier height. First, we use first-principles calculations to relax the metal-MoSe₂-metal structures. Next, we calculate the transmission functions of the structures using Green's function method shown in *Figure* 2.2. We then calculate the E_b for electrons

by measuring the $E_c - E_F$ for electrons and $E_F - E_V$ for holes from the transmission function, where E_F is the Fermi energy, $E_c(E_V)$ refers to the corresponding energy levels at the start of non-zero transmission above (below) the Fermi level. As an example, the work function of gold (111) is 5.1 eV and the ionization potential of a single layer of MoSe₂ is 5.22 eV [109]. Therefore, the SM rule predicts a barrier height of 0.12 eV and a p-type transport, whereas our first-principles calculation indicates a barrier height of 0.26 eV and an n-type transport. Similarly, the calculated barrier height is n-type for Cu, while the SM rule predicts p-type barrier height. *Table 2.1* summarizes the calculated potential barrier height of metal-5 MoSe₂-metal structure, and a range of barrier height predicted by the SM rule for Au, Pt, Cu, and Ni. The table also shows the transmission gap E_g for MoSe₂ in each structure, where $E_g = E_c - E_V$. We note that it is more difficult to extract this information from the local density of states as the screening effect of the metal on its adjacent layer results in a tail in the density of states, hence we define the transmission



Figure 2.2 Transmission function of metal₁-5 MoSe₂-metal₂ SSTI structure. (b) Transmission function T(E) and thermal transmission window $T(E) * \left(-\frac{df(E)}{dE}\right)$ at 300K and 1000K of Cu-5 MoSe₂-Cu structure.

Metal contact	Au	Pt	Cu	Ni
5L MoSe2	0.89	0.89	0.87	0.80
Transmission gap (eV)				
Barrier Height (eV)	0.26	0.42	0.10	0.30
(Calculated)	(n type)	(p type)	(n type)	(n type)
Barrier Height (eV)	0-0.14	0-0.12	0.62 (n-type)	0-0.20
(SM rule)	(p-type)	(p-type)	0.14(p-type)	(p-type)

Table 2.1 Calculated bandgap & barrier height of metal-5 MoSe₂-metal SSTI structure

gap instead of bandgap. From the calculated potential barrier heights listed in the table, we see that Cu makes low energy contact for MoSe₂, which becomes n-type, with a barrier height of 0.10 eV. Therefore, it is expected that the Cu-MoSe₂-based SSTI device to have the highest electrical conductance among the studied metals.

Next, we study the effect of the number of MoSe₂ layers on metal-MoSe₂ contact resistance. The energy states of the metal significantly affect the energy states of the adjacent layers. This screening effect damps with distance and hence it is expected that the barrier height to be dependent on the number of layers. Here, we calculate the potential barrier height for Au-MoSe₂-Au SSTI structure where the number of layers of Table 2.2 Variation of barrier height with the numbers of MoSe₂ layers

Number of layers	3 layers	4 layers	5 layers	6 layers
Barrier Height (eV)	0.20	0.23	0.26	0.32

MoSe₂ varied from 3 to 6 layers in the heterostructure. *Table 2.2* shows the potential barrier height for the Au-3-6 MoSe₂-Au SSTI structure. We see that the SSTI structure with 3 layers of MoSe₂ shows the lowest barrier height of 0.2 eV, therefore, expected to show the highest electrical conductance as more electrons will overcome the energy barrier. We note that the transmission gap closes for 1 and 2 layers and transport is dominantly through tunneling.

Next, we evaluate the performance of the Au-3-6 MoSe₂-Au SSTI structure. *Figure 2.3(a)* shows the transmission function of the structure containing 3-6 layers of MoSe₂. *Figure*



Figure 2.3. (a) Transmission function (b) electrical conductance (c) Seebeck coefficient and (d) power factor times temperature of heterostructure containing 3-6 layers of MoSe₂. The inset of figure (a) shows a close-up of the transmission functions.

2.3(*b*) and *Figure* 2.3(*c*) show the electrical conductance (σ) and Seebeck coefficient (S) of all the structures. The electrical conductance of the structure with 3 layers of MoSe₂ is maximum and electrical conductance decreases as the number of MoSe₂ layers in the structure increases. This is consistent with the barrier height of the structures as shown in *Table* 2.2. Also due to the increase in the number of thermally excited electrons, the electrical conductance increases as the temperature increases as shown in *Figure* 2.3(*b*). The Seebeck coefficient increases with the number of MoSe₂ layers in the heterostructure because the transmission gap increases with the number of layers. The power factor times temperature (PFT= σS^2T) is a parameter that is used to characterize the power generated



Figure 2.4 Power factor time temperature (PFT) of 3-6 layers of MoSe2 for (a) 200-500 K (b) 500-750K (c) 750-970K (d) 970-1200K.

by the SSTI device is shown in *Figure 2.3(d)* for all the structures. The PFT is optimum for the structure with 3 layers of MoSe₂ at the temperature range of 200-500K and 970-1200K while structures with 4 and 5 layers of MoSe₂ show optimum PFT at the temperature range of 500-750K and 750-970K respectively. A breakdown of the PFT for each of these temperature ranges is shown in *Figure 2.4*. The maximum power factor for the structure with 3 layers of MoSe₂ is 327 MWm⁻²K⁻¹ at 1200K. For comparison, our previously calculated structure Au-Gr-3 WSe₂-Gr-Au, Pt-Gr-3 WSe₂-Gr-Pt showed a PFT of 0.83 MWm⁻²K⁻¹ and 60 MWm⁻²K⁻¹ respectively at 800K [66] and Sc-WSe₂-3 MoSe₂-WSe₂-Sc showed a PFT of 427 MWm⁻²K⁻¹ at 1200K [39]. Note that the unit used here is for 2D structures and is different from those used for bulk thermoelectric power factors.

2.2.2 Asymmetric MoSe₂-based SSTI

In VSTI, two dissimilar metals with work function differences larger than 1 eV are used as cathode and anode and the output power is proportional to the work function difference between the metals. The solid-state thermionic devices designed so far have similar metallic contact as cathode and anode [39,66,73]. Therefore, the effect of asymmetric metallic contact with different work functions on the device performance is not understood. In this section, we evaluate and compare the performance of two sets of symmetric and asymmetric SSTI devices. In the first set of calculations, we evaluate the performance of symmetric Au-5 MoSe₂-Au, symmetric Pt-5 MoSe₂-Pt, and asymmetric Au-5 MoSe₂-Pt structures and in the second set of calculations, we evaluate the performance of symmetric Au-3 MoSe₂-Au, symmetric Cu-3 MoSe₂-Cu, and asymmetric Au-3 MoSe₂-Cu structures. Since in the previous part we identified 3-5 layers as



Figure 2.5. Local density of states of (a) Au-5 MoSe₂-Au (b) Pt-5 MoSe₂-Pt (c) Au-5 MoSe₂-Pt and their corresponding transmission functions.

optimally performed devices, for all calculations in this section, 3 or 5 layers of MoSe₂ are used.

Figure 2.5 shows the local density of states (LDOS) of symmetric gold, symmetric platinum, and the asymmetric structure with one side gold and another side platinum and their corresponding transmission functions. Gold and platinum are chosen since they have similar work functions. From the LDOS we see that the Fermi level E_F is located near the conduction band of the gold and gold-platinum asymmetric structure which means these structures are n-type while the Fermi level of the platinum structure is located near the valence band making it p-type. The transmission function, Seebeck coefficient, electrical conductance, and the power factor times temperature for all three structures are shown in *Figure 2.6*. As can be seen from the LDOS and the transmission function, the

gold structure has a lower barrier height compared to the other two structures. Therefore, the gold structure shows higher electrical conductance values as shown in *Figure 2.6(b)*. The platinum structure shows a positive Seebeck coefficient while the gold and the gold-



Figure 2.6. Transmission function (b) Seebeck coefficient (c) electrical conductance and (d) power factor times temperature of the gold, platinum, and gold-platinum asymmetric structure containing 5 layers of MoSe₂. The black line represents the gold structure, the blue line represents the platinum structure, and the red line represents the gold-platinum asymmetric structure. The inset of figure (a) shows a close-up of the transmission functions.

platinum asymmetric structure show a negative Seebeck coefficient, as shown in *Figure* 2.6(c), which is consistent with the p-type and n-type barrier height of the respective structures. The platinum structure shows a maximum Seebeck coefficient of 620 μ V/K at

620K while the maximum Seebeck coefficient of the gold and gold-platinum asymmetric structure is -792 μ V/K and -795 μ V/K at 572K and 740K respectively. The presence of the bandgap in these structures contributes to the large Seebeck coefficients. The PFT of all three structures is shown in *Figure 2.6(d)*. The high electrical conductance due to low barrier height and the high Seebeck coefficient of the gold structure results in the highest PFT at high temperatures. The low electrical conductance combined with the low Seebeck coefficient makes the platinum structure the worst performing among the three structures while the PFT of the platinum-gold asymmetric structure is in between the PFT of the gold and platinum structure.

In the previous set of calculations, we see that while the gold and gold-platinum asymmetric structure is n-type, the platinum structure is p-type. For the next set of



Figure 2.7. Local density of states of (a) Au-3 MoSe₂-Au (b) Cu-3 MoSe₂-Cu (c) Au-3 MoSe₂-Cu and their corresponding transmission functions.

calculations, we find another metal contact that has a very close work function to gold and creates a structure that is n-type doped. We choose copper for this calculation which has a work function value of 4.53-5.10 eV. Therefore, Au-3 MoSe₂-Au, Cu-3 MoSe₂-Cu are the symmetric structures and Au-3 MoSe₂-Cu is the asymmetric structure for these calculations. The local density of states and the corresponding transmission function of



Figure 2.8. (a) Transmission function (b) electrical conductance (c) Seebeck coefficient and (d) power factor times temperature of the gold, copper, and gold-copper asymmetric structure containing 3 layers of MoSe₂. The blue line represents the gold structure, the red line represents the copper structure, and the black line represents the gold-copper asymmetric structures. The inset of figure (a) shows a close-up of the transmission functions.

symmetric gold, symmetric copper, and a gold-copper asymmetric structure are shown in *Figure 2.7*. The Fermi level E_F for all these structures is close to the conduction band which means all the structures are n-type doped. The energy barrier height of the copper structure is significantly lower than the other two structures. The electrical conductance of all the structures is shown in *Figure 2.8(b)*. The electrical conductance of the copper structure is very high compared to the other two structures due to the significantly lower barrier height. The n-type doping of all the structures can be further verified by the negative Seebeck coefficient as shown in *Figure 2.8(c)*. The maximum Seebeck coefficient of the gold, copper, and gold-copper asymmetric structures are -451 μ V/K, -321 μ V/K, and -373 μ V/K respectively at 1200 K. The PFT of the gold, copper, and gold-copper asymmetric structures are 327 MWm⁻²K⁻¹, 917 MWm⁻²K⁻¹, and 373 MWm⁻²K⁻¹ respectively at 1200 K (*Figure 2.8(d)*). The PFT of the copper structure is the highest among all the SSTI structures that have been calculated so far [39,66,110].

We note that the transport properties of the asymmetric structure are always in between the two symmetric ones. The only exception is the Seebeck coefficient in the range of 600K to about 1000K wherein the asymmetric structure shows a Seebeck coefficient smaller than both symmetric counterparts.

From these two sets of calculations, we see that the PFT of the asymmetric structure is in between the PFT of its symmetric counterpart. Although the asymmetry of the metallic contact improves the performance of VSTI devices, the asymmetry of metallic contact does not affect the performance of SSTI devices. This is possibly due to the difference in the operating temperature and barrier height between the two types. One has to keep in mind that given the nanoscale thickness of these devices only a very small temperature difference can be maintained between the electrodes. Since the optimal operating temperatures of symmetric structures are very different, the performance of the asymmetric structure can never be superior to the symmetric ones unless their barrier height is the same. Whereas the VSTI barrier height is a few eVs, the ideal barrier height of SSTIs is only on the order of meV. Given the small temperature difference which can be maintained in these structures, we can linearize the theory of thermionic transport, and define equivalent Seebeck coefficient and power factor. Upon doing so, the asymmetric structure shows average properties, in between the two symmetric counterparts similar to how averaging is done in thermoelectric structures. The most important parameter in these structures seems to be the barrier height itself. The lower the barrier height, the higher the power factor. We know the optimum barrier height is about 2K_bT which corresponds to 50 meV at room temperature and 100 meV at 600K. The latter is close to the barrier height of the Cu structure.

2.3 Effect of Electron-Phonon Scattering

Finally, since we are describing electron transport using a coherent formalism and have neglected inelastic scatterings, our results are only approximate at very high temperatures where the electron mean free path can become shorter than the barrier thickness. In practice, the electrical conductance and power factor should start decreasing with T at high enough temperatures. We calculated the mean free path (MFP) of bulk MoSe₂ along the z-axis at different temperatures from first-principles to estimate the effect of inelastic electron-phonon scattering on the transport properties. The energy-dependent electron-phonon scattering rates and MFP is shown in *Figure 2.9*. The electron mean free path at the bottom of the conduction band at 300K is 200Å and at 1000K is 35Å. The length of the 3 layers and 5 layers of MoSe₂ devices are 19.35Å and 32.25Å



Figure 2.9. (a) Electron-phonon scattering rate for bulk MoSe2. (b) Electron mean free path calculated along the z-axis.

respectively. Therefore, up to 1000K, the inelastic electron-phonon scattering should not affect the performance of the 3 layers and 5 layers of MoSe₂-based SSTI devices. We would



Figure 2.10 Band structure of (a) bulk (b) single layer (c) 2 layers (d) 3 layers (e) 4 layers (f) 5 layers of MoSe₂. The bulk band structure (in brown) is superimposed on the band structures of 1-5 layers (in blue) of MoSe₂.

like to point out that the mean free path of bulk MoSe₂ was merely performed as a guideline. We simply compared the bulk mean free path with the length of the device and claimed since the bulk mean free path is larger than the size of the device, therefore, our coherent transport calculation is justifiable. The band structure of the 3-5 layers of MoSe₂ is similar to that of the bulk MoSe₂ as shown in *Figure 2.10*. The significant difference in band structure is only true for monolayer and bilayer MoSe₂ which we have avoided in this work.

2.4 Effect of Defects

We have developed the tools and methodology to compute the thermionic transport properties of SSTI devices based on 2D vdW heterostructures from the first principles. The remaining task is to include the effect of imperfections in the calculation. The most important effects are lattice mismatch and impurities such as vacancies and foreign atoms or molecules or eventual oxide layers that can exist at interfaces. In this work, we investigate the effect of point defects such as vacancies and substitutional defects on the performance of the MoSe₂-based SSTI device performance. The point defects that are considered in this work are the substitution of a Mo atom by a W atom, the substitution of a Se atom by an S atom, Se vacancy, and Mo vacancy.

2.4.1 Mo and Se Substitution

First, we investigated the effect of the substitutional defect on the performance of the Au-MoSe₂-Au structure containing 3 layers of MoSe₂. We substituted a Mo atom with a W



Figure 2.11 (a) Transmission function (b) electrical conductance (c) Seebeck coefficient and (d) power factor times temperature of the Au-MoSe₂-Au structure containing 3 layers of MoSe₂. The black line represents the SSTI structure with no point defect, the red line represents the structure where a Mo atom is substituted by a W atom, and the blue line represents the structure where a Se atom is substituted by a S atom.

atom and a Se atom with an S atom. The transmission function, Seebeck coefficient, electrical conductance, and the power factor times temperature of the non-defective and defective structures are shown in Figure 2.11. We can see that the electrical conductivity and Seebeck coefficient is not significantly affected by the substitutional point defect. Consequently, the PFTs of these three structures are very similar.



Figure 2.12 (a) Transmission function (b) electrical conductance (c) Seebeck coefficient and (d) power factor times temperature of the Au-MoSe₂-Au structure containing 3 layers of MoSe₂. The black line represents the SSTI structure with no point defect, the red line represents the structure with a Se vacancy in the first layer, and the blue line represents the structure with a Se vacancy in the second layer.

2.4.2 Mo and Se Vacancy

Next, we investigate the effect of vacancy defects on thermionic transport. We created Se vacancy and Mo vacancy by removing one Se atom and one Mo atom respectively from the structures. The transmission function, Seebeck coefficient, electrical conductance, and the power factor times temperature for the Se vacancy are shown in *Figure 2.12* and for Mo vacancy in shown in *Figure 2.13*. From *Figure 2.12(a)* and *Figure 2.13(a)*, we can see that the transmission gap increases due to both Se vacancy and Mo vacancy. However,

the increase in the transmission gap due to Mo vacancy is higher than the Se vacancy. Consequently, the electrical conductivity significantly decreases in both types of defective structures as can be seen in Figure 2.12(*b*) and Figure 2.13(*b*). While at high temperature the electrical conductivity in Se vacant structures decreases by approximately three times, and the electrical conductivity in Mo vacant structure decreases by approximately five times. The Seebeck coefficient also decreases in both types of defective structures. As a result, while both the PFT of the Se vacant structure and the PFT of the Mo vacant structure fall considerably, the decrease in the Mo vacant



Figure 2.13 (a) Transmission function (b) electrical conductance (c) Seebeck coefficient and (d) power factor times temperature of the Au-MoSe₂-Au structure containing 3 layers of MoSe₂. The black line represents the SSTI structure with no point defect, the red line represents the structure with a Mo vacancy.

structure is far higher. The reduction of PFT is mainly contributed by the significant decrease in the electrical conductivity in both types of defective structures.

We calculated the partial density of states of bulk MoSe₂ as shown in Figure 2.14 in order to explain why the effect of Mo vacancy is significantly greater than the Se vacancy. The Au-MoSe₂-Au SSTI structure with 3 layers of MoSe₂ is an n-type structure. The transmission function above the Fermi level will thus be most impacted by the vacancy of the atoms that contribute the most to the density of states above that level. The majority of the contribution of the density of states of MoSe₂ above the Fermi level comes from the



Figure 2.14 Partial density of states of bulk MoSe2. The d orbital of Mo contributes the most to the density of states, followed by the p orbital of Se.

d orbital of Mo, followed by the p orbital of Se as shown by the red and blue lines in *Figure 2.14* respectively.

2.5 Summary

We used first-principle density functional theory (DFT) combined with real-space Green's functions formalism to evaluate the performance of SSTI devices with a varying number of MoSe₂ layers and with a variety of metallic electrodes. Among the studied metals, copper makes the lowest energy contact for electron transport while platinum makes low energy contact for hole transport with MoSe2. The Cu-3 MoSe2-Cu structure shows an extremely large PFT of 917 MWm⁻²K⁻¹ at 1200K which is the largest power factor calculated for thermionic structure based on TMDs. Since the barrier height can be tuned with the number of layers, we investigated the contact barrier dependence on the number of layers by studying the contact between gold and 3 to 6 layers of MoSe₂. We found that Au with 3 layers of MoSe₂ shows the lowest barrier height, hence, making better ohmic contact. Furthermore, we evaluated the performance of solid-state thermionic devices with 3-6 layers of MoSe₂ sandwiched between two gold contacts and evaluated how their performance changes with the number of layers. Structures with 1 & 2 layers of MoSe₂ are not included as the transport in these structures is dominated by tunneling of carriers which is not desirable for SSTI devices. We find that SSTI devices with 3 layers of MoSe₂ show optimum performance at the temperature range of 200-500K and 970-1200K while devices with 4 and 5 layers of MoSe₂ show optimum performance at the temperature range of 500-750K and 750K-970K respectively. Therefore, the number of layers can be optimized for a given target operating temperature. Next, we studied the performance of

two sets of asymmetric SSTI. Although an asymmetric metallic electrode enhances the efficiency of a VSTI device, we find that asymmetry of the electrode does not play any role in improving the performance of SSTI devices because the temperature difference across the device is very small, and one is in the linear regime. The most important parameter seems to be the energy barrier height and the structure with the lowest barrier height (0.10 eV) shows the highest performance. We also estimated the electron mean free path at the Fermi level and across the MoSe₂ planes to be 200 Å, and 35Å at 300K and 1000K respectively which is larger than the thickness of the structures considered here. Finally, we investigated the impact of point defects, namely substitutional and vacancy defects, on the performance of MoSe₂-based SSTI devices. We find that, whereas both Mo vacancy and Se vacancy have a significant impact on device performance, the effect of Mo vacancy is considerably greater. The substitutional defect, on the other hand, has a minor impact on device performance.

Chapter 3: Thermoelectric properties of bulk MoSe2: effect of vdW interaction, electron-phonon interaction, and ionized impurity scattering

Thermoelectric materials can convert heat energy directly to electricity and vice versa. Thermoelectric materials are considered to have great potential for power generation, energy-saving, and heat management [111–116]. Devices made of thermoelectric materials are extremely simple, have no moving parts, use no greenhouse gases, have a quiet operation, are environmentally friendly, and are highly reliable [117,118]. Because of these excellent features, thermoelectric devices have attracted extensive interest for nearly two centuries. Solid-state thermoelectric devices are generally based on heavily doped semiconductors such chalcogenides [119,120], zintl phases [121], as clathrates [122], complex oxides [123], and skutterudites [124,125], and can be used for cooling applications or electricity generation directly from a heat source. The efficiency of these devices is determined by a dimensionless figure-of-merit $ZT = (S^2\sigma/k)T$ where Z is the figure-of-merit, *T* is the absolute temperature, *S* is the Seebeck coefficient, σ is the electrical conductivity, and k is the total thermal conductivity with contributions from the lattice (k_L) and the electrons (k_e) [126]. Besides the traditional power generator and cooling applications, thermoelectric materials can also be applied to active cooling [3,127], where large thermal conductivity and power factor are both desired to transfer heat from hightemperature heat sources to low-temperature heat sinks, and in thermal switches where heat flux is required to adjust based on ambient conditions [128].

Two-dimensional (2D) layered materials such as transition metal dichalcogenides (TMDCs) are good candidates for thermoelectric [64,129–135] as well as thermionic [66,67,74,136] energy conversion applications because of their large Seebeck coefficients and low thermal conductivities. Due to weak van der Waals interactions, the thermal conductivity in the cross-plane direction is small making them ideal candidates for nanoscale cooling [68,69,137] and power generation. Another important feature of 2D materials is that the thermoelectric properties such as electrical conductivity and Seebeck coefficient depend on the number of layers as the band structure and the bandgap change with it. In the case of MoSe₂ its bulk has an indirect bandgap of 0.80 eV while monolayer MoSe₂ has a direct bandgap of 1.55 eV [79,80,138].

MoSe₂, a TMDC material, consists of a transition metal Mo, sandwiched between two chalcogen layers of Se in which Mo's and Se's are covalently bonded within the plane. However, the Se layer constructs weak van der Waals (vdW) interaction with the next Se layer perpendicular to the plane to construct bulk MoSe₂. Therefore, it is important to include the van der Waals interaction in the theoretical calculation to correctly obtain the thermoelectric transport properties of MoSe₂. It is expected that the inclusion of vdW interaction in the theoretical calculation affects the cross-plane transport properties significantly.

Thermoelectricity in semiconductors is the response of electron and phonon currents to temperature gradients. The interaction between the electrons and phonons plays a crucial role in this response. To maximize the thermoelectric response, one needs to selectively heat electrons and minimize the electron-phonon interaction to avoid heat leakage to the lattice. Only the energy delivered by the electrons is the conversion of heat to electrical
energy, the part delivered by phonons is wasted. In practice, phonons always exist at finite temperatures and take some of the input heat directly from the source and some through electron-phonon energy exchange. Both, lower the performance and serve as heat leaks. Electron-phonon interaction is an important phenomenon in condensed matter physics beyond thermoelectricity. Many experimental observations such as temperature-dependent band structures, zero-point renormalization of the bandgap in semiconductors, conventional phonon-mediated superconductivity, phonon-assisted light absorption, Peierls instability [139], the Kohn effect [140], temperature-dependent electrical resistivity as well as traditional superconductivity [141] are caused by the electron-phonon interaction. The role of electron-phonon interactions in the transport properties of systems with strong electron-phonon correlations is one of the central issues in the theory of strongly correlated systems.

Electron-phonon scattering plays a central role in electron transport in relatively pure materials [142]. While the impurity and defects lower the electron mobility, their values are not intrinsic and depend on the quality of the material growth and the number of impurity and defect centers. In contrast, electron-phonon interaction is an intrinsic property of a given semiconductor and hence the first step in evaluating the potential of a semiconductor for thermoelectric applications is to evaluate the electron-phonon interaction. Over the years, several different open-source codes have been developed to compute the electron-phonon scattering rate from first-principles calculations [106,143–146]. These fully first-principles approaches to calculating the electron-phonon interaction employing density functional perturbation theory (DFPT) combined with Wannier interpolation [147] can now produce highly accurate electron lifetimes and have

shown close agreement with experimental measurements of electron mobility and conductivity of intrinsic samples [106,145].

In the case of doped semiconductors, it is important to include ionized impurity scattering in addition to electron-phonon interactions. The carrier density in a doped semiconductor is determined by the relative position of the impurity states to the band edges (the binding energy) and the temperature. When ionized, the charged impurity centers scatter the free carriers via Coulomb interactions, affecting their lifetimes. At low temperatures, when phonon effects are minimal, carrier scattering by ionized impurities is the dominant scattering determining the carrier mobility. In heavily doped semiconductors, this regime might be extended to room temperatures. Therefore, it is important to incorporate ionized impurity scattering along with electron-phonon scattering in the theoretical transport calculation to accurately predict experimental results.

In this work, we theoretically evaluate the effect of electron-phonon scattering (EPS) and ionized impurity scattering (IIS) on the electronic and thermoelectric properties of bulk MoSe₂ in the in-plane and cross-plane direction at room temperature without and with including the effect of vdW interaction. We obtain the EPS rates from the first-principle calculations and the IIS rates using Brooks-Herring [148] approach. The electronic and thermoelectric transport properties such as mobility (μ), electrical conductivity (σ), and Seebeck coefficient (*S*) of bulk MoSe₂ at room temperature in the in-plane and cross-plane direction are calculated by solving the linearized electron Boltzmann transport equation (BTE) under the relaxation time approximation (RTA) with the aid of the EPS rates and IIS rates evaluated at different Fermi Level positions. We compare the calculated in-plane mobility and electrical conductivity with experimentally obtained values. Finally, we use our developed method to optimize the in-plane power factor times temperature (PFT) of MoSe₂ with respect to carrier concentration and temperature.

3.1 Computational Details

We compute the EPS rates in bulk MoSe₂ using first-principles calculations. The EPS rates are calculated using the PERTURBO package [145]. In the preparation stage, five calculations are performed before calculating the electron-phonon scattering rates using PERTURBO. (i) A self-consistent (scf) DFT calculation, (ii) a phonon calculation using DFPT (iii) a non-self-consistent (nscf) DFT calculation (iv) obtain the Wannier functions (v) compute the e-ph matrix elements at the coarse k and q points (determined by the nscf step and the phonon step respectively) grids of Brillouin zones. The DFT and DFPT calculations are performed using the QUANTUM ESPRESSO package [103]. The Wannier functions are obtained using the Wannier90 package [99].

For the scf and nscf calculations, the norm-conserving pseudopotentials [104] with the Perdew-Burke-Ernzerhof (PBE) [92] functional for the exchange-correlation are used. We used the non-local van der Waals DFT functional (vdW-DF-optb86) [99,100] to correctly take the vdW interaction into account. A 12×12×4 mesh and an 18×18×6 Monkhorst-Pack k-point mesh are used for the self-consistent and non-self-consistent field calculations, respectively and the cutoff energy of the plane wave is chosen as 60 Ry. The convergence threshold of energy is set to be 10⁻¹² Ry. Lattice was relaxed with the force convergence threshold of 1.0e⁴ Ry/Bohr. The obtained relaxed lattice constants of bulk MoSe₂ in the

hexagonal structure are a=b=3.31 Å and c=12.89 Å. Our calculated lattice constants match the experimentally reported value in the literature [96]. The dynamical matrices and phonon perturbations are computed on a 6×6×2 q-point mesh in the phonon calculations using DFPT. The Wannier90 package [99] is employed to obtain the Wannier functions. For MoSe₂ the Wannier function consists of d_{xy}, d_{xz}, d_{yz}, d_{z2}, d_{x2-y2} orbitals on each Mo atom and p_x, p_y, p_z orbitals on each Se atom, leading to the wannierization of a total of 22 bands. Then the e-ph matrix elements on the coarse k-point and q-point Brillouin zone grid is obtained by the PERTUBO package.

Finally, to obtain the EPS rates (τ_{e-ph}), the PERTURBO package [145] is employed to interpolate the electron-phonon coupling matrices as well as electron and phonon eigenvalues obtained by DFT and DFPT calculations from coarse to fine k and q point meshes (40×40×40) using the Wannier interpolation scheme [107]. In addition, and for comparison and validation, the EPS rates are also computed using the electron-phonon Wannier (EPW) [106] package based on maximally localized Wannier functions [107,149], which allows accurate interpolation of electron-phonon couplings from coarse grids to arbitrarily dense grids. The EPS rates calculated using these two packages show similar values.

We calculated the IIS rates (τ_{imp}) using the Brooks-Herring approach for different doping concentrations [148]. The IIS rate is given by,

$$\tau_{imp}(E) = \frac{8\pi^3 \hbar^3 \varepsilon_r^2 \varepsilon_0^2}{N_I q^4} \left[\ln(1+Y^2) - \frac{Y^2}{1+Y^2} \right]^{-1} DOS(E) v^2(E)$$

where $\Upsilon^2 = 4\pi^2 L_D^2 \hbar DOS(E) v(E)$, \hbar is the reduced Plank constant, ε_r is the relative permittivity, ε_0 is the permittivity of free space, N_I is the impurity concentration, q is the

electronic charge, L_D is the Debye length, DOS(E) is the density of states, and v(E) is the group velocity. To obtain the effect of both EPS and IIS scattering both are combined using Matthiessen's rule ($\tau^{-1} = \tau_{e-ph}^{-1} + \tau_{imp}^{-1}$). The electron mobilities, electrical conductivities, and the Seebeck coefficients are calculated using the PERTURBO [145] code based on the BTE under the RTA.

3.2 Result and Discussion

3.2.1 Band structure and Phonon Dispersion

The electronic band structures of bulk MoSe₂ with and without the inclusion of vdW interaction are shown in *Figure 3.1(a)*. The band structure calculated in this work is in agreement with the previous calculation [150]. The bulk MoSe₂ shows an indirect bandgap of 0.80 eV. This is in agreement with the previously reported theoretical value [80,138]. The calculated phonon dispersions using DFPT with and without the



Figure 3.1. (a) Electronic band structure and (b) phonon dispersion of bulk MoSe2 without (red) and with (blue) the inclusion of vdW interaction.



Figure 3.2 The band structure of MoSe2. Results from DFT calculations (blue solid lines) and Wannier interpolation (red solid lines) are overlaid.

inclusion of vdW interaction are shown in *Figure 3.1(b)*. The DFT band structure was then interpolated using the maximally localized Wannier function. The DFT calculated band structures and the band structure obtained from Wannier interpolation show very good agreement as shown in *Figure 3.2*. We observe that the effect of vdW interactions is minimal on the band structure and the phonon dispersions.

3.2.2 Mobility and Electrical Conductivity

We focus on the n-type samples and study the electron-phonon interaction within the conduction band. *Figure 3.3(a)* shows the calculated EPS rates obtained from the EPW and PERTURBO codes together with the electronic density of states (DOS) with respect to the



Figure 3.3 (a) Electron-phonon scattering rates in MoSe₂ calculated using EPW and PERTURBO code together with the electronic density of states. (b) Electron-phonon scattering rates and ionized-impurity scattering rates with carrier concentration between 10¹⁶ and 10¹⁸ cm⁻³ at 300 K.

conduction band minimum (CBM). The EPS rates obtained from these two codes show close agreement. The scattering rates versus electron energy show a similar trend to that of the electronic DOS, consistent with the fact that the DOS regulates the phase space for electron-phonon scattering [151]. The IIS rates for the carrier concentration of 10¹⁶, 10¹⁷, and 10¹⁸ cm⁻³ at 300K along with the EPS rates are shown in *Figure 3.3(b)*.

Using our calculated scattering rates, the room-temperature electron mobilities and electrical conductivities are calculated using the BTE under the RTA. In this work, we mainly focus on electron transport in the in-plane and cross-plane directions at room temperature. The electron transport properties namely the mobility and conductivity are calculated for four combinations as shown in *Figure 3.4* and *Figure 3.5*: (i) without vdW interaction and inclusion of only EPS rates (red curves), (ii) with vdW interaction and inclusion of the combination of EPS and IIS rates (green curves), and (iv) with vdW interaction and



Figure 3.4 The (a) in-plane and (b) cross-plane mobility vs carrier concentration are calculated using the Boltzmann transport equation under the constant relaxation time approximation. The in-plane electrical mobilities are compared with the in-plane experimental Hall mobilities from literature.

inclusion of the combination of EPS and IIS rates (black curves). *Figure 3.4* shows the room temperature electron mobility in the in-plane and cross-plane direction for the carrier concentration range of 10¹⁶ to 10¹⁸ cm⁻³. Our calculated in-plane electron mobility at room temperature with the inclusion of only EPS rates and without vdW interaction is 192 cm²/Vs while including the vdW interaction is 200 cm²/Vs. These values are independent of the carrier concentration. The obtained cross-plane mobility with the inclusion of only EPS rates and without including the vdW interaction is 2.47 cm²/Vs while with including the vdW interaction is 2.47 cm²/Vs while with including the vdW interaction is 1.46 cm²/Vs. We can see that the effect of vdW interaction on the in-plane mobility is small while the cross-plane mobility decreased by a factor of 1.7. This is expected as Mo's and Se's are covalently bonded within the plane while the Se layer constructs weak vdW interaction with the next Se layer in the cross-plane direction in the MoSe² structure and to accurately predict the electronic transport in the cross-plane direction this vdW interaction needs to be accounted for in the calculations.

The theoretical mobility with the inclusion of only EPS rate is relatively insensitive to carrier concentration within the carrier concentration range of 10¹⁶ to 10¹⁸ cm⁻³. The experimentally measured in-plane room temperature Hall mobilities of single-crystal MoSe₂ are extracted from literature for different carrier concentrations. Within the range of carrier concentration from 3x10¹⁶ to 1.4x10¹⁷ cm⁻³, the Hall mobility varies from ~55 to ~175 cm²/Vs as shown in *Figure 3.4(a)*. The calculated in-plane mobility is overestimated compared to all the experimentally measured values. This is because we only included the EPS rates in the transport calculation which is the dominant scattering mechanism at low carrier concentration. However, as the carrier concentration increases, the contribution of the IIS rates in the transport properties is no longer negligible. Therefore, we need to include both the EPS rates and IIS rates in the transport calculation to correctly predict the experimental results. We can see from *Figure 3.4(a)* that with the inclusion of both EPS rates and IIS rates in the transport calculation, mobility gradually decreases as the carrier concentration increases in the in-plane and cross-plane directions. Furthermore, we can see from *Figure 3.4(a)* that the in-plane theoretical mobility closely matches the experimental mobility with the inclusion of both EPS rates and IIS rates thus confirming that the IIS rates need to be accounted for in the transport calculation to accurately predict electronic transport properties.

Next, we calculate the in-plane and cross-plane electrical conductivities at room temperature for the same four combinations. The calculated in-plane and cross-plane room temperature electrical conductivity for carrier concentrations from 10¹⁶ to 10¹⁸ cm⁻³ are shown in *Figure 3.5*. First, we calculate the in-plane and cross-plane electrical conductivities with the inclusion of only EPS rates. The in-plane and cross-plane electrical



Figure 3.5 The (a) in-plane and (b) cross-plane electrical conductivity vs carrier concentration are calculated using the Boltzmann transport equation under the constant relaxation time approximation. The in-plane electrical conductivity is compared with the electrical conductivity of single crystal MoSe₂ from the literature.

conductivities increase as the carrier concentrations increase, which is consistent with the behavior of semiconductor materials. The inclusion of vdW interaction does not affect the in-plane electrical conductivity as shown by the overlap of red and blue lines in *Figure* 3.5(a). However, the vdW interaction reduces the cross-plane electrical conductivity as shown in *Figure* 3.5(b). We compare our calculated in-plane electrical conductivity with the experimentally measured in-plane electrical conductivity of single crystal $MoSe_2$ [152–155]. Our calculated in-plane values are larger than the experimental values as shown in *Figure* 3.5(a). This is consistent with the fact that other scattering mechanisms are present in real materials along with EPS whereas we only included the EPS rates in the transport calculation. Therefore, we included the combination of both EPS rate and IIS rate in the transport calculation. We can see from *Figure* 3.5 that the inclusion of IIS rates along with EPS rates has a small effect on the electrical conductivity at low carrier concentration but significantly modifies it as the carrier concentration becomes large. Now, our calculated in-plane electrical conductivity values closely match the

experimental values as shown in *Figure 3.5(a)* implying that the inclusion of both the EPS rate and IIS rate is important in the transport calculation of bulk MoSe₂ at room temperature.

3.2.3 Seebeck Coefficient

The in-plane and cross-plane Seebeck coefficients are calculated using the BTE under the RTA. In this case, only the theoretically calculated EPS rates from the first principles are used to estimate the relaxation time. To carry out the quantitative comparison, we calculate the Seebeck coefficient using the constant relaxation time approximation (CRTA) employing the BoltzTrap code [108]. *Figure 3.6*(a) and *Figure 3.6* show the room temperature in-plane and cross-plane Seebeck coefficient vs chemical potential with respect to the conduction band minimum (CBM) calculated using RTA and CRTA. The



Figure 3.6 Room temperature Seebeck coefficient vs chemical potential in the (a) in-plane and (b) cross-plane direction. The conduction band minima calculated from Boltztrap and Perturbo code are taken as the reference point, zero. The red star represents the experimentally measured Seebeck coefficient.

Seebeck coefficient from RTA and CRTA show very good agreement confirming that the Seebeck coefficient is not sensitive to the details of relaxation times. The calculated Seebeck coefficients with and without including the vdW interaction are also shown in Figure 3.6. The Seebeck coefficient value decreases as the chemical potential increases, which is consistent with the fact that higher chemical potential represents higher carrier concentration which contributes to the reduction of the Seebeck coefficient. The crossplane Seebeck coefficient is larger than the in-plane Seebeck coefficient for the same chemical potential. In the case of the Seebeck coefficient, there is no effect of vdW interaction in the in-plane direction while there is a small but insignificant effect in the cross-plane direction. Agarwal et al. reported experimentally measured room temperature Seebeck coefficient of -960 μ V/K at a carrier concentration of 1.78x10¹⁶ cm⁻ 3 [156]. The chemical potential that corresponds to this carrier concentration is 0.21 eV below the CBM. In *Figure 3.6(a)*, the experimental Seebeck coefficient is shown as a red star. The calculated Seebeck coefficient of -1035 µV/K at room temperature at the chemical potential of 0.21 eV below the CBM is a reasonable estimate of the experimentally measured value. The inclusion of the combination of both the EPS rates and IIS rates in the Seebeck calculation does not have any effect on the Seebeck coefficients further confirming the insensitiveness of the Seebeck coefficient on the details of relaxation times.

3.2.4 Power Factor Optimization

After reproducing the experimental in-plane transport properties of MoSe₂ with reasonable accuracy, we used our developed method to optimize the PFT with respect to carrier concentration and temperature. *Figure 3.7(a)* shows the optimized in-plane power



Figure 3.7 (a) In-plane power factor times temperature vs carrier concentration of bulk $MoSe_2$ at 300K. (b) In-plane power factor times temperature vs temperature of bulk $MoSe_2$ at a carrier concentration of 1.5×10^{20} cm⁻³.

factor with respect to carrier concentration at 300K. The in-plane PFT reaches a maximum value of 0.6 Wm⁻¹K⁻¹ at a carrier concentration of 1.5×10^{20} cm⁻³ at 300K. Then we fixed the carrier concentration at 1.5×10^{20} cm⁻³ and varied the temperature from 300K to 1200K. *Figure 3.7(b)* shows in-pane PFT vs temperature at a carrier concentration of 1.5×10^{20} cm⁻³. The PFT shows a maximum value of 1.07 Wm⁻¹K⁻¹ at 1000K.

3.3 Summary

In summary, we calculated the electron-phonon scattering rates of bulk MoSe₂ using two full first principle-based codes, PERTURBO and EPW. The ionized impurity scattering rates are calculated using the Brooks-Herring method. The calculated rates are then used to obtain the in-plane and the cross-plane electronic and thermoelectric properties of bulk MoSe₂ at room temperature with and without including the vdW interaction using the BTE under the RTA. The calculated in-plane and cross-plane electron mobility with the inclusion of only electron-phonon scattering rates at room temperature without and with incorporating the vdW interaction is relatively insensitive to carrier concentration for a carrier concentration range of 10¹⁶ to 10¹⁸ cm⁻³. The in-plane mobilities are not affected by the vdW interaction while the cross-plane mobilities are reduced by 1.7 times thus confirming that the inclusion of vdW interaction is important to accurately predict the cross-plane transport properties of MoSe₂. The theoretically calculated in-plane electron mobilities and electrical conductivity values are overestimated compared to the experimental mobilities when electron-phonon scattering rates are only included. At high doping levels, the electron transport is affected by ionized impurity scatterings in addition to the electron-phonon scattering. We were able to reproduce the experimentally measured in-plane electron mobilities and electrical conductivities after the inclusion of both rates and with no fitting parameters. The Seebeck coefficients are calculated by solving the linearized electron BTE under the RTA with the aid of the first-principles electron-phonon scattering rates evaluated at different Fermi Level positions. To compare the calculated Seebeck coefficient under RTA, the Seebeck coefficients are again calculated using BTE under CRTA. The RTA and CRTA Seebeck coefficients show a good agreement indicating that the Seebeck coefficient is not sensitive to the details of the relaxation time. The inclusion of both the electron-phonon scattering rates and the ionized-impurity scattering rates in the Seebeck calculation did not influence the Seebeck coefficients, further proving the insensitivity of the Seebeck coefficient to the specifics of relaxation times. Finally, we used our developed method to optimize the PFT in terms of carrier concentration and temperature. We find that $MoSe_2$ shows a maximum PFT of 1.07 $Wm^{-1}K^{-1}$ at 1000K with a carrier concentration of 1.5×10^{20} cm⁻³.

Chapter 4: Theoretical and experimental thermionic transport across gold-graphene-WSe² van der Waals Heterostructures

Solid-state thermionic (SSTI) power generators can be viewed as intermediate between vacuum-state thermionic converters and thermoelectric power generators. Like many other heat engines, these devices can work either as power generators where they convert input heat to electricity, or coolers where applied electricity is used to pump heat. The SSTI power generators and refrigerators were first proposed by Shakouri [19] and Mahan [21] independently as an alternative to vacuum state thermionic converters. These devices are made by inserting a semiconducting layer between metallic electrodes. The semiconducting layer forms an energy barrier for charge carriers allowing only hot ones to pass [64,157,158]. This current flow is referred to as thermionic current. The SSTI devices are similar to vacuum state thermionic ones wherein the vacuum is replaced by the semiconducting layer. Due to the lower energy barrier, the SSTI devices operate at temperatures much smaller than the vacuum state thermionic devices. The SSTI devices are also very similar to thermoelectric devices. The most important difference is that the thermionic transport in SSTI devices is ballistic, whereas the thermoelectric transport is diffusive. Like thermoelectric devices, it is possible to define an equivalent figure of merit, ZT for SSTI devices. The figure of merit concept is borrowed from the thermoelectric field and is defined as $ZT = \frac{\sigma S^2 T}{\kappa}$, where σ is the electrical conductivity, S is the Seebeck coefficient and κ is the thermal conductivity. We note that the energy conversion

efficiency and the coefficient of performance (COP) equations of SSTI devices are not the same as the ones for thermoelectric devices [20,21]. Only after linearizing the equations (that is under small temperature drops and small voltage drops), an analogy to thermoelectric modules could be drawn. In this analogy, the Seebeck coefficient is the energy barrier height (in units of volt) divided by the temperature plus a constant. It can be shown numerically that thermoelectric equations can reproduce thermionic results accurately, which is a remarkable observation by Mahan [44]. Theoretical investigations had conflicting predictions comparing the efficiency of SSTI converters to those of thermoelectric devices [19–21,51,76]. In SSTI converters, in order to maintain ballistic transport of the hot electrons, the semiconducting layer thickness, L, should be equal to or less than the electron mean free path, λ . On the other hand, a minimum length, L_t , is needed to suppress the tunneling of electrons, which is undesirable since low energy electrons (with energies smaller than the chemical potential, μ) act as holes and lower the efficiency of the electron transmitting device (similar to bipolar effect in the case of thermoelectric transport). Thus, the semiconducting layer thickness should satisfy the condition: $L_t < L < \lambda$.

Recently, highly efficient SSTI converters made out of 2D layered materials were proposed theoretically and computationally [39,73,76]. In these structures, the in-plane atoms are covalently bonded while the layers in the cross-plane direction, are weakly bonded by van der Waals forces. Due to weak interlayer bonding, it is possible to stack different 2D materials on top of each other without any strain that would otherwise develop because of lattice mismatch in the presence of a strong bonding [55]. The bandgap of 2D materials can be tuned by applying strain, electric field, and also by

changing the number of stacked layers. Arsenene, the monolayer of arsenic, for example, has been reported to show a smooth transition from semi-metallic to semiconducting state for a different number of stacked layers [159]. It is also reported that arsenene, an indirect bandgap semiconductor can be converted to a direct bandgap semiconductor by applying compressive and tensile strain along its a-axis [159]. Another important property of 2D layered heterostructures is their low value of thermal conductance in the cross-plane direction which is the result of the weak van der Waals interlayer bonding. In solid-state thermionic devices, the thermal conductance should be minimized, and extremely small values of 0.1 $MWm^{-2}K^{-1}$ are desirable for achieving high efficiency [42]. The main challenge is to achieve these small conductance values at small length scales to preserve the ballistic nature of thermionic transport. Extremely small conductance values have already been demonstrated in several 2D layered structures and at nanometer length scales. For example, Yuan *et al.* reported thermal conductance values smaller than $1 MWm^{-2}K^{-1}$ across seven layers of MoS₂ [59]. Zhang *et al.* estimated the interfacial thermal conductance across monolayer and bilayer MoSe₂ to be of the order 0.1-1 $MWm^{-2}K^{-1}$ [160]. Massicotte *et al.* reported a cross-plane thermal conductance of $0.5 MWm^{-2}K^{-1}$ across graphene-WSe₂-graphene heterostructure that were tested for photo-thermionic emission [61]. Chen et al. reported a low thermal conductance of 2.36 $MWm^{-2}K^{-1}$ for Graphene-h-BN-graphene heterostructure [37]. In this structure, h-BN forms too high of an energy barrier for electrons and results in poor electronic properties. Therefore, the structure's figure of merit at room temperature is only on the order of 10⁻ ⁶. To our knowledge, this is the only experimentally measured ZT for layered structures across a few nanometers.

Due to the lack of well-established measurement methods [77,161], currently, there are very few experimental studies focused on the efficiency of the solid-state thermionic converters made out of 2D van der Waals heterostructures. In this work, we study thermionic transport across a gold-graphene-3 layer of WSe₂-graphene-gold (Au-Gr- $3WSe_2$ -Gr-Au) structure computationally and experimentally. We report a new experimental technique that combines the thermoreflectance and cooling curve measurements to extract the equivalent figure merit of the SSTI converter. Although our measured room temperature figure of merit is small (ZT = 1.5×10^{-3}), this value is three orders of magnitude higher than the previously reported value for similar types of 2D heterostructures [37]. The experimental values are in close agreement with the theoretical values calculated for this structure.

4.1 Materials and Methods

4.1.1 Device Fabrication

A bottom graphene layer, 3 layers of WSe₂, and a top graphene layer were mechanically exfoliated and transferred on the substrate in sequence using a polydimethylsiloxane (PDMS)-assisted transfer method. The thickness of WSe₂ was identified by using optical contrasts on an optical microscope image of the WSe₂ on the PDMS where thicknesses of reference samples (from 1 to 5 layers) were measured by atomic force microscopy (AFM) and their optical contrasts in the green channel of a charge-coupled device camera were served as reference values. Metal electrodes (Ti/Au-3nm/100nm) were deposited by using a general photolithography process and electron-beam evaporation. The fabricated

device was annealed at 200°C in a vacuum chamber overnight to achieve the Ohmic contact between metal and graphene.

4.1.2 Transport Characterization

The I-V curve of the device is measured using the two probe method. The thermoreflectance measurement is based on the relative change in the reflectivity (due to change of refractive index) of a device surface as a function of change in temperature, which can be represented by the following first-order relationship [162]:

$$\frac{\Delta R}{R_o} = \left(\frac{1}{R_o} \frac{\delta R}{\delta T}\right) \Delta T = C_{\rm th} \Delta T$$

where ΔR is the change in reflectivity, **R** is the reflected light, **C**_{th} is the thermoreflectance calibration coefficient and ΔT is the change in temperature. The calibration coefficient is typical of the order of 10⁻² to 10⁻⁵ and dependent on the sample material, the wavelength of the illuminating light, the angle of incidence (and thus, by extension, the surface roughness), and the composition of the sample in the case of multi-layer structures. Therefore, calibration for each material is required to determine the exact value of the calibration coefficient. The calibration method consists of heating the sample using an external thermoelectric (TE) heating stage and a micro-thermocouple to record the induced temperature change. The sample is heated at two distinct temperatures where the reflectance distribution of the surface is measured. By measuring the change in reflectance, the thermoreflectance coefficient can be calculated at each location across the sample surface. The measured calibration coefficient using 530nm LED on the overlap region of our sample is $2.0 (\pm 0.3) \times 10^{-4}$.

Thermoreflectance measurement is carried out on the sample using the Microsanj NT220B system. The thermoreflectance measurement system consists of a pulse generator, a signal generator, and a control unit. A 530nm green LED was used as an illuminator and was focused onto the sample's top surface through a beam splitter and a high magnification objective. The reflected light that contained the information on the sample's surface temperature change was collected by a charge-coupled device (CCD) detector. A 100µs voltage pulse was applied to the metallic contacts and the temperature response of the sample was measured at 90µs. Steady-state conditions were achieved after 50 to 70µs.

We use time-domain thermoreflectance (TDTR) to characterize the conductance of the Gr-3WSe₂-Gr structure. Our two-tint implementation of the technique is discussed elsewhere in the literature [163], along with the associated analysis of the technique [164–166]. We first coat a nominal 80 nm Al transducer onto our Gr-3WSe₂-Gr structure, which has been mechanically exfoliated previously onto silicon with a thermal oxide of 300 nm. The thickness of the Al was confirmed via picosecond acoustics [167,168], while its thermal conductivity was determined from reference specimens placed near the Gr-3WSe₂-Gr sample during deposition. The effective $1/e^2$ pump/probe radii are ~1.5µm. The measured conductance at the Al-Gr-SiO₂ interface is found to be 20 MW m⁻²K⁻¹, while that of the Al-Gr-3WSe₂-Gr-SiO₂ interface is 9 MWm⁻²K⁻¹. Because these two measurements reflect the series resistances of the structures, we can

use these values to determine the thermal conductance of the Gr-3WSe₂-Gr structure alone. Doing so allows us to extract a conductance of 17 MW m⁻²K⁻¹ for the structure.

4.1.3 Computational Methods

To study the structural and electronic properties of the Au-Gr-WSe₂-Gr-Au van der Waals heterostructure, we used the state-of-the-art density functional theory-based first-principles calculations, as implemented in the Siesta package [91]. We used the exchange-correlation functional of Perdew-Burke-Ernzerhof [92] revised for solids [93] and standard basis set, namely, double zeta plus polarization (DZP). Real space mesh cutoff energy was set to 300 Ry. A single k point in the cross-plane direction whereas a $5 \times 5 \times 1$ k mesh in the basal plane was used for the Brillouin zone sampling. The in-plane lattice constants were fixed to the relaxed gold <111> plane while the graphene and WSe₂ lattices were adapted accordingly ($2\sqrt{3}a_{Au<111>} = 4a_{Gr} = \sqrt{7}a_{WSe_2}$, a is the lattice constant). The cross-plane direction was relaxed without any constraint. The forces of all the atoms were relaxed within 0.01 eV/Å. The ballistic transport properties were calculated using the real space Green's function method as in the TranSiesta implementation [101]. Phonon thermal conductance was calculated using Green's function method simplified for the 1D model [73].

4.2 Results

4.2.1 Electrical Transport

Au-Gr-3WSe₂-Gr-Au device was fabricated on Si/SiO₂ substrate where the device structure is illustrated in *Figure 4.1A*. A bottom graphene layer, a 3-layers WSe₂, and a top graphene layer were mechanically exfoliated and transferred on the substrate in sequence



Figure 4.1 Au-Gr-3WSe₂-Gr-Au device. (A) Illustration of the cross-section of the Au-Gr-3WSe₂-Gr-Au structure. The three layers of WSe₂ flake are sandwiched by the top and bottom graphene layers on a Si/SiO₂ substrate, and contact metals (Ti/Au) are deposited on the top and bottom graphene layers. (B) Optical microscope image of an Au-Gr-3WSe₂-Gr-Au device. The three layers of WSe₂, top graphene, and bottom graphene are highlighted by red, white, and black dashed lines, respectively. Scale bar, 20mm. (C) I-V curve of the fabricated Au-Gr-3WSe₂-Gr-Au device.

using a polydimethylsiloxane (PDMS)-assisted transfer method. The thickness of WSe² was identified by using optical contrasts on an optical microscope image of the WSe² on the PDMS where thicknesses of reference samples (from 1 to 5 layers) were measured by atomic force microscopy (AFM) and their optical contrasts in the green channel of a charge-coupled device camera were served as reference values. Metal electrodes (Ti/Au-3nm/100nm) were deposited by using a general photolithography process and electron-beam evaporation. The fabricated device was annealed at 200°C in a vacuum chamber overnight to achieve the Ohmic contact between metal and graphene. The optical microscope image of the fabricated device is shown in *Figure 4.1B*, and *Figure 4.1C* shows the current-voltage characteristic measured across the top and bottom metal contacts, indicating a near-Ohmic contact. Our further analysis shows that the measured value is dominated by the contact resistance between Au/Ti and graphene (see supplementary materials section).

The room-temperature Seebeck coefficient of this structure is measured by the set-up schematically shown in *Figure 4.2A*. A small external heater was placed close to one of



Figure 4.2 Seebeck measurement. (A) Schematic of the Seebeck measurement setup. (B) Seebeck voltage measured versus applied temperature difference. The measured Seebeck coefficient is $72 \pm 12 \mu V/K$.

the metallic pads to create a local hot spot. We then used two thermocouples and two electrical probes directly connected to the gold pads (contacts) to simultaneously measure the temperature differential and the Seebeck voltage across the Au-Gr-WSe₂-Gr-Au device. The device-level Seebeck coefficient can be estimated by linearly fitting the measured Seebeck voltage (μ V) with respect to the measured temperature differential Δ T (°K) as shown in *Figure 4.2B*. It is noted that the data suffer from a large noise due to the non-uniformity of the induced temperature gradient across the sample. Nevertheless, our obtained experimental Seebeck coefficient ~ 72±12 μ V/K is in good agreement with the theoretically calculated value of 86 μ V/K using first principles and Green's function calculations.

We note that the measured Seebeck coefficient should be interpreted as the device-level Seebeck coefficient and includes contributions from the graphene ribbons as well as the Gr-3WSe₂-Gr overlap region. While it is not possible to separate the contribution of these two regions, we note that the majority of the Seebeck signal is from the overlap region. The thermal resistance of the overlap region is much larger than that of the graphene ribbons, hence the majority of the temperature drop is in the overlap region.

Thermionic transport across Au-Gr-WSe₂-Gr-Au structure with 3-5 layers of WSe₂ is studied computationally using first-principles calculations combined with real-space Green's function formalism. The schematic of the studied structure is shown in *Figure 4.3* and the local density of states of the structure is shown in *Figure 4.3B*. The energy barrier height is about 0.1 eV. It is expected that the optimal barrier height for thermionic application is around $2k_BT$ [20], therefore it is expected that this device works best at temperatures above 600°K. To reduce the energy barrier, one way is to replace gold with another metal with a larger work function. *Figure 4.3C* shows the calculated local density of states for platinum with a larger work function which is a better match to the work function of the current structure and hence has a lower energy barrier. In addition, platinum has a larger density of the states at the Fermi level resulting in higher carrier conductance. The electronic transmission function of both gold and platinum structures is shown in *Figure 4.4A*. Both structures show a clear gap when more than 3 layers of



Figure 4.3 Electronic structure of Au/Pt-Gr-WSe₂-Gr-Au/Pt.(A) Ball-stick model for the configuration of Au/Pt-Gr-WSe₂-Gr-Au/Pt. The yellow, green, gray, and brown balls denote Au/Pt, Se, W, and C atoms, respectively. (B) Contour plot of the LDOS of the Au-Gr-WSe₂-G.

WSe₂ are present indicating that three layers are enough to suppress the tunneling current. Using the density of the state and the transmission function, the electronic transport properties could be calculated using linear response integrals. The results indicate a very small electrical conductance value of 3.5×10^{-5} in units of quantum



Figure 4.4 Transport properties of Au/Pt-Gr-WSe₂-Gr-Au/Pt.(A) Electron transmission function in the cross-plane direction of the gold structure (solid blue line) and the platinum structure (red dotted line). (B) Calculated Seebeck coefficient (S, red line) and electrical conductance (G, blue line) versus temperature of both gold and platinum structure. The red circle is the experimentally measured Seebeck coefficient at room temperature. (C) Phonon transmission function in the cross-plane direction of the gold structure (solid blue line) and the platinum structure (red dotted line). (D) Calculated electronic thermal conductance (Ge, red line) and lattice thermal conductance (Gph, blue line) versus temperature.

conductance for Au-Gr-3WSe₂-Gr-Au structure. This value is equivalent to a resistance times area of $3.7 \times 10^{-10} \Omega m^2$ which is too small for efficient performance. The conductance is greatly enhanced when gold is replaced by platinum as shown in Figure 4.4B due to the lower energy barrier of the platinum structure. The calculated equivalent

Seebeck coefficient of Au-Gr-3WSe₂-Gr-Au structure is 86 μ V/K at room temperatures consistent with our experimentally measured value and increases to 292 μ V/K at high temperatures (T~700°K) as shown in *Figure 4.4B*.

4.2.2 Thermal transport

Due to the large size of the supercell, full first-principles calculations of lattice thermal conductance values are too costly for the current structure. Therefore, we used a simpler 1D model as described in our previous publication [73]. The calculated phonon thermal conductance of Au-Gr-3WSe₂-Gr-Au is about 14 MWm⁻²K⁻¹. Due to the ballistic nature of transport, at temperatures above 200°K, the thermal conductance values do not change significantly as shown in Figure 4.4D. The electronic part of the thermal conductance is an order of magnitude smaller compared to the lattice part at room temperatures but reaches 0.2 MWm⁻²K⁻¹ at 680K. Finally, overall ZT is small. The calculated electronic and phononic transmission functions, the Seebeck coefficient, and the electrical and thermal conductance is the main drawback of the current structure. To demonstrate the importance of metallic contact, we also report theoretical results of replacing gold with platinum. Due to improved conductance values, the platinum structure shows much larger ZT values as shown in the supplementary materials.

To check the validity of the theory, we used time-domain thermoreflectance (TDTR) measurements to experimentally measure the thermal conductance of the fabricated device [163]. We deposit a nominal 80 nm thick aluminum layer via electron-beam

evaporation to serve as a transducer for the Gr-3WSe₂-Gr device. The measured resistance thus encompasses contributions from the Al-Gr interface, the Gr-3WSe₂-Gr structure, and the Gr-SiO₂ interface. The measured conductance accounting for each of these contributions is determined to be $9 \text{ MWm}^{-2}\text{K}^{-1}$. We also measure the conductance of the Al-Gr-SiO₂ interface and determine this to be 20 MW m⁻² K⁻¹.

Using a series resistor model, discussed further in the Supplementary Materials, the thermal conductance of the Gr-WSe₂-Gr layer can be extracted to be 17 $MWm^{-2}K^{-1}$. This is in good agreement with the theoretically calculated value. We note that the Au-Gr contacts are not included in the experiment and if included, they will lower the overall thermal conductance value.

Finally, we evaluate the device-level ZT by directly measuring the cooling curve of the device using a thermoreflectance imaging technique. We borrow the cooling curve concept from the thermoelectric field. This measurement is done routinely for testing the device performance of thermoelectric devices. The principle is as follows: A temperature difference develops as a result of applying an electric current to a Peltier module. This temperature difference is due to the Peltier effect and the Joule heating. The temperature difference is measured at a steady state for a range of applied currents. It is shown that the maximum cooling (ΔT_m) is achieved when the cold side is fully isolated (zero heat flux), the hot side is connected to a heat sink (constant temperature boundary conditions) and the current is equal to $I_{opt} = \frac{ST_C}{R}$ where T_C is the temperature on the cold side, and R is the resistance of the device. Under these conditions, ΔT_m is proportional to the ZT of the device following Eq. (E4) [169,170]:

$$ZT = \frac{2\Delta T_m}{T_c} \tag{E1}$$

To perform cooling curve measurements, we use the thermoreflectance technique wherein a pulsed voltage is applied across the device and the 2D temperature profile of the device is obtained by mapping the local changes in the reflectance coefficient to the local temperature. To help visually perceive the thermal condition in the device under bias for thermoreflectance imaging, we demonstrate the temperature mapping of the



Figure 4.5 Thermal imaging of the Joule heating inside the structure and cooling curve. (A) Joule heating: 2D temperature map of the Au-Gr-WSe2-Gr-Au device under a relatively high-voltage 2 V obtained using the thermoreflectance method. Joule heating dominates in the Gr-WSe2-Gr junction and leaks through the graphene ribbon and gold contacts. (B) Cooling curve: The temperature difference between the substrate and top of the active device in Kelvin versus applied voltage at small applied voltages.

device under a relatively large pulsed voltage of 2V, shown in *Figure 4.5A*. Joule heating of up to 9°C is observed at the top surface of the Gr-WSe₂-Gr junction. The hot spots

indicate the inhomogeneity or defects at the interface. It is observed that the heat is mostly generated in the active layers and leaks through the graphene ribbons and gold contacts. *Figure 4.5B* shows the cooling curve obtained by using the thermoreflectance imaging technique under low bias voltages up to ~0.06V. Using Eq. E1, we can estimate an equivalent ZT to be 1.5×10^{-3} for the Au-Gr-3WSe₂-Gr-Au structure. The boundary conditions used to obtain Eq. E4 is not satisfied with our experiment. First, the device is fabricated on a SiO₂ layer, which cannot dissipate the heat effectively and cannot serve as a perfect heat sink. Second, the cold side is not thermally isolated and there is a small heat leak due to convection since the measurement is not performed in a vacuum. Therefore, our measured ZT is considered to be underestimated for this device structure. While still too small for practical application, our measured ZT already shows three orders of magnitude enhancement compared with the previously reported ZT values for similar nanometer-thick 2D layered heterostructures [37].

4.3 Summary and Discussion

To summarize, we have used first-principles calculations combined with Green's function formalism to estimate the thermionic performance of Au-Gr-1 to 5 layers of WSe₂-Gr-Au structures. We further fabricated the device and measured its performance to validate the theory. The calculated transmission function indicated a clear suppression of tunneling current for structures with more than 3 layers of WSe₂. Therefore, 3 layers are enough to build a thermionic device. The calculated barrier height is 0.1 eV indicating that this device operates best at temperatures above 600°K. The electronic conductance and the Seebeck coefficient, both increases with temperature as shown in *Figure 4.4B*. The

room temperature calculated Seebeck coefficient is in close agreement with the experimentally measured value of 72 μ V/K signifying the accuracy of the calculations. In the cross-plane direction, the thermal conductivity of the WSe₂ layered structure has been reported to be as low as 0.05 W m⁻¹ K⁻¹, which is among the lowest possible thermal conductivity values in a solid [171]. This ultra-low thermal conductivity, along with the large thermal boundary resistance values reported for interfaces of 2D layered heterostructures, points to small values for the thermal conductance of the studied structure.

The calculated lattice thermal conductance of 14 MWm⁻²K⁻¹ for Au-Gr-3WSe₂-G-Au is close to the measured value of 17 MWm⁻²K⁻¹ for Gr-3WSe₂-Gr. The thermal conductance at Au-Gr contacts is low and is about 20 $MWm^{-2}K^{-1}$. It is shown that the limited phonon density of states in Au, is the determining factor in thermal transport at Au-Gr interfaces [172,173]. If we add the thermal resistance of the Au-Gr contacts in series to the Gr-3WSe₂-Gr, we obtain a value of 6.3 MWm⁻²K⁻¹. The experimentally measured conductance value is smaller than the theoretically calculated one due to the inevitable presence of defects. Values for similar structures have been reported in the literature. Massicotte et al. reported a conductance of 0.5 MW m⁻² K⁻¹ for Au-Gr-4WSe₂-Gr-Au [61]. However, we note that the conductance reported reflects that of electron-phonon coupling at Gr-hBN interfaces, a parallel process to the phonon-mediated conductance across these interfaces. Thus, we cannot make direct comparisons between values determined in our work and those found in the literature. The contribution of electronphonon coupling to the conductance of 3- and 4-layer WSe₂ are reported to be similar due to the ballistic nature of transport in these layers [61], however, the total thermal

conductance across metal-WSe₂-substrate interfaces have been shown to decrease following an increase in the number of WSe₂ layers [174]. The trend in the latter is consistent with the ultralow thermal conductivity of WSe₂ [171], as the resistances compound follows an increase in the number of layers.

The I-V curve of the fabricated structure indicates a near-Ohmic contact. The overall electrical conductance value calculated for the Au-Gr-3WSe₂-Gr-Au is small. For the fabricated structure with an area of roughly $3 \mu m \times 3 \mu m$, the resistance is about 40Ω . Our contact resistance measurements indicate Au-Ti-Gr contact varies from device to device and has a range from 0.5 to $2 k\Omega$. In other words, contact resistance is the dominant resistance in the experiment. If we use the measured Seebeck coefficient, the calculated resistance, and the measured thermal conductance, we obtain a ZT of 7×10^{-4} for the current structure which is twice smaller than the directly measured ZT value using thermoreflectance measurements. There are many sources of error when calculating ZT from the three transport properties. First, while TDTR measurements are reliable for these measurements, we used a resistive model to add the thermal resistance of Au-Gr and Gr-3WSe₂-Gr which only gives a rough idea about the overall thermal resistance of the device. Second, we were not able to extract the electrical conductance of the device due to the large contact resistance and hence we used the theoretical value for it. Finally, there are sample variations due to the presence of defects and we note that the TDTR measurement was performed on a different sample.

The directly measured ZT value using the thermoreflectance method, 1.5×10^{-3} , is small but it is significantly larger compared with other similar structures. We have recently measured the ZT of monolayer and bilayer WSe₂ layers sandwiched between gold and

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graphite and only observed ZT values on the order of 10^{-5} due to the dominance of the tunneling current. Similarly, ZT of Gr-hBN-Gr is reported to be on the order of 10^{-6} . Our measured ZT value is also consistent with the small calculated ZT values for this structure at room temperatures. As discussed before, the studied structure is suitable for elevated temperatures. To improve the ZT values at room temperatures, structures with lower electron energy barriers are needed. The barrier height of the current structure is 0.1eV. If we replace the gold contacts with another metal that can form a lower energy barrier (~0.05eV), we can extend the high performance of the device to room temperatures. We studied several possible metals. The most optimistic one for this structure is platinum. Transport properties of Pt-Gr-3WSe₂-Gr-Pt are reported in *Figure 4.4*. The main advantage of Pt is to lower the energy barrier and therefore improve the electrical conductance. As shown in *Figure 4.4B* two orders of magnitude enhancement in the electrical conductance is expected when replacing Au with Pt without deteriorating other transport properties.

Chapter 5: Morphology and Seebeck Coefficients of Electrodeposited Bi₂Se₃ films grown onto Au(111)/Si Substrates

5.1 Introduction

V-VI chalcogenide compounds such as Bi₂Ch₃ (Ch = S, Se, or Te) and the homologous series based on Sb, exhibit a wide range of properties and functionalities. These materials and in particular their alloys have been long studied for thermoelectric (TE) applications around room temperature. $Bi_{2-x}Sb_xTe_3$ and $Bi_2Te_{3-x}Se_x$ are the two main p-type and n-type thermoelectric compounds respectively, used in commercial thermoelectric modules designed for room-temperature applications [8,175–178]. The thermoelectric module's power generation efficiency and the Peltier refrigerators' coefficient of performance are increasing function of the TE materials figure of merit, zT, where the figure of merit zT = $\$S^2T/\$$ (where \$ is conductivity, S the Seebeck coefficient, T the absolute temperature and \$ the thermal conductivity). $Bi_{2-x}Sb_xTe_3$ compounds have shown zT values close and larger than unity [125,179–183]. While in general the reported values for $Bi_2Te_{3-x}Se_x$ are smaller, the peak value of zT is still reported to be larger than unity [184–188].

Some of these semiconducting intermetallic compounds have been recognized as threedimensional (3D) topological insulators (TIs) [189]. This new form of electronic structure in matter exhibits strong spin-orbit coupling and symmetry that contribute to generating an insulator behavior in the bulk and conducting electronic states at surfaces and interfaces [190–192]. Bi₂Se₃, in particular, has been among one of the first 3D topological insulators being identified [189]; this compound exhibits a rhombohedral phase (r-Bi₂Se₃) and a small direct bandgap of about 0.2-0.3 eV [193–196] if grown at a relatively high temperature of the order of 200°C or above. However, growth at or below 70°C results in the crystallization of a metastable orthorhombic structure (o-Bi₂Se₃) [197], homologous to that of the compounds Bi₂S₃ [198], Sb₂S₃ [199], and Sb₂Se₃ [200]. These crystal structures have larger band gaps, of the order of 0.9 - 1.2 eV, suitable for solar cells and photonic applications [201,202]. However, the growth of a purely o-Bi₂Se₃ is difficult and rarely reported in the literature [203–205].

Electrodeposition from nitric acidic electrolytes in particular results in a mixed-phase rhombohedral/orthorhombic variable with the relative phase fraction and the conditions of growth [205]. The conductivity of these materials is highly dependent on defect formation during growth, among which two types of Se vacancies are the dominant donor defects [206]. This results in a propensity for n-type defects, and therefore n-type conduction; the conductivity, in particular, is heavily dependent on the condition of synthesis due to the variation of defect density. Among the two phases, r-Bi₂Se₃ is widely studied for thermoelectric applications [205,207–213]. The r-Bi₂Se₃ shows a large value of the Seebeck coefficient which makes it suitable for thermoelectric applications. The existing literature reported a Seebeck coefficient value for undoped n-type r-Bi₂Se₃ in the range of -110 μ V/K to -120 μ V/K [208,214–216]. On the other hand, due to the growth issues, the only reported Seebeck coefficient of the pure orthorhombic phase by Tumelero *et. al.* shows a much higher value of -350 μ V/K consistent with the large bandgap of this phase [205].
In this chapter, we focus on the morphology and Seebeck coefficients of electrodeposited Bi₂Se₃ films on Au (111)/Si substrate with film thickness ranging from 0.54 μ m to 5.72 μ m. The films form continuous layers, seemingly through an anomalous Stransky-Krastanov (layer plus island) growth process, resulting in the formation of smooth films up to about 740 nm, followed by a significant roughening afterward. XRD patterns confirmed that the films are purely rhombohedral when the thickness is below 1.84 μ m while films are mixed-phase when the thickness is 1.84 μ m and above. The experimentally measured Seebeck coefficient shows a maximum value of -184 μ V/K at the thickness of 1.84 μ m which is considered to be the onset of o-Bi₂Se₃ on top of the r-Bi₂Se₃. Furthermore, we theoretically calculated the Seebeck coefficients of bulk r-Bi₂Se₃ and o-Bi₂Se₃ separately from the first principle density functional theory (DFT) and showed that the experimental Seebeck coefficients match with the value of r-Bi₂Se₃ for 1.84 μ m and above thickness while falling between the values of pure r-Bi₂Se₃ and o-Bi₂Se₃ for 1.84 μ m and above thicknesses.

5.2 Experimental Details

5.2.1 Electrodeposition

Bi₂Se₃ films were grown onto 100 nm sputtered Au(111)/n-type Si (100) substrates. The electrolyte for electrodeposition consisted of 5 mM Bi(NO₃)₃, 5 mM SeO₂, and 0.5 M HNO₃ to increase the electrolyte conductivity and the solubility of the ionic species. The solution pH ranged from 0.2 to 0.4. The potential window to deposit Bi₂Se₃ films was between -0.1 V and -0.25 V vs. SCE. Beyond this potential, the film deposited with an applied potential of -0.3 V appeared to have cracks on the surface. The morphology of films that could

deposit in this potential window exhibited variation in morphology (Figure 7.9) and the Bi:Se atomic fraction for the films deposited within this potential window was found to be 38:62 (Figure 7.10). However, the films deposited at -0.1 V were gray in color and appeared to be most planar and smooth from SEM images (Figure 7.11). Thus, -0.1 V was chosen for potentiostatic deposition of Bi₂Se₃ on the Au/Si substrates.

Electrodeposition experiments were carried out using the EG&G potentiostat/galvanostat by applying a constant potential of -0.1 V vs. SCE, with a front contact to the Au layer. A platinum mesh was used as the counter electrode (CE). To deposit films in a wide range of thicknesses, the charge density during each experiment varied between 2 C/cm² and 13 C/cm² corresponding to 0.74 μ m and 5.72 μ m, respectively. The Faradaic efficiency was estimated to be around 80% by comparing the experimental thickness measured by SEM cross-sections against the thickness calculated assuming a 100% deposition efficiency. Film thickness in some cases is only indicative, due to the different morphologies of the films. The measured thickness was an average of 16 different measurements taken from two different samples grown under the same conditions.

5.2.2 Characterization

The stoichiometry of Bi₂Se₃ films was measured by an Energy Dispersive Spectroscopy (EDS) instrument, integrated with a Scanning Electron Microscope (SEM, FEI Quanta 650). The SEM was also used to image the morphology and microstructure of the films. The crystal structure of the films was identified with an X-ray diffractometer (PANalytical Empyrean) with a Cu K α source (wavelength, λ = 0.154 nm), both in a

Bragg-Brentano and grazing incidence modes. The average grain size of Bi₂Se₃ films was calculated using the Scherrer equation below where k, B, and θ are the dimensionless shape factor, line broadening at the full width half maximum (FWHM) point of the diffraction features in the XRD pattern and the Bragg angle, respectively.

$$d = \frac{K\lambda}{BCos\theta} \tag{1}$$

Hall measurements are typically the preferred method for obtaining in-plane carrier density and mobility profiles of semiconductor thin films. Since the accuracy of carrier density profiles depends on conduction solely through the film, a non-conductive substrate is an absolute requirement for this method. Electrodeposition, on the other hand, requires the growth of thin films on a conductive substrate. Hence to perform inplane conductivity and mobility measurements, the films need to be transferred to insulating substrates.

As a consequence, in this work, we focus on cross-plane electrical transport properties. An electrochemical technique, Mott-Schottky analysis, is more suitable for cross-plane carrier density analysis and was performed to obtain carrier density profiles of the Bi₂Se₃ films using a BioLogic SP-150 instrument in the frequency range of 10 Hz to 1 kHz. A 0.1 M phosphate buffer solution (PBS) was used as the electrolyte for the Mott-Schottky measurements. Carrier concentration, N_d in cm⁻³, is determined from Eq. 2, where ε is the permittivity of Bi₂Se₃ in F/cm, ε_0 is the permittivity of free space, A is the 2-D area exposed to the electrolyte, q is the charge of an electron in C, and m is the rate of the C⁻² (cm⁴µF⁻²) change versus applied potential (V vs. RHE). [217]

$$N_d = \frac{2}{\varepsilon \varepsilon_o A^2 q m} \tag{2}$$

The cross-plane electrical conductivity measurement on these samples proved to be difficult to measure. The measured values were dominated by contact resistance. To eliminate the contact resistance, usually, the transfer length measurement (TLM) is used in which resistance of samples of different thicknesses is measured and the contact resistance is extracted from the resistance versus thickness curve. However, since the mobility of the films depends on the thickness of the film (as the morphology depends on the thickness), it is not possible to separate the contact resistance using the TLM in our samples. The Seebeck coefficients were measured in the cross-plane direction using a homemade experimental setup. A 200 nm thick Au layer was deposited on the Bi₂Se₃ films as top contact for the Seebeck measurement. To obtain the Seebeck coefficient, a temperature gradient was applied to the sample along the cross-plane direction by placing the sample on top of a Peltier module. Two thermocouples and two voltage probes were used to measure the temperature difference and the Seebeck voltage across the films respectively. The Seebeck coefficient was obtained by linearly fitting the Seebeck voltage curve with respect to the temperature difference ($S = -\Delta V / \Delta T$). All Seebeck and resistance measurements were carried out at room temperature.

5.3 Computational Details

We used density functional theory (DFT) calculation to calculate the theoretical Seebeck coefficients under constant relaxation time approximation. The Seebeck coefficient values of the rhombohedral phase and the orthorhombic phase were calculated separately. The rhombohedral unit cell of the bulk Bi₂Se₃ exhibits a space group of $R\bar{3}m$ with five atoms in the trigonal unit cell, while the orthorhombic unit cell has a space group *Pnma* with 20 atoms in the unit cell. The band structure and density of states were calculated using the plane wave DFT code, Quantum-ESPRESSO (QE) [103], treating exchange-correlation functional with generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) [92] and modified Perdew-Burke-Ernzerhof (PBEsol) [93] functional. Scalar relativistic and fully relativistic pseudopotentials are used throughout the calculation. We set the plane-wave kinetic energy cut-off at 80 Ry with a charge density of 800 Ry for both crystal structures. A 6×6×6 Monkhorst-Pack grid of k-points for the rhombohedral phase and 9×3×3 for the orthorhombic phase was used to sample the Brillouin zone [218]. The geometry relaxation calculations were performed as a result of the Born Oppenheimer approximation. [219] In this stage, the lattice parameters and the atomic coordinates were determined by minimizing the energy function within the adopted numerical approximations using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [220]. In the self-consistent calculation, the convergence threshold for energy is set to 10⁻¹⁰ eV. The band structures and density of states of the orthorhombic and rhombohedral phases are shown in Figure 5.6. Finally, the Seebeck coefficient calculation is based on the BoltzTrap [108] package with the semi-classical Boltzmann transport method in the constant relaxation-time [221] approximation. Within the constant relaxation-time approximation, the Seebeck coefficient can be obtained directly from the electronic structure without any adjustable parameters.

5.4 Results & Discussion



Figure 5.1 Surface morphology of electrodeposited Bi₂Se₃ films with varying thicknesses.

Figure 5.1(a) shows the surface morphology of the Bi₂Se₃ films having thicknesses in the range of $0.74 - 5.72 \mu$ m. Planar film deposition was observed in the early stage of growth. As the films grew in thickness, crystallized nuclei of micron-scale started to appear on the planar films. The average crystal nuclei increased with the overall film thickness; furthermore, the density of nuclei increased, and the nuclei also increased in size, forming elongated particles. The number density of these crystals presents on the surface gradually increased and at a film thickness of ~1.84 μ m, the Bi₂Se₃ films were completely



Figure 5.2 Cross-section of Bi2Se3 films for varying thickness.

covered with crystalline features approximately 1 μ m in length. A close-up image of one of these crystals is shown in the inset of *Figure 5.1*.

Cross-sections for the various films are shown in Figure 5.2. The films with 440 nm thickness exhibit occasional nuclei grown on the surfaces (not shown here). Around a 740 nm thickness, these nuclei transform into lamellar irregular features that result in an increase of roughness at a thickness of about 770 nm. Thicker films (1 to 5 um) in contrast exhibit features similar to tip shapes, mostly directed in the perpendicular direction. Based on the previous SEM morphology analysis the growth mode of these films is most likely a Stransky-Krastanov mode, where the film grows initially in an epitaxial layer-bylayer, and later, beyond a critical layer thickness, which depends on the strain and the chemical continues potential of the deposited film, growth through the nucleation and coalescence of adsorbate islands. The formation of nuclei on top of the smooth Bi₂Se₃, however, occurs on a much larger scale than the usual Stransky-Krastanov, whereby few monolayers are sufficient to complete the Stransky-Krastanov growth mode. If so, we assume that the initial growth does not fully progress in an epitaxial manner, but instead follows a smooth growth where dislocations allow a quasi-epitaxial growth.

The XRD pattern of the films is shown in *Figure 5.3*. The films corresponding to 0.74 μ m thickness show diffraction features at 20 positions of 24.83°, 28.98°, 43.4°, and 52.79° which correspond to rhombohedral (labeled as R) planes of (001), (015), (110) and (024), respectively. However, numerous new diffraction features appear in the XRD pattern of Bi₂Se₃ films having a thickness of 1.84 μ m, all of which corresponded to the orthorhombic (labeled O) crystal planes. The crystal structure of the Bi₂Se₃ as a function of thickness

shows a dominant presence of the orthorhombic phase with respect to the rhombohedral accompanied by a gradual narrowing of the reflections from the (001), (015), (110, 0111), and (024) planes suggesting the formation of larger grains in the rhombohedral phase. This is confirmed by the calculation of average grain sizes based on the Scherrer equation. The average grain size for the characteristic (015) rhombohedral plane has been included in *Table 5.1*. For further analysis, the films with thicknesses from 1.84 μm and beyond



Figure 5.3 XRD pattern of the Bi2Se3 with film thicknesses between 0.74 μ m and 5.7 μ m electrodeposited on Au (111) substrates.

Deposited charge	Average	Average grain size	Carrier
density (C/cm ²)	thickness	(nm)	concentration
	(µm)		(cm-3)
2	0.74	12.9	$1.2 \ge 10^{18}$
4	1.84	25.9	$3.04 \ge 10^{18}$
9	3.97	22.2	5.67 x 10 ¹⁸
13	5.72	30	1.04 x 10 ¹⁹

Table 5.1 Average film thickness, grain size, and carrier concentration in Bi₂Se₃ films.

were assumed to exhibit a mixture of semiconducting orthorhombic and semi-metallic rhombohedral phases while those below $1.84 \mu m$ and less were assumed to be pure rhombohedral.

The Mott-Schottky method was used to estimate the surface carrier concentration of the films; these data show a monotonic increase by an order of magnitude, starting from 1.2 x 10^{18} cm⁻³ for a 0.74 µm thick film, up to 1.04×10^{19} cm⁻³ for 5.72 µm films. The $1/C^2$ vs. potential plot used to determine the carrier concentration for the films is shown in *Figure 5.4*, and N_d values are included in *Table 5.1*. The positive slope of the Mott-Schottky plots confirms the n-type conductivity of the films (*Figure 5.4*), as validated by the negative Seebeck coefficients. This is consistent with Se-rich films. The atomic ratio of Bi:Se in these electrodeposited films was 38:62. Under such Se-rich conditions, Se-antisites (Se_{Bi}) show the lowest formation energy and therefore the most likely point defect, leading to n-type



Figure 5.4 Mott-Schottky plots of the Bi2Se3 with film thicknesses between 0.74 μ m and 5.72 μ m electrodeposited on Au (111) substrates.

conductivity in rhombohedral Bi₂Se₃. [206] In the case of the pure orthorhombic phase, Se antisites (Se_{Bi}) are more likely owing to lower formation energies in Se-rich films, thus leading to an n-type conductivity. [222]

The variation of experimentally measured room temperature Seebeck coefficients (S) as a function of Bi₂Se₃ film thickness is shown in *Figure 5.5*. The negative sign of the Seebeck values indicates n-type conduction in the films. The room temperature Seebeck coefficient for 0.74 μ m thick films was around -90.5 μ V/K which gradually increased to a maximum of -184.5 μ V/K when the film thickness reached 1.84 μ m. The Seebeck coefficient of the films decreases beyond this thickness value to -100.8 μ V/K for a film thickness of 5.72 μ m.

Previous reports on experimental Seebeck coefficients of Bi₂Se₃ are summarized in *Table* 5.2. A majority of the existing literature reports Seebeck coefficients between -100 μ V/K and -120 μ V/K for n-type conductivity. The increase of surface roughness in the morphology of the films due to crystal formations in the 0.74 – 1.84 μ m film range was also taken into consideration to explain the increasing Seebeck coefficient trend. The presence of porosity in the film morphology may result in enhanced scattering of low energy carriers with higher efficiency compared to planar structures; this results in an



Figure 5.5 Experimentally measured Seebeck coefficients of the Bi2Se3 films with film thickness between 0.74 μ m to 5.72 μ m.

enhanced Seebeck effect. [223] The only reported Seebeck coefficient of the pure orthorhombic phase shows a much higher value of -350 μ V/K which is significantly Table 5.2 Reported Seebeck coefficients of Bi2Se3.

Deposition Method	Film type	Crystal	Seebeck
		Structure	Coefficient
			(µV/K)
Solvothermal	Nanostructures	R*	-115 [208]
Electro don ocition	Eilere	R	+26.46 [213]
Electrodeposition	FIIMS	M^*	+6.53 [213]
Aqueous Chemical	Nanostructured films	R	-119 [227]
Growth			
Electrodeposition	Films	O*	-350 [205]
MOCVD	Films	R	-120 [214]
MBE	30 quintuple layers	-	-104.3 [215]
Aqueous Chemical	Nanostructured films	R	-113 [216]
growth			
Electrodeposition	Films	R	+20 [228]

*The rhombohedral, mixed-phase and orthorhombic crystal structures are denoted as R, M, and O

higher than those observed for the rhombohedral phase. [205] Thus, the emergence of a dominant orthorhombic phase in our films (higher in phase fraction) around 1.84 μ m thickness was most likely the factor that contributed to the improvement of the Seebeck coefficient.

To further explain the variation of Seebeck coefficients, we theoretically calculated the Seebeck coefficients. In theory, it is not feasible to calculate the Seebeck coefficients of mixed-phase Bi₂Se₃ using first-principles calculations. Instead, the Seebeck coefficients of bulk r-Bi₂Se₃ and o-Bi₂Se₃ are calculated separately. The films are thick enough to be considered bulk. Since the exact volume fractions are not known, we can only determine the range of the Seebeck coefficient variations. The differential conductivity $\sigma(E)$, the conductivity σ , and the Seebeck coefficient *S* are given respectively by Eq. 3 – 5.

$$\sigma(E) = q^2 g(E) v^2(E) \tau(E) - - - (3)$$

$$\sigma = \int \sigma(E) \left(-\frac{\partial f}{\partial \varepsilon} \right) dE - - - (4)$$

$$S = -\frac{1}{qT} \frac{\int \sigma(E) (E - \mu) \left(-\frac{\partial f}{\partial E} \right) dE}{\int \sigma(E) \left(-\frac{\partial f}{\partial E} \right) dE} - - - (5)$$

Where *E* is the energy, g(E) is the density of states, *q* is the electronic charge, v(E) is the group velocity, $\tau(E)$ is the relaxation time, *f* is the Fermi-Dirac distribution function, μ is the chemical potential and T is the temperature. For metals and degenerate semiconductors, the Seebeck coefficient can be approximated by the Mott formula. [224]

$$S = \frac{\pi^2}{3} \left(\frac{\kappa_B^2 T}{e} \right) \left(\frac{d \log \sigma(E)}{dE} \right)_{E=\mu} - - - (6)$$

Thus, the electronic band structure and density of states of material play a key role in determining the thermoelectric properties of the system in question. The r-Bi₂Se₃ and the



Figure 5.6 Theoretically calculated band structure and density of states of (a) rhombohedral phase Bi2Se3 and (b) orthorhombic phase Bi2Se3.

o-Bi₂Se₃ have completely different electronic band structures and density of states as shown in *Figure 5.6*. The r-Bi₂Se₃ shows a narrow bandgap of 0.24 eV while the o-Bi₂Se₃ shows a wide bandgap of around 0.95 eV. The calculated bandgaps of r-Bi₂Se₃ and o-Bi₂Se₃ are consistent with previous theoretical and experimental bandgaps of 0.2-0.3 eV [193–196] and 0.9-1.2 eV [201,202] respectively.

The Seebeck coefficient depends mainly on the position of the Fermi level (carrier concentration) and the energy dependence of the density of state and the relaxation times. Owing to their different electronic structure, the r-Bi₂Se₃ and o-Bi₂Se₃ give rise to a different range of Seebeck coefficients which are plotted as a function of carrier concentration in *Figure 5.7a*. The Seebeck coefficients of r-Bi₂Se₃ and o-Bi₂Se₃ are extracted for each film using the carrier concentration values that are obtained from the Mott-Schottky analysis.

The theoretical Seebeck coefficients of the pure r-Bi₂Se₃ and o-Bi₂Se₃ are shown in *Figure 5.7b* along with our experimental Seebeck coefficients of the mixed phases. Our observed experimental values match those for the pure rhombohedral phase in the 0.74 – 1.02 μ m thickness range. However, for films with 1.84 μ m thickness, the experimental Seebeck coefficient matches that for the pure orthorhombic phase more closely. For thicker films (3.97 μ m and 5.72 μ m) the experimental values were within the limits set by the theory for pure r-Bi₂Se₃ and o-Bi₂Se₃. These results agree with our conclusions about the mixed-phase structure of films based on the analysis of XRD patterns.

The increasing trend of carrier concentration with film thickness (*Figure 5.5d*) would generally lead to decreasing Seebeck coefficient values. However, in our study, we observe that this trend holds only in the $1.84 - 5.72 \mu m$ thickness range, where a mixture

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of rhombohedral and orthorhombic phases co-exists. On the other hand, the increasing

Figure 5.7 (a) Theoretically calculated Seebeck coefficient vs. carrier or doping density plots and (b) comparison of experimental measurements of mixed-phase Bi₂Se₃ films (black squares) and theoretical Seebeck coefficients of pure rhombohedral (red circles) and pure orthorhombic (purple triangles) phases of Bi₂Se₃ films.

Seebeck coefficient trend is observed in the $0.74 - 1.84 \mu m$ thickness range, where the onset of crystal formation and growth of the orthorhombic phase in the films occurred. The phase fraction of the films could not be estimated with a reasonable degree of certainty by analyzing data from XRD pattern and Raman spectroscopy, which limited our ability to match the observed values to the predicted Seebeck coefficient values with higher accuracy.

5.5 Summary

The electrodeposited Bi₂Se₃ films upon nucleation form continuous layers following the Stransky-Krastanov (layer plus island) growth process and resulting in the formation of smooth films up to about 700 nm thickness. In later stages, film growth is dominated by the formation of crystals which coalesce together to form a rougher film. XRD patterns confirmed that the films are purely r-Bi₂Se₃ below 1.84 μ m thickness while they are mixed-phase Bi₂Se₃ for 1.84 μ m thickness and beyond. The Seebeck coefficient shows n-type conductivity, exhibiting a maximum value of -184 μ V/K at 1.84 μ m thickness. First-principles calculations were implemented to calculate the band structure of the rhombohedral and orthorhombic phases and the obtained bandgaps closely replicate those of the experiment. The Seebeck coefficient values were calculated using constant relaxation times. From the theoretically obtained Seebeck coefficients, it is shown that the experimental Seebeck coefficients match the values of the rhombohedral phase when the film thickness is below 1.84 μ m while falling between the Seebeck coefficients of pure rhombohedral and orthorhombic phase when the film thickness is 1.84 μ m and above.

Chapter 6: Summary

The primary objective of this dissertation is to theoretically design highly efficient SSTI devices based on 2D vdW heterostructures. This work also theoretically investigates the effect of asymmetry of the electrode, electron-phonon interaction, and defects on the SSTI device performance. Knowing the mean-free path of electrons in the bulk version of the 2D semiconductor material used as the channel in the SSTI device, the size effect, and the importance of electron-phonon interaction in nanoscale thermionic devices are evaluated. The highly accurate electron-phonon scattering rates of the bulk form of the 2D semiconductor channel are computed from the first-principles in order to determine the effect of electron-phonon interaction on the performance of the 2D vdW-based SSTI device. The calculated electron-phonon scattering rates are then utilized to investigate the effect of electron-phonon interaction on thermoelectric transport of the same bulk semiconductor from full first-principles calculations. In addition, in this work, the first SSTI device based on 2D vdW heterostructures is fabricated and characterized in collaboration with experimental groups.

Solid-state thermionic structures made from layered van der Waals heterostructures have shown promising thermal-to-electrical energy conversion efficiencies theoretically. These structures are further studied using first-principles calculations combined with Green's function method in this dissertation. By calculating the electron-phonon relaxation length, ballistic transport in these structures is confirmed. The effect of the number of layers, the energy barrier, the asymmetry of the contacts, and defects on the performance of MoSe₂-based thermionic converters are also studied in this work. It is demonstrated that making a low-energy barrier and low-resistance metallic contact is the key to highperformance thermionic diodes, and copper is identified as the optimum metallic contact for MoSe₂-based devices. It is further shown that, unlike the vacuum-based thermionic diodes, asymmetry does not result in improved performance within the linearized transport theory. Finally, we investigated the impact of point defects, namely substitutional and vacancy defects, on the performance of MoSe₂-based SSTI devices. We find that, whereas both Mo vacancy and Se vacancy have a significant impact on device performance, the effect of Mo vacancy is considerably greater. The substitutional defect, on the other hand, has a minor impact on device performance.

In the preceding section of this dissertation, the MoSe₂ is used as the 2D semiconducting channel in SSTI devices. To obtain the effect of electron-phonon scattering on the performance of MoSe₂-based SSTI devices, the highly accurate electron-phonon scattering of the bulk form of MoSe₂ is calculated from the first-principles. The computed electron-phonon scattering rates are utilized to further investigate their effect on the thermoelectric transport of bulk MoSe₂. In this work, the thermoelectric properties of bulk MoSe₂ within relaxation time approximation including electron-phonon and ionized impurity interactions using first-principles calculations and at room temperatures are studied. The anisotropy of this two-dimensional layered metal dichalcogenide is studied by calculations of electron mobility in the cross-plane and the in-plane directions. The cross-plane mobility is found to be two orders of magnitude less than the in-plane mobility. The inclusion of van der Waals interactions further lowers the carrier mobility in the cross-plane direction but minimally affects the in-plane one. The results for in-plane electrical mobility and conductivity are in close agreement with experimentally

reported values indicating the accuracy of the calculations. The Seebeck coefficient calculations show that this coefficient is primarily dictated by the band structure. The details of relaxation times and inclusion of van der Waals interactions only slightly change the Seebeck coefficient. The in-plane thermoelectric power factor reaches a maximum value of 20 μ Wcm⁻¹K⁻² at a carrier concentration of 1.5x10²⁰ cm⁻³ at 300K. In the future, this work can be extended to include electron-electron scattering and defect scattering to more accurately capture material properties.

In this work, thermionic cooling across gold-graphene-WSe₂-graphene-gold structures is also studied computationally and experimentally. Graphene and WSe₂ layers were stacked, followed by deposition of gold contacts. The I-V curve of the structure suggests near-ohmic contact. A hybrid technique that combines thermoreflectance and cooling curve measurements are used to extract the device ZT. The measured Seebeck coefficient, thermal and electrical conductance, and ZT values at room temperatures are in agreement with the theoretical predictions using first-principles calculations combined with realspace Green's function formalism. This work lays the foundation for the development of efficient thermionic devices.

Lastly in this dissertation, as a separate route, it is investigated how polymorphism in Bi₂Se₃ allows it to be tuned for unique thermoelectric properties. The commonly reported rhombohedral structure is a topological insulator, a narrow gap semiconductor with a bandgap of 0.2–0.3 eV, and has been widely studied for thermoelectric applications. The alternative orthorhombic structure is a semiconductor with a larger bandgap of 0.9–1.2 eV. The opportunity to fabricate a mixture of these orthorhombic and rhombohedral structures provides a chance for materials engineering to optimize its electrical and

thermal properties. In this work, the morphology and the Seebeck coefficient of mixedphase, Se-rich, n-type Bi2Se₃ films were prepared by electrodeposition using an acidic bath. Post-nucleation formation of smooth films was observed to be followed by the emergence of crystals and continued growth through the coalescence of the newly formed crystals. The room temperature Seebeck coefficients of the films were also observed to vary as a function of the film thickness, increasing from -90 μ V/K (0.74 µm thickness) to a maximum of -184.4 μ V/K (1.84 µm thickness) and gradually decreasing to -100.8 μ V/K (5.72 µm thickness). Analysis of XRD patterns for the Bi2Se₃ films showed that the thickness dependence of Seebeck coefficients was related to the transition from pure rhombohedral to a mixture of orthorhombic and rhombohedral phases. The thickness-dependent Seebeck effect was further discussed by the computational study of the Bi2Se₃ band structures and Seebeck coefficients of pure rhombohedral and pure orthorhombic structures.

Chapter 7: Appendices

Supplementary Materials

Supplementary materials of Chapter 2 Gold-platinum symmetric and asymmetric structure with 3 layers of MoSe₂

In chapter 2, we presented the SSTI performance of gold-platinum symmetric and asymmetric structures with 5 layers of MoSe₂. Here, we evaluate the performance of gold-platinum symmetric and asymmetric structures with 3 layers of MoSe₂. The local density of states (LDOS) of symmetric gold, symmetric platinum, and the asymmetric structure with one side gold and another side platinum and their corresponding transmission



Figure 7.1 Local density of states of (a) Au-3 MoSe2-Au (b) Pt-3 MoSe2-Pt (c) Au-3 MoSe2-Pt and their corresponding transmission functions.



Figure 7.2 Transmission function (b) Seebeck coefficient (c) electrical conductance and (d) power factor times temperature of the gold, platinum, and gold-platinum asymmetric structure.

functions are shown in Figure 7.1. From the LDOS we see that the Fermi level E_F is located near the conduction band of the gold and gold-platinum asymmetric structure which means these structures are n-type while the Fermi level of the platinum structure is located around the middle of the gap. The transmission function, Seebeck coefficient, electrical conductance, and the power factor times temperature for all three structures are shown in *Figure 7.2*. We can see from the LDOS and the transmission function that the gold structure has a lower barrier height compared to the other two structures. Because of the lower barrier height, the gold structure shows significantly higher conductance at high temperatures as shown in *Figure 7.2(b)*. From *Figure 7.2(c)* we can see that the gold structure shows the highest Seebeck coefficient while the platinum structure shows the lowest Seebeck coefficient. *Figure 7.2(d)* shows the power factor times temperature (PFT) of all three structures. The combination of high electrical conductance and high Seebeck coefficient makes the PFT of the gold structure significantly higher at high temperatures compared to the other two structures. The platinum structure shows the lowest PFT due to low electrical conductance and the lowest Seebeck coefficient. Similar to the gold-platinum asymmetric structures with 5 layers of MoSe₂, the PFT of the structure with 3 layers of MoSe₂ falls in between the symmetric gold and symmetric platinum structure.



Figure 7.3 Transmission function (b) Seebeck coefficient (c) electrical conductance and (d) power factor times temperature of the Cu-3 MoSe₂-Cu and Cu-5 MoSe₂-Cu structures. The blue line represents the 3-layer structure, and the red line represents the 5-layer structure.

SSTI performance comparison of Cu-3 MoSe₂-Cu and Cu-5 MoSe₂-Cu structure

Among all our calculations, the SSTI structure with 3 layers of MoSe₂ with Cu contact showed the highest PFT. We showed that SSTI structures with 3-5 layers of MoSe₂ with metal contact show optimum performance. In the main manuscript, we presented the performance of the copper structure with 3 layers of MoSe₂. Here, we compare the SSTI performance of the copper structure with 3 and 5 layers of MoSe₂. Figure 7.3 shows the transmission function, electrical conductance, Seebeck coefficient, and PFT of both structures. From *Figure 7.3(a)* we can see that the 3-layer structure has a lower barrier height compared to the 5-layer structure. The 3-layer structure has higher electrical conductance compared to the 5-layer structure as shown in Figure 7.3(b) due to the lower barrier height of the 3-layer structure. However, the 5-layer structure has a higher Seebeck coefficient compared to the 3-layers structure as shown in Figure 7.3(c) due to the higher transmission gap of the 5-layer structure. Because of the high electrical conductance and low Seebeck coefficient of the 3-layer structure and low electrical conductance and high Seebeck coefficient of the 5-layer structure, both structures have similar PFT over the entire temperature range as shown in Figure 7.3(d).

Electron-Phonon Scattering rate and mean free path (MFP) of bulk MoSe₂

Figure 7.4(*a*) shows the full phonon dispersion that is used to calculate the electronphonon scattering rates. Figure 7.4(*b*) shows the energy-dependent electron-phonon scattering rate $\tau(E)$ of bulk MoSe₂ from 300K to 1000K. The energy-dependent electron



Figure 7.4 Full phonon dispersion of MoSe₂ used to calculate the electron-phonon. (b) Electron-phonon scattering rates. The solid lines show the fitted curve. (c) Electron group velocity along the z-axis.

group velocity v(E) along the z-axis is shown in Figure 7.4(*c*). The energy-dependent electron MFP Λ along the z-axis is obtained by: $\Lambda = 2\tau(E)v(E)$.

Supplementary materials of Chapter 4

Series Resistor Model

We model the resistances of the interfaces as measured via TDTR using a series resistor

model. The Al-Gr-3WSe₂-Gr-SiO₂ conductance values can be modeled as follows:

$$\frac{1}{h_{k,measured,Al-Gr-3WSe2-Gr-SiO2}} = \frac{1}{h_{K,Al-Gr}} + \frac{1}{h_{K,Gr-3WSe2-Gr}} + \frac{1}{h_{K,Gr-SiO2}}.$$
 (S1)

In this equation, $h_{K,measured,Al-Gr-3WSe2-Gr-SiO2}$ is the conductance measured via TDTR of the device, while $h_{K,Al-Gr}$ and $h_{K,Gr-SiO2}$ are representative of the associated conductance values with the Al-Gr and Gr-SiO₂ interfaces, respectively. The variable $h_{K,Gr-3WSe2-Gr}$ encompasses the intrinsic resistances of the graphene and WSe₂, as well as the associated resistances at the two Gr-WSe₂ interfaces. Similarly, the Al-Gr-SiO₂ conductance values are governed by the equation

$$\frac{1}{h_{k,measured,Al-Gr-SiO2}} = \frac{1}{h_{K,Al-Gr}} + \frac{1}{h_{K,Gr-SiO2}}.$$
 (S2)

So long as the cross-plane thermal conductivity of the graphene layer is on the order of 1 W m⁻¹ K⁻¹, it will have a negligible contribution to the measured conductance, hence the negligence of the contribution from the graphene layer. By subtracting Eq. S2 from Eq. S1, the conductance of the Gr-3WSe₂-Gr layer can be extracted to be

$$\frac{1}{h_{K,Gr-3WSe2-Gr}} = \frac{1}{h_{k,measured,Al-Gr-3WSe2-Gr-SiO2}} - \frac{1}{h_{k,measured,Al-Gr-SiO2}}.$$
(S3)



Figure 7.5 Time-domain thermoreflectance measurement. Best fits for the Al-Gr-SiO₂ and Al-Gr-3WSe₂-Gr-SiO₂ interfacial regions.



Figure 7.6 Figure of merit (ZT) of Au-G-WSe2-G-Au structure and Pt-G-WSe2-G-Pt structure. (A) Calculated ZT vs temperature of Au-G-WSe2-G-Au structure shown by the solid blue line. The red circle is the experimentally measured ZT at room temperature. (B) Calculated ZT vs temperature of Pt-G-WSe2-G-Pt structure.



Figure 7.7 Repeatable cooling curve measurement. (A) Optical image of the first sample. (B) Cooling curve of the first sample. (C) Optical image of the second sample. (D) Cooling curve of the second sample.

Analysis of contact resistance

We extract the contact resistances from two-probe and four-probe resistance measurements from sample 1 and sample 2 as shown in Figure 7.8 to get a range of the contact resistance value.

The method explained here uses sample 1. First, we measure two probe resistance (see Table 7.1) between contact 2 and contact 3 which include the resistance of contact 2 (R₂),



Figure 7.8 Contact resistance measurement. The optical image of the samples fabricated to measure the contact resistance. (A) Sample 1. (B) Sample 2.

the resistance of contact 3 (R₃), and resistance of graphene flake between contact 2 and contact 3 (R₂₃). We can write,

$$R_2 + R_3 + R_{23} = 3500\Omega \quad (S4)$$

From the four-probe resistance measurements (current supplied between contact 1 and contact 4 and voltage measured between contact 2 and contact 3 (see Table 7.2)) we get only the resistance of graphene flake (520 Ω) between contact 2 and contact 3 (R₂₃). By subtracting the value of R₂₃ (520 Ω) from Eq. S4 we get,

$$R_2 + R_3 = 2980\Omega$$
 (S5)

Similarly, we can write,

$$R_2 + R_4 = 1870\Omega$$
 (S6)

No.	Resistance measured between contacts	Sample 1 Resistance (Ohm)	Sample 2 Resistance (Ohm)
1	2-3	3500	3500
2	2-4	2800	2100
3	3-4	2400	2400

Table 7.1 Two probe resistance data for sample 1 and sample 2 (see *Figure 7.8*).

Table 7.2 Four probe resistance data for sample 1 and sample2 (see *Figure 7.8*).

No.	Current supplied between contacts	Voltage measured between contacts	Resistance (Ohm) Sample 1	Resistance (Ohm) Sample 2
1	1-4	2-3	520	27
2	1-5	2-4	930	72
3	2-5	3-4	425	44

Table 7.3 Contact resistances.

Sample	Contact 2 resistance, R2 (Ohm)	Contact 3 resistance, R3 (Ohm)	Contact 4 resistance, R4 (Ohm)
Sample 1	1437.5	1542.5	432.5
Sample 2	1900.0	1572.0	784.0

 $R_3 + R_4 = 1975 \,\Omega$ (S7)

Solving equations S5, S6 and S7 we get the contact resistance of contact 2 (R₂), contact 3 (R₃), and contact 4 (R₄), which are summarized in Table 7.3 below. Similarly, we can extract the contact resistance values for Sample 2. From our contact resistance analysis, we see that the contact resistance varies from ~0.5k Ω to ~2.0k Ω .

Film 8 12 5 Substrate -0.15 V -0.1 V -0.3 V -0.25 V -0.2 V

Supplementary materials of Chapter 5

Figure 7.9 Physical appearance of electrodeposited Bi₂Se₃ films on Au/Si substrates at potentials varying from -0.1 V to -0.3 V vs. SCE.



Figure 7.10 SEM images of Bi₂Se₃ film surface electrodeposited with applied potentials of -0.1 to -0.3 V vs. SCE



Figure 7.11 Current density vs. time profile for electrodeposited Bi₂Se₃ film

Experimental Characterization Methods

Thermoreflectance imaging

In chapter 5, thermoreflectance imaging is used to obtain the temperature profile of the SSTI device. Thermoreflectance imaging is a non-invasive technique based on the physics of light reflectance which responds proportionally to the material's temperature change [225], as the refractive index of the sample surface changes with temperature (ΔT) resulting in a change in the reflection intensity ($\Delta R/R$) following the relation expressed as $\frac{\Delta R}{R} = \chi \Delta T$ [226] where χ is the thermoreflectance coefficient, which mainly depends on the studied material and the wavelength of the illuminated light. Except for some well-documented elemental materials such as Au, Pt, Si, etc, the thermoreflectance coefficient



Figure 7.12 Working schematic diagram of a Microsanj thermoreflectance imaging system.

needs to be calibrated to obtain the absolute temperature values. The schematic diagram of the thermoreflectance imaging system (MicroSanj) in our laboratory is shown in Figure 7.12. It has a control unit that generates and synchronizes a LED light source for illumination, and a pulsed electrical current is applied to the measuring device. The temperature change due to the applied current modifies the reflection intensity, which can be captured by a charge-coupled device (CCD) camera and sent back to the control unit for analysis. The synchronized diagram for a typical transient thermoreflectance measurement can be found in Ref. [225]. A precise lock-in of the light and electrical signals allows the system to capture the transient temperature mapping under bias. However, since the proportional reflectivity change corresponding to the temperature change is usually very small being on the order of 10⁻⁴ [225], the signal measured by the CCD camera is averaged over many device thermal excitation cycles to improve the

signal to noise ratio. Using this technique, we can measure either transient or steady-state temperature profile of the device surface under pulsed voltage bias.



Figure 7.13 Home-built Seebeck coefficient measurement setup

Home-built Seebeck Measurement setup

In chapter 5, the Seebeck coefficients of Bi₂Se₃ samples are measured using a home-built setup as shown in *Figure 7.13*. To measure the Seebeck coefficients of the film we deposited a gold pad on top of the film. To create a cross-plane temperature difference in the sample, we placed it on top of a thermoelectric module. Two voltage probes were used to measure the Seebeck voltage and two thermocouples were used to measure the temperature difference. We tested the accuracy of the setup by measuring the Seebeck coefficient of some known samples.

Publications and Presentations

Book Chapter

 <u>Md Golam Rosul</u>, Md Sabbir Akhanda, Mona Zebarjadi, *Thermionic energy conversion*, <u>IOP Publishing</u>, 2020

Journal Articles

- <u>Md Golam Rosul</u>, Xiaoming Wang, Keivan Esfarjani, Mona Zebarjadi, Low-resistance contact in MoSe2-based solid-state thermionic devices, Phys. Rev. B 105, 115412 (2022).
 <u>DOI</u>
- 3. <u>Md Golam Rosul</u>, Mona Zebarjadi, Effect of electron-phonon interaction on the thermoelectric properties of bulk MoSe₂. <u>arXiv:2204.02596</u>
- Md Golam Rosul, Doeon Lee, David H. Olson, Naiming Liu, Xiaoming Wang, Patrick
 E. Hopkins, Kyusang Lee, Mona Zebarjadi, *Thermionic transport across gold-graphene-WSe2 van der Waals heterostructures, Science Advances, 2019;5: eaax7827 DOI*
- Rasin Ahmed^{*}, <u>Md Golam Rosul^{*}</u>, Yin Xu, Mona Zebarjadi, Giovanni Zangari, Morphology and Seebeck coefficient of Bi₂Se₃ films electrodeposited on Au (111) substrates, Electrochimica Acta, 368 (2021) 137554 (*Equal contribution) <u>DOI</u>
- Tianhui Zhu, Peter Litwin, <u>Md Golam Rosul</u>, Farjana Ferdous Tonni, Stephen John McDonnell and Mona Zebarjadi, *Transport Properties of Few-Layer NbSe2: from Electronic Structure to Thermoelectric Properties, Material Today Physics* (2022). <u>DOI</u>
Naiming Liu, Tianhui Zhu, <u>Md Golam Rosul</u>, Jon Peters, John E Bowers, Mona Zebarjadi, Thermoelectric Properties of Holely Silicon at Elevated Temperatures, Materials Today Physics, 14 (2020) 100224 <u>DOI</u>

Conference Presentations

- 8. <u>Md Golam Rosul</u>, Rasin Ahmed, Mona Zebarjadi, Giovanni Zangari, Study of Thermoelectric Properties of Mixed Phase Bi₂Se₃ Films Made by Electrodeposition, in MRS spring meeting and exhibit (Phoenix, AZ, April 2019)
- 9. Mona Zebarjadi, <u>Md Golam Rosul</u>, Solid State Thermionic Devices based on 2D van der Waals Heterostructure, in 3rd Annual Energy Harvesting Society Meeting (Falls Church, VA, September 2019)
- Md Golam Rosul, Doeon Lee, David H. Olson, Naiming Liu, Xiaoming Wang, Patrick
 E. Hopkins, Kyusang Lee, Mona Zebarjadi, van der Waals heterostructure based solidstate thermionic coolers, Virtual Conference on Thermoelectrics (Virtual Conference on Thermoelectrics, July 2020)
- 11. <u>Md Golam Rosul</u>, Xiaoming Wang, Mona Zebarjadi, Solid-state thermionic devices: Effect of asymmetry on the device performance (TMS 2021 Annual Meeting and Exhibition, March 2021)
- 12. <u>Md Golam Rosul</u>, Xiaoming Wang, Keivan Esfarjani, Mona Zebarjadi, Asymmetric MoSe₂-based solid-state thermionic devices (AVS Mid-Atlantic Virtual Chapter Meeting 2021, April 2021)

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