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Phonon and Electron Properties of Transition Metal Dichalcogenides – Applications in High-Temperature Electronics

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Electrical Engineering

by

Chenglong Jiang

December 2016

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Committee Chairperson

University of California, Riverside
I would like to express my sincere gratitude for people who I met during my Ph.D. study and who helped me to achieve such success. First of all, I would like to thank my doctoral advisor, Professor Alexander A. Balandin for giving me continuous guidance, support and encouragement during the past four years. Dr. Balandin provided me with great opportunities to work on both fundamental science and cutting-edge technological research projects. He guided me with his wisdom and knowledge to lead my research in the right direction. His high standard towards research is very impressive and it has been a pleasure to work in his laboratory.

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Dedicated

to my parents
Transition metal dichalcogenides are layered van der Waals materials with a number of unique electrical and thermal properties. These materials are of interest from both fundamental science and practical application points of view. In this dissertation, I describe results of my research of the phonon and electron properties of layered transition metal dichalcogenides as well as devices based on these materials. In the first part of this dissertation, I report on the phonon and thermal properties of thin films of tantalum diselenide grown by chemical vapor transport method. The Raman optothermal measurements revealed that the room temperature thermal conductivity in these films decreases with decreasing thickness suggesting strong phonon – boundary scattering. The measurements of electrical resistivity of the field-effect devices with TaSe$_2$ channels have indicated that heat conduction is dominated by acoustic phonons in these van der Waals films. In the framework of this dissertation research, I fabricated of MoS$_2$ thin-film transistors and investigated their high-temperature current-voltage characteristics. The
measurements revealed that MoS$_2$ transistors remain functional to temperatures of at least as high as 500 K and after two month of aging. The comparison of the direct current and pulse measurements has demonstrated that the direct current sub-linear and super-linear output characteristics of MoS$_2$ thin-films devices result from the Joule heating and the interplay of the threshold voltage and mobility temperature dependences. At temperatures above 450 K, a kink in the drain current occurs at zero gate voltage irrespective of the threshold voltage value. This intriguing phenomenon was attributed to the slow relaxation processes in thin films. The results of this dissertation contribute to better understanding of properties of two-dimensional materials, and reveal their potential for electronic applications.
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Chapter 1

Introduction

1.1 Background

From 1947 John Bardeen and Walter Brattain at AT&T’s Bell lab demonstrated the first transistor on germanium with 25 µm to 1971 Intel introduced the first commercial microprocessor on silicon with 10 µm minimum feature size, and to 14 nm Fin Field Effect Transistor (FinFET) technology today, the feature size of transistors has been shrink for ~2000 times [1]. As the channel width of transistors decreasing to nanometer range, the power dissipation become very essential for modern semiconductor industry. Figure 1 shows the road map of feature size development of semiconductor industry. Because the devices are pushing the limitation of materials, research about how to decrease the dissipation power and increase the thermal conductivity of materials becomes more and more popular [2]. Besides of room temperature application of semiconductors, semiconductors are also need in extreme conditions. As the development of electronics in combusting chamber sensing, chemical reaction monitoring, aerospace applications etc. some semiconductor devices have been found that can be operated under those either extreme high or low temperature [3]. The Table 1.1 shows the performance of current commercial semiconductors devices that fulfill the requirements of those extreme conditions. Since the traditional semiconductors is not cost effective to large
Figure 1.1 Plot of years of logic industry “Node Range” labeling. Data extracted from ITRS Reports Executive Summary from 2001 to 2015.

Table 1.1 Traditional semiconductor working temperature ranges.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Bandgap (eV)</th>
<th>Working temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.1</td>
<td>Below 300 °C (SOI)</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Below 200 °C</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>Below 400 °C</td>
<td>[5]</td>
</tr>
<tr>
<td>SiC</td>
<td>2.9 (6H) 3.26</td>
<td>Below 800 °C (6H)</td>
<td>[5]</td>
</tr>
<tr>
<td>GaN</td>
<td>3.45</td>
<td>Below 1000 °C</td>
<td>[5]</td>
</tr>
</tbody>
</table>

volume application, and the band gap management can be achieved by produce different number of layers of two-dimensional materials, it is an opportunity for researchers to seek for better performance and cost effective semiconductors that can be large apply in extreme conditions [3].
1.2 Transition Metal Dichalcogenides

Since 2004 the graphene has been discovered by mechanical exfoliated method [6], it is unique thermal and electron properties has been well studied [7, 8]. The “graphene-like” mechanical exfoliation method has inspired our researchers to conduct research on other two-dimension materials with interesting properties. As a group, layered van der Waals materials can be mechanically or chemically exfoliated by breaking the relatively weak bonding force between the layers. The resulting thin films can be re-stacked into superlattice-type structures with various properties [9-11]. Layered transition metal dichalcogenides (TMD) is an interesting subgroup of inorganic van der Waals materials. TMD materials has a form MX$_2$, where M can be Mo, W, Nb, Ta, or Ti and X=S, Se, or Te. Figure 1.2 shows the position of mentioned elements and some TMDs. TMD materials have some interesting phonon and electron properties. TMD materials also belongs semiconductor, semi-metal or topological insulator. Interesting property also
observed from TMD materials that is charge density wave effects in the temperature range from \(~100\text{K}\) to room temperature. The recently research also indicated that the transition temperature of titanium diselenide thin films are increasing when we thinner down the thin film of TiSe\(_2\). The recent research about Bismum telluride and other topological insulators shows that these quasi-2D crystals of Bi\(_2\)Te\(_3\) have electrical and thermal properties that are substantially different from those of bulk Bi\(_2\)Te\(_3\) [11, 12]. Another research conducting on MoS\(_2\) shows the band gap level and structure changed since they thinner down MoS\(_2\) from multilayer to single layer. All the interesting phenomena mentioned above and etc., showed us the interesting properties of TMDs and indicated the potential applications of those materials.

1.3 Thermal Conductivity of Thin Films

As the devices dimension shrinking down to nanometer range, thermal effect becomes very important for channel materials. So, it is critical to investigated thermal conductivity of semiconductor thin films. There are several methods to measure thermal conductivity of thin films, including 3\(\omega\), opto-thermal Raman, etc. During the measurement, the substrates also play very important role. According to phonon boundary condition, when we thinner down the thin films and narrow down dimensions of materials. The phonon boundary is decreasing and during the meantime the phonon scattering is increasing, and this process will dramatically decrease thermal conductivity of materials. Not only phonon scattering influences the value of thermal conductivity, but also electron can carry some heat. So in order to sort out either phonon or electron
contribution to the thermal conductivity of semiconductors, four probe measurement should be performed on thin films, and use Wiedemann–Franz law to determine the electron contribution of thermal conductivity. The first exam thin film material is graphene. It has an ultra-high thermal conductivity. But MoS$_2$ and TaSe$_2$ showed the predicted results that is thermal conductivity is decreasing during thinner down thin films. Also, to find more suitable material to be future channel materials for semiconductor industry, more materials should be studied.

1.4 High Temperature Applications of Semiconductors

Many electronic components for control systems and sensors are required to operate at temperature of ~500 K. Examples of the high temperature applications include turbine engine control in aerospace and energy generation or the oil-field instrumentation. The availability of transistors and circuits for high temperature (T $\geq$ 500 K) operation is limited. Devices made of SiC, GaN, and other conventional large-band-gap semiconductors hold promise for extended high-temperature operation but are still not cost-effective for high volume applications. There is a need for new material systems that can be used for fabrication of field-effect transistors (FETs), thin-film transistors (TFT), and chemical FET and TFT based sensors functional at high temperatures. Recent advances in the exfoliation and growth of quasi two-dimensional (2D) layered materials—referred to as van der Waals materials—have resulted in a surge of interest to their possible device applications [2, 9, 12, 14]. One of the most promising materials among the layered transition-metal dichalcogenides (TMD) is MoS$_2$ [15, 16]. A single
atomic layer of MoS2 shows a direct band gap of $E_g = 1.9$ eV while bilayer and bulk MoS$_2$ exhibits an indirect band gap of $\sim 1.6$ eV and $\sim 1.3$ eV, respectively [17, 18]. The interest to MoS$_2$ thin films and devices based on this material is explained by the relatively large energy band gap of MoS$_2$, large on-off ratio of MoS$_2$ TFT [19], low levels of flicker noise in MoS$_2$ TFT [20] and relatively high thermal conductivity of MoS$_2$ thin films compared to thin films of other TMDs [21]. It was also shown that MoS$_2$ TFT can be used as selective gas and chemical sensors [22].
References


Chapter 2

Metrology

2.1 Mechanical Exfoliation of van der Waals Materials

Mechanical exfoliation of 2D material was first developed by Novoselov in 2004 to produce graphene [1]. Later on, this method has been widely used to produce other 2D materials thin film, like MoS$_2$ [2], black phosphorous [3], TaSe$_2$ [4], and etc. The principle of this method is using the viscosity of tape to break the Van der Waals force between layered materials to make thin films of those 2D materials. Van der Waals force is a weak bond between two layers of 2D materials. The first tape has been proved that can be used for exfoliation of 2D materials is scotch tape. Later on, researchers found out Nitto tape can also do exfoliation and also provide a relatively clean surface of substrate.

In order to do exfoliation of 2D materials, first you have to have some high quality single crystal bulk 2D materials. After placing some bulk materials on the tape, the material has to be cleaved for several times by fording the tape. Then the tape will have some area covered by materials. After examining the whole area of 2D material, the area with more transparency is picked and placed on top of substrate that 2D materials supposed to sit on. After gently rubbing the contact area of tape and substrate for several minus, slowly remove the tape from the substrate. Because the exist of Van der Waals force between substrate and 2D material. Some flake will remain on top of substrate. The whole exfoliation process is completed. The schematic of entire mechanical exfoliation process
Figure 2.1 Schematic of mechanical exfoliation process.

Figure 2.2 Optical microscope image of TaSe₂ thin films. Thinner sample has dark blue color, and the cold color indicates the sample is very thick.

is showed in Figure 2.1. Since the dimension of exfoliated flakes on substrate is usually in micro meter range. We need optical microscope to identify the position of exfoliated flake. The 2D materials have different light absorbing rate. For example, single layer graphene can observe \(-3\)% of visible light [5]. This is a roughly method to know how many layers of the exfoliated flakes. Figure 2.2 shows the optical microscope image of exfoliate TaSe₂ thin films. The thinner layer shows a dark blue color. With increasing of
layers of thin film flakes, the color is changing from dark blue to light blue and turning into gold color. This method is fast only for roughly identify the thickness of thin film flakes, and prepare for further examination or fabrication process. The accurate thickness of thin films has to be determined by AFM measurement. Because the AFM measurement is time consuming, I also develop another rapid method to measure the thickness of thin films. This method is detail describe in chapter 3 of this dissertation. Compared mechanical exfoliation method to chemical exfoliation, Molecule Beam Epitaxy, chemical vapor deposition method, mechanical exfoliation method has the advantage that it can provide thin films with higher crystal quality, less defect of flake and less contamination of flake surface [6]. Even though mechanical exfoliation method has some disadvantage like, exfoliated flakes are not uniform every time, flake dimension is very small, and not cost efficiency of large scale production, researchers can use this high quality thin films flake to investigate the properties of materials with less disrupt like defects, contaminations, and etc. So in order to study the pure properties of materials, mechanical exfoliation method is used during my Ph.D. research.

2.2 Raman Spectroscopy

Solid state materials are formed by single atoms. Different stacking ways of atoms forms different crystal structure of materials. Each solid-state material has it unique crystal structure and parameters. When the atoms in different crystal structure, they vibrate in different ways. There are four vibration modes of 2D thin film materials which is showed in Figure 2.3 [7]. The vibration modes separate into in-plane vibration mode
Figure 2.3 Schematic of TMD thin films main vibrational modes.

and out-of-plane vibration mode. The vibration of atoms in crystal excite phonons into crystal. Raman is the technique to detect phonon properties of materials. When the photon hit the atom of material, there are scattered by phonons, electrons and etc. This scattering separated into two different type by energy conservation, the elastic scattering and inelastic scattering. The schematic of two scattering mode is shown in Figure 2.4. The elastic scatting is the electron is excited to a higher energy level by photon and jump back to the same energy level and emit a photon. The absorbed and emitted photons are at same energy level and energy is conserved. So elastic scattering cannot be used to investigate properties of materials. The inelastic scattering is separated into stoke and anti-stoke scatting. The difference between elastic and inelastic scattering is the electron return to a different energy level compared with original energy level. If it returns to a
Figure 2.4 Schematic of photon and phonon scattering.

higher energy level compared with original energy level, then it is stoke scattering, otherwise it is anti-stoke scattering. Since usually anti-stoke scattering emitted very low energy photons, it appears at very low frequency level of Raman spectrum. So it need very low frequency cut-off filter to detect. Since the setup we have in lab has a ~110 cm\(^{-1}\) cut-off frequency, the anti-stoke Raman is not studied in this dissertation. The vibration modes are described before, but not all vibration mode is Raman active. Some of the activation mode is infrared active, and some are not selected by Raman selection Rules [8]. Because the vibration modes and crystal structure are different, every material has it is unique Raman spectrum. Raman is very sensitive with crystallinity, so Raman can be not only to determine the materials, but also determine the quality of materials. Since the sample we examined are very thin, and laser light of Raman has several hundred-
Figure 2.5 Raman spectrum of single layer, bi-layer and multi-layer MoS$_2$.

I also developed a method to measure thickness of 2D materials by using peak ratio of material and silicon substrate. The detail is described in chapter 3. The accuracy of Raman spectrum can be narrow down to 0.1 cm$^{-1}$ by using Gauss or Lorentz curve fitting [9], so using Raman method to measure thickness of 2D materials is very accurate. Another example of Raman determine thickness is MoS$_2$. Figure 2.5 shows the Raman spectrum from single layer to multilayer MoS$_2$. The difference between two Raman peak is increasing by increasing the number of layers of flake. This is because when more layers stacking, the space between layers is decreasing.
Figure 2.6 Raman spectrum of TaSe$_2$ thin films at temperature from 80 K to room temperature.

and also maybe Coulomb interaction between layers get stronger between layers [10]. Another application of Raman is measure the temperature of sample. Figure 2.6 shows the TaSe$_2$ sample with different temperature. The peak position changed by increasing the temperature. The main reason of peak position changing is the phonon energy is increasing by increasing the temperature and also graphene has bond length decreases and graphene experiences thermal contraction instead of expansion [11]. This method also developed into opto-thermal method to measure thermal conductivity of materials. The details are described in next section. The advantage of Raman is rapid and accurate characterization of materials, and Raman is widely used in academia and industry.
2.3 Raman Opto-Thermal Method

The Raman Opto-Thermal method to measure thermal conductivity of thin films was develop in our lab [7, 9, 12, 13]. We are the first used this method to measure the thermal conductivity of graphene. By this method, thermal conductivity of graphene is determined as 3000 W/mK at room temperature. The schematic of Raman opto-thermal method is shown in Figure 2.7. In order to calculated thermal conductivity of thin films,

First, the thin film is placed in a cold-hot cell which use liquid nitrogen and heater to maintain the chamber at certain temperature from liquid nitrogen temperature up to 600 °C. The temperature control has a 0.1 °C accuracy. The Raman spectrum is taken from liquid nitrogen temperature to 600 °C with a 10 °C step. Since the phonon energy is depended on material’s temperature, peak positions at different temperature range can be

![Figure 2.7 schematic of Raman opto-thermal method.](image-url)
fitted to a linear equation. By this step, we know the temperature coefficient of measured material. The 488 nm laser of Raman can accurate exquisite spectrum information and heat the thin film. The spectrum of different laser power is taken in order to heat sample into different temperature. The difference of temperature at different laser power is determined by using the peak position of two spectrum and temperature coefficient that calculated before. Another information that can be extracted from Raman spectrum is the laser light absorb ratio by comparing the Si peak intensity of Si/SiO\(_2\) substrate and with thin film on top of Si/SiO\(_2\) substrate. With the above information, the numerical modeling method can be used to calculated thermal conductivity of thin film.

The modeling of heat diffusion thin films on Si substrate was performed using the finite element method implemented in COMSOL software package with the Heat Transfer Module. The substrate consists of 0.5mm Si and 300 nm SiO\(_2\) layer. The radius of the Si/SiO\(_2\) used in the simulated domain is 100 \(\mu\)m. The thickness and radius of thin films varied for different flakes according to the values obtained experimentally. The radius of laser spot size is 0.5 \(\mu\)m. The heat conduction was simulated by solving numerically Fourier’s law \(-\nabla \cdot (K \cdot \nabla T) = Q\) where \(K\) is the thermal conductivity, \(T\) is the absolute temperature, and \(Q\) is the power density of the heat source. The thermal conductivity values of Si and SiO\(_2\) used in the simulation were 140 W/mK and 1.4 W/mK, respectively. The absorbed laser power density along z direction can be described by the following function \(Q(z) = Q_0 \cdot \alpha \cdot exp(-\alpha \cdot z)\), where \(Q_0\) is the laser power density at the top surface of the sample, \(\alpha\) is the absorption coefficient of thin film obtained in previous steps. For a given dissipation power and sample geometry, the
numerical modeling generates a temperature profile in the sample structure. Due to the axial symmetry of the simulation domain around z direction, the temperature profile in the whole sample structure can be fully represented by the simulation results in z-\( r \) cross-section, where \( r \) is coordinate in the cylindrical coordinate system. The thermal conductivity of thin films was determined via the iteration approach as described in [12].

2.4 Transition Metal Dichalcogenides Devices Fabrication

To measure the electron properties of thin films, devices fabrication technique has to be performed on thin films samples [14-16]. The schematic of the entire process is showed in Figure 2.8. Since the exfoliated thin films are very small compare with landmark on Si/ SiO\(_2\) substrate, another small alignment mark has to be fabricated before final contact. The fabrication process includes spin coating of resistance, E-beam Lithography, metal deposition and lift-off. Spin coating speed is using Headway SCE spin coater to spread a thin layer (usually few hundred nanometer) of resistance. The spinning is carried on with 4000 rpm speed for 40 second to guarantee the uniformity and thickness of MMA layer. After 10 minus baking at 180 °C on hot plate, the solvent in liquid phase resistance will be completely removed. The second layer which is PMMA is deposit by using the same procedure with MMA. The reason of depositing two different polymer layers is that the develop rate of MMA and PMMA are different, MMA is faster than PMMA. During the same development time after expose to e-beam, MMA develop faster and form a wider trench than PMMA. After the metal deposition process, this wider trench help to prevent metal layers at contact area and resistance covered area
Figure 2.8 Schematic of device fabrication process.
connect with each other. After resistance deposition, E-beam Lithography is started on LEO SUPRA 55 e-beam lithography machine. The writing pattern is designed and aligned previously on DesignCAD 2000 software. The e-beam writing procedure including align the pattern and beam position together. This step make sure the pattern is writing on the same position as designed. The Neabity software turned a SEM machine to a e-beam lithography machine. E-beam lithography requires certain amount of electron hitting the resistance, for PMMA, the amount is from 400 to 800 µC/m². The electron beam voltage should be 20 KeV and above, and also the beam current should be no less than 70 µA to guarantee the quality of e-beam expose. The exposure time is calculated automatically by software with combination of exposure area, input area dose and measured current of electron beam. After e-beam lithography, the sample is developed in a solution with1:3 mixture ratio of MIBK and IPA. The developing time can be varied from tens of seconds to several minus, which depends on the developer and area dose during e-beam writing. The MIBK (1) : IPA (3) developer can give the finest resolution of developing compare with other ratio of mixture or pure MIBK. Either the pattern at the designed position or not is confirmed by using optical microscope. The contrast of exposed area and unexposed area is different. For most of the time, the development procedure can not completely remove the resistance. There will be very small amount of resistance remained on the exposed area. Small power of oxygen plasma treatment for 10-20 second will completely remove the residue of resistance and help to form the better metal to semiconductor contact. The substrate should be transfer very fast to E-Beam Evaporator machine to prevent oxidation of thin film at contact area. E-beam Evaporation
is performed on Temescal BJD-1800 e-beam evaporator. In order to form a ohmic contact between metal electrodes and semiconductor, the metal has to be carefully chosen. According to the law, the working function of metal is similar to electron affiliation of semiconductor can form an omic contact. After the e-beam evaporator chamber pump down to $10^{-6}$ Torr, the metal should be started to deposit with a very small rate like 0.5 to 1 Å/s. The small deposition rate can prevent the damage of semiconductor surface and improve the deposition quality of contacting area. After metal deposition, the sample is soaked in acetone for at least four hours to completely remove the unexposed resistance. The metal layer which deposit on top of unexposed resistance area will be removed and left only exposed area with metal contacts. Even though the sample has been dipped in solvent for a very long time, it is not guaranteed the resistance is fully removed by solvent. Thermal annealing is also needed for some device fabrication process. The thermal annealing for long time with nitrogen or argon gas protection will help with removing residues and also can improve the quality of metal semiconductor contacts. With all the steps described above, the device is ready for characterization.

2.5 Various Device Characterization Methods

Device characterization including electron properties characterization and metrology characterization. To measure the electron properties of devices, the devices have been put into Lakeshore probestation which is sitting on optical table to avoid vibration influence on device characterization. Lakeshore probestation can pump down to $10^{-4}$ Torr. The vacuumed chamber of Lakeshore can provide a more stable testing environment.
Lakeshore probestation also equip with temperature control system. With the help of liquid nitrogen or helium and a heating stage, the testing temperature of sample can be changed from 7 K to 400 K. The temperature control system can make the chamber temperature stabilized with a $\pm 0.05$ K accuracy. The electron properties characterization is conducting on Angilent B1500 semiconductor analyzer. The semiconductor analyzer is capable to do two to four terminal measurement, pulse measurement, and etc. Figure 2.9 shows the temperature dependence transport measurement of MoS$_2$ devices.

Metrology characterization includes verify the thickness of thin films and precise length and width dimensions. All the metrology characterization are conducted after

![Figure 2.9 Transport measurement of MoS$_2$ device at room temperature, 200 K and 100 K.](image)

Figure 2.9 Transport measurement of MoS$_2$ device at room temperature, 200 K and 100 K.
Figure 2.10 The AFM and SEM picture of MoS$_2$ devices.
electron or phonon properties characterization because the metrology characterization tool may introduce defects or contaminations to thin films. The thickness of thin films is measured by AFM. Figure 2.10 (a) shows the AFM measurement of MoS$_2$ thin film. The AFM is operated under tapping mode which the AFM tip keeps a certain distance between sample surface. The sample surface is not leveled during measurement. After manually level the AFM image, the software can accurately extract thickness data of thin films. Even though AFM is not a time-consuming method, but it is a very reliable method to measure thickness of thin films. Although Raman can also determine the thickness of thin films, it is still need AFM to verify the thickness. To measure the length and width dimension of devices, SEM can provide more accurate data than optical microscope. Since it has been proved that the electron irradiation can influence the properties of devices, SEM measurement has to be done after all other measurement has been finished. The Si/SiO$_2$ wafer is insulator, so the surface charging has a great influence on SEM measurement. The solution is keeping the electron beam voltage as low as possible, usually 1 to 5 KeV can give a better image contrast. By lower down the scanning speed, the image has better resolution. Figure 2.11 (b) shows the SEM image of a MoS$_2$ device. The metrology and electron properties characterization provides the detail and accurate information to extract other parameter like electron mobility.
References


Chapter 3

Phonon and Thermal Properties of Exfoliated TaSe$_2$ Thin Films

3.1 Introduction and Motivations

In this paper, we report on the physical properties of TaSe$_2$ films prepared by “graphene-like” mechanical exfoliation. We focus on their phonon and thermal properties, which are essential for the metrology of such films and for possible device applications. Indeed, apart from graphene and hexagonal boron nitride, layered van der Waals materials typically have rather low values of thermal conductivity, $K$ [1-3]. Thin films of such materials should have even lower $K$ values due to phonon–boundary scattering. However, because the thermal conductivity in such materials is strongly anisotropic (substantially larger in-plane) and the cleaved surfaces can be rather smooth, the change in $K$ due to film thinning is difficult to predict. The degraded thermal conductivity can become a major impediment for practical applications due to unavoidable power dissipation and self-heating effects. The contribution of electrons to thermal transport in thin films of metal dichalcogenides is also not known precisely. Thus the main goals of this study are to characterize the phonon spectrum, the relative contributions of phonons and electrons to heat conduction and the extent of thermal conductivity degradation in TaSe$_2$ thin films.
The crystal structure of TaSe$_2$ consists of Se-Ta-Se layers containing Ta in trigonal prismatic coordination. The weak interlayer van der Waals bonding permits the facile mechanical delamination and exfoliation of such crystals, and it also leads to several TaSe$_2$ polytypes that differ in the relative orientation of the layers and their stacking arrangements. In this work, we specifically examine 2H-TaSe$_2$. The structure of this polytype has a two-layer repeat pattern (AcA BcB), within which the trigonal prismatic units are rotated $60^\circ$ with respect to each other [4, 5].

**3.2 Material Synthesis and Sample Preparation**

The 2H-TaSe$_2$ crystals used in this study were derived from 3R-TaSe$_2$ powder according to standard methods. Briefly, we first prepared TaSe$_2$ from the elements. After two firing cycles at 700 and 900 °C, the product consisted of mostly 3R-TaSe$_2$ with traces of the 2H-TaSe$_2$ form, which is typical for this synthetic route [5]. Then this material was heated in the presence of I$_2$ within a sealed ampule with a 100 °C temperature gradient; these “chemical vapor transport” conditions [6] resulted in clusters of metallic gray crystals. As shown in Figures 1(a), 1(b), and 1(d) inset, these crystals have lateral dimensions of approximately 200–800 lm and thicknesses of approximately 5 to 30 µm. Powder X-ray diffraction (XRD) reveals that the major phase of crystallized material is the 2H-TaSe$_2$ polytype; as shown in Figure 1(c), the experimental diffraction pattern matches literature data for 2H-TaSe$_2$ very well [7, 8]. In addition, we observe traces of 3R-TaSe$_2$, in line with common observations of polytype mixtures within Ta-Se systems [4, 5]. The presence of this minor component does not affect subsequent samples that are
Figure 3.1 Characterization of 2H-TaSe₂ crystals grown by the chemical vapor transport method: (a) Optical microscopy image. (b) SEM image. (c) Powder X-ray diffraction data. The top red trace shows the pattern from as-grown TaSe₂ crystals; the primary component is 2H-TaSe₂ (database comparison shown at bottom) with traces of 3R-TaSe₂ (marked with *). (d) Energy dispersive X-ray spectroscopy data for a 2H-TaSe₂ crystal (SEM (inset)). (e) XPS spectra showing the Ta 4f photoelectric peaks from 2H-TaSe₂ crystals before and after peel-off from surface layers. The spectrum of Ta₂O₅ on Ta foil is included for reference. (f) XPS spectra showing the Se 3d photoelectric peaks from 2H-TaSe₂ crystals before and after peel-off from surface layers. Reprinted from: Z. Yan, C. Jiang, T. R. Pope, C. F. Tsang, J. L. Stickney, P. Goli, J. Renteria1, T. T. Salguero and A. A. Balandin, J. Appl. Phys. 114, 204301 (2013); http://dx.doi.org/10.1063/1.4833250 with permission from AIP Publishing LLC.
samples that are derived from the mechanical delamination of 2H-TaSe$_2$ single crystals. Both energy-dispersive X-ray spectroscopy (EDS) and electron probe microanalysis (EPMA) data confirm that the composition of the crystals is within a few percent of the ideal stoichiometry (Figure 3.2 (d)). Several factors that may contribute to the observed variation include: (i) EPMA data were collected from a non-ideal crystal surface, which introduces additional error, (ii) incorporation of oxide impurities, and/or (iii) possible non-stoichiometry, which is known in the range of $x < 0.03$ and $0.25 < x < 0.64$ for 2H-Ta$_{1-x}$Se$_2$ [5, 9]. In particular, X-ray photoelectron spectroscopy (XPS) indicates that the TaSe$_2$ crystal surfaces become oxidized upon exposure to air. Figures 1(e) and 1(f) show XPS data for the Ta 4f and Se 3d photoelectric peaks from a series of samples. By comparison with a reference sample of Ta foil that exhibits both Ta metal and its native oxide Ta$_2$O$_5$ [10], we can see that 2H-TaSe$_2$ crystals also contain Ta oxide. However, upon mechanical delamination of surface layers from the 2H-TaSe$_2$ crystals, the only remaining visible species is TaSe$_2$.

Thin films of 2H-TaSe$_2$ were prepared on Si/SiO$_2$ substrates following the standard “graphene-like” approach [11-13]. The thickness $H$ of the films ranged from a few trilayers to $H = 300$ nm. The Se-Ta-Se atomic trilayer has a thickness 6.359 Å and the lattice parameter 3.434 Å (see Figure 3.2). The crystal structure of 2H-TaSe$_2$ belongs to the space group D6h4 and it has a unit cell consisting of two Se-Ta-Se trilayers. We used Raman spectroscopy as a metrology tool to verify the quality of the crystals and determine the thicknesses of the flakes. Raman spectroscopy (Renishaw InVia) was
Figure 3.2 Crystal structure of 2H-TaSe$_2$ (a) and schematic of its main vibrational modes. Reprinted from: Z. Yan, C. Jiang, T. R. Pope, C. F. Tsang, J. L. Stickney, P. Goli, J. Renteria1, T. T. Salguero and A. A. Balandin, J. Appl. Phys. 114, 204301 (2013); http://dx.doi.org/10.1063/1.4833250 with permission from AIP Publishing LLC.
Figure 3.3 (a) Raman spectrum of the exfoliated thin films of TaSe$_2$ on Si substrate. The data is shown for the films thickness ranging from ~260 nm to below 30 nm. The characteristics $E_{2g}$ and $A_{1g}$ peaks of TaSe$_2$ are clearly observed. The intensity of Si peak at 522 cm$^{-1}$ is increasing with the decreasing thickness of TaSe$_2$ film. (b) The ratio of the intensity of Si peak to $E_{2g}$ peak in Raman spectrum of TaSe$_2$. The calibrated intensity ratio can be used for nanometrology of TaSe$_2$ films. The insets show optical microscopy images of two flakes of TaSe$_2$ with substantially different thickness. The thinner flakes appear blue in color whereas the thicker flakes appear yellow. Reprinted from: Z. Yan, C. Jiang, T. R. Pope, C. F. Tsang, J. L. Stickney, P. Goli, J. Renteria1, T. T. Salguero and A. A. Balandin, J. Appl. Phys. 114, 204301 (2013); [http://dx.doi.org/10.1063/1.4833250](http://dx.doi.org/10.1063/1.4833250) with permission from AIP Publishing LLC.
performed in the backscattering configuration under 633 nm laser excitation. An optical microscope (Leica) with a 50× objective was used to collect the scattered light. To avoid possible self-heating effects, the excitation laser power for Raman spectroscopic measurements was kept low at P < 0.5 mW (on the sample surface).

3.3 Raman Metrology of van der Waals Thin Films

Figure 3(a) shows Raman spectra of TaSe$_2$ for nine exfoliated thin films with different thicknesses $H$ ranging from a few nm to >250 nm. The thicknesses of the exfoliated films were measured by atomic force microscopy (AFM). The 2H-TaSe$_2$ crystal possesses 12 zone center lattice vibrational modes. Four of these modes ($E_{2g}^2$, $E_{1g}$, $E_{12g}^1$, and $A_{1g}$) are Raman active. The atomic displacements for these vibrational modes are shown in Figure 3.3 (b). The $A_{1g}$ and $E_{12g}^1$ modes can be clearly seen in the Raman spectra at ~ 235 cm$^{-1}$ and ~ 207 cm$^{-1}$, respectively (see Figure 3.3 (a)). The modes with the energy lower than 130 cm$^{-1}$ are blocked by the Rayleigh filter of the spectrometer. There have been few reports of Raman data for TaSe$_2$ [14-17]. In contrast, earlier studies used bulk TaSe$_2$ samples and focused on the lower frequency portion of the spectrum [14-16]. Comparison of our data with that in Ref. 17 indicates that the peak positions and mode assignments are consistent.

The pronounced Si peak from the substrate appears at 522 cm$^{-1}$. The intensity of the Brillouin zone-center Si peak is proportional to the interaction volume. It explains why the peak intensity is increasing with decreasing thickness of TaSe$_2$ film placed on top of Si substrate. The ratio of the intensity of Si peak to that of $A_{1g}$ or $E_{2g}$ can be used for
Figure 3.4 (a) Evolution of Raman spectrum of 2H-TaSe$_2$ thin film with temperature. A new peak appears in the spectra at about 250 cm$^{-1}$ after temperature decreases below 220 K. The peaks shift their position with temperature. (b) Temperature coefficients $\Gamma_1$ and $\Gamma_2$ for $E_{2g}$ and $A_{1g}$ Raman peaks of 2H-TaSe$_2$, respectively. The temperature coefficients can be used for the extraction of the thermal conductivity of thin films using the Raman optothermal method. Reprinted from: Z. Yan, C. Jiang, T. R. Pope, C. F. Tsang, J. L. Stickney, P. Goli, J. Renteria1, T. T. Salguero and A. A. Balandin, J. Appl. Phys. 114, 204301 (2013); http://dx.doi.org/10.1063/1.4833250 with permission from AIP Publishing LLC.
determining the thickness of the exfoliated film. Figure 3.3 (b) presents the ratio of the intensity of the Si peak to that of the E\textsubscript{2g} peak, I(Si)/I(E\textsubscript{2g}), as a function of thickness H. This ratio decreases exponentially with increasing film thickness and can be fitted with the equation $I(Si)/I(E_{2g}) = 11.2 \exp(-H/54.9) - 0.11$ (here the thickness H is in the units of nm). The obtained dependence can be used as a calibration curve for the Raman-based nanometrology of TaSe\textsubscript{2} films. The approach can be extended to other layered van der Waals materials. From a practical perspective, the Raman metrology of exfoliated films are easier and faster than AFM inspection.

The temperature dependence of Raman spectra of 2H-TaSe\textsubscript{2} was studied in the temperature range from 83 K to 613 K. The sample with exfoliated TaSe\textsubscript{2} flake was put in a cold-hot cell where the temperature was controlled externally with 0.1°C accuracy. Figure 3.4 (a) shows the Raman spectrum of a typical TaSe\textsubscript{2} flake measured at different temperatures. The Raman peak positions of both A\textsubscript{1g} and E\textsubscript{12g} modes move to lower wavenumber range (red shift) when temperature increases. The Raman peak positions of TaSe\textsubscript{2} A\textsubscript{1g} and E\textsubscript{12g} modes at the different temperatures are shown in Figure 3.4 (b). In the measured temperature range, the temperature dependence of A\textsubscript{1g} and E\textsubscript{12g} modes can be represented by a linear relation $\omega = \omega_0 + \Gamma T$, where $\omega_0$ is the frequency of Raman peak when temperature T is extrapolated to 0 K, and $\Gamma$ is the first-order temperature coefficient. The extracted temperature coefficients of A\textsubscript{1g} mode and E\textsubscript{12g} mode are $\Gamma_1 = 0.013$ cm\textsuperscript{-1}/°C and $\Gamma_2 = 0.0097$ cm\textsuperscript{-1}/°C, respectively. The softening of A\textsubscript{1g} and E\textsubscript{2g} modes with increasing temperature is in agreement with the report for bulk 2H-TaSe\textsubscript{2} [14].
However, a direct quantitative comparison of the temperature coefficients is not possible because our data are for thin films rather than bulk and for a different temperature range.

### 3.4 Thermal Properties of TaSe$_2$ Thin Films

The obtained temperature coefficients characterize the inharmonicity of the TaSe$_2$ crystal lattice. They also can be used to extract the thermal conductivity data using the Raman optothermal technique, which was originally developed for graphene [14]. The data presented in Figure 3.4 (b) can be used as calibration curves for determining the local temperature rise in TaSe$_2$ flakes. The temperature is extracted from the shift of Raman peak positions. In a sense, the Raman spectrometer is thus used a thermometer. For the thermal measurements, we intentionally increase the intensity of the excitation laser so that it induces a local heating of the sample. The low thermal conductivity of TaSe$_2$ allows one to achieve local heating at the power level of about 1–2 mW. Figure 3.5 (a) shows a characteristic Raman mode of the tested TaSe$_2$ flake at low and high excitation power. The Raman peak position of E$_{2g}$ peak shifts from 209.1 cm$^{-1}$ to 207.7 cm$^{-1}$ as the power increase by 90%. The calculated change in the local temperature introduced by laser is ~144°C. The measurements were repeated using another Raman peak of TaSe$_2$ to ensure reproducibility of the local temperature measurement. The temperature rise for a known dissipated power and sample geometry allows one to determine the thermal conductivity [18]. We have used the finite element method (FEM) to simulate the heat dissipation in the samples under test. The thermal conductivity was determined via the iteration approach. For the first simulation run, the thermal
Figure 3.5 (a) Shift and broadening of the Raman peaks of 2H-TaSe$_2$ as a result of local heating with the excitation laser. (b) Intensity ratio of the Si Raman peak from the substrate without thin film to that of the substrate covered with 2H-TaSe$_2$ thin film. The data allow one to estimate the amount of power absorbed by the film. The inset shows a model used for extraction of the thermal conductivity of thin films of 2H-TaSe$_2$. Reprinted from: Z. Yan, C. Jiang, T. R. Pope, C. F. Tsang, J. L. Stickney, P. Goli, J. Renteria1, T. T. Salguero and A. A. Balandin, J. Appl. Phys. 114, 204301 (2013); http://dx.doi.org/10.1063/1.4833250 with permission from AIP Publishing LLC.
conductivity of TaSe$_2$ flake was assumed to have the value of $K_0$. The numerical simulation with the assumed value of thermal conductivity resulted in the modeled temperature rise $\Delta T_0$. The simulated temperature rise was compared with the experimental temperature rise $\Delta T$. If $\Delta T_0$ was larger (smaller) than $\Delta T$, the assumed value of the thermal conductivity $K$ was increased (decreased) in the next run until the simulated temperature rise matched the experimental data and the final value of $K$ was obtained. This procedure also requires the knowledge of the power dissipated in the thin film. The power level at the sample surface is measured directly with a detector. The absorption coefficient in the thin film can be deduced from the ratio of the integrated Raman intensity of Si peak from the substrate with TaSe$_2$ films placed on top of it to the Si peak of the substrate not covered with the TaSe$_2$ peak (see Figure 3.5 (b)). One can see that this ratio decreases when the film thickness increases and goes all the way to zero, which means that all laser power is absorbed in the film. The film thickness dependence of the Si peak intensity ratio can be fitted by an exponential decay function $I_{51}(H)/I_{510} = 1.06 \exp(-H/27.1) - 0.04$, where $H$ is the film thickness in unit of nm, and the extracted absorption coefficient, $a$, is 27.1 nm$^{-1}$. The details of the FEM based procedure for extraction of thermal conductivity have been described in Ref. 19.

The inset to Figure 3.5 (b) presents a schematic of the simulated sample structure. The radius of simulated domain size is 100 $\mu$m and the radius of TaSe$_2$ flake and the laser spot are 4 $\mu$m and 0.5 $\mu$m, respectively. The thicknesses of TaSe$_2$ flakes used for extraction of thermal conductivity were $H = 45$ nm, $H = 55$ nm, and $H = 85$ nm. The thickness of the silicon dioxide layer and silicon substrate were 300 nm and 0.5 mm,
respectively. The silicon substrate was placed on an ideal heat sink so that the temperature at the bottom side was fixed at 300 K. The adiabatic conditions were assumed at other external boundaries. For the TaSe$_2$ flake with H = 45 nm we obtained the experimental shift in the Raman peak position $\Delta \omega = 1.4$ cm$^{-1}$ as the power on the sample surface changed from 0.11 mW to 1.15 mW. This corresponds to a local temperature rise of $\Delta T = 144$ K. The software-enhanced resolution of the micro-Raman spectrometer in these measurements was estimated to be 0.1 cm$^{-1}$, which sets the experimental error at about 10%. Errors related to radiative losses were estimated to be less than 10% due to the relatively fast time scale of the measurements. The results of the measurements are summarized in Table 3.1. One can see that the room temperature thermal conductivity in these films decreases from its bulk value of about 16 W/mK to ~9 W/mK in 45 nm thick films. Although the electrical and thermal transport properties of graphite intercalation compounds and MX$_2$ materials were studied even earlier than mechanically exfoliated graphene [20], only a few prior reports have addressed the thermal properties of TaSe$_2$ and related materials [21-23]. It has been reported that the room temperature thermal conductivity of bulk 2H-TaSe$_2$ is ~16 W/mK [23]. Our results for mechanically exfoliated thin films are consistent with the prior measurements for bulk 2H-TaSe$_2$ [21-23].

Table 3.1 Thermal conductivity of exfoliated 2H-TaSe$_2$ thin films at room temperature.

<table>
<thead>
<tr>
<th>Thickness H (nm)</th>
<th>45</th>
<th>55</th>
<th>85</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (W/mK)</td>
<td>9</td>
<td>11</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>
For practical applications, it is important to understand whether the heat conduction is dominated by the phonon or electron contributions. To determine this distinction, we fabricated four-terminal devices with the channels implemented with thin film 2H-TaSe$_2$. We used electron beam lithography to define the top metal contacts for the electrical measurements. The top contacts were fabricated with 10 nm of Ti and 100 nm of Au. Figure 3.6 shows the current-voltage (I-V) characteristics of a representative device. The insets show the optical microscopy image of the 2H-TaSe$_2$ device and the linear region used for extraction of the electrical conductivity $\sigma$. The channel lengths, widths, and thicknesses were 9 $\mu$m, 6.5 $\mu$m, and 80 nm, respectively. The experimentally determined conductivity of the 2H-TaSe$_2$ channel was $\sigma = 0.365$ $1/\Omega$m for this device. Using the Wiedemann–Franz law, $K/\sigma T = (\pi^2/3)(k_B/e)^2$, we estimated that the contribution of electrons to thermal conductivity of thin films of intrinsic 2H-TaSe$_2$ is $\sim 3\times 10^{-6}$ W/mK. This means that the heat conduction is dominated by phonons. The electrical conductivity of the synthesized 2H-TaSe$_2$ samples before exfoliation was substantially higher. However, the thermal transport was still dominated by the phonons.

Our data indicate that the thermal conductivity starts to decrease when the film thickness becomes comparable to the phonon mean free path in the material. The latter suggests that the observed decrease of the thermal conductivity, as compared to bulk value, is related to the acoustic phonon–boundary scattering. This is a non-trivial conclusion because one may have expected that in exfoliated thin films of van der Waals materials the smooth interfaces of the cleaved films will lead to negligible phonon—boundary scattering. It also is known that the thermal conductivity in MX$_2$ materials is
Figure 3.6 Current-voltage characteristic of a two-terminal device with 2H-TaSe$_2$ channel. The upper inset shows optical microscopy image of the device. The lower inset shows the small bias region of I-V curve used for determining the resistivity of the exfoliated flake of 2H-TaSe$_2$. Reprinted from: Z. Yan, C. Jiang, T. R. Pope, C. F. Tsang, J. L. Stickney, P. Goli, J. Renteria1, T. T. Salguero and A. A. Balandin, J. Appl. Phys. 114, 204301 (2013); http://dx.doi.org/10.1063/1.4833250 with permission from AIP Publishing LLC.

strongly anisotropic (much larger in plane K) and thus variations of thickness may not necessarily produce strong effects. Our results indicate that the thermal transport in exfoliated films on substrates is dominated by extrinsic effects, such as boundary scattering, rather than by the intrinsic lattice dynamic properties of van der Waals films.
3.5 Conclusions

We investigated the phonon and thermal properties of 2H-TaSe₂ thin films prepared by the mechanical delamination of crystals. We have established that the intensities of Raman peaks from the films and the Si substrate can be used for the robust and fast nanometrology of TaSe₂ thin films. The Raman nanometrology method can be readily extended to other layered van der Waals materials. We also found that the thermal conductivity of the exfoliated thin films of 2H-TaSe₂ is dominated by phonon contributions and reduced substantially compared to the bulk value. The Raman optothermal measurements indicate that the room temperature thermal conductivity in these films decreases from its bulk value of ~16W/mK to ~9W/mK in 45 nm thick films. These results suggest that thermal issues need to be taken into account in proposed device applications of TaSe₂, other metal dichalcogenide and van der Waals materials.
References


Chapter 4

High-Temperature Performance of MoS$_2$

Thin-Film Transistors: Direct Current and Pulse Current-Voltage Characteristics

4.1 Introduction and Motivations

Many electronic components for control systems and sensors are required to operate at temperature of 500 K. Examples of the high temperature applications include turbine engine control in aerospace and energy generation or the oil-field instrumentation. The availability of transistors and circuits for high temperature (T>500 K) operation is limited [1]. Devices made of SiC, GaN, and other conventional large-band-gap semiconductors hold promise for extended high-temperature operation [2-4], but are still not cost-effective for high volume applications. There is a need for new material systems that can be used for fabrication of field-effect transistors (FETs), thin-film transistors (TFT), and chemical FET and TFT based sensors functional at high temperatures. Recent advances in the exfoliation and growth of quasi two-dimensional (2D) layered materials—referred to as van der Waals materials—have resulted in a surge of interest to their possible device applications [5-8]. One of the most promising materials among the layered transition-metal dichalcogenides (TMD) is MoS$_2$ [9, 10]. A single atomic layer of MoS$_2$ shows a
direct band gap of \( E_g = 1.9 \) eV while bilayer and bulk MoS\(_2\) exhibit an indirect band gap of 1.6 eV and 1.3 eV, respectively [11-13]. The interest to MoS\(_2\) thin films and devices based on this material is explained by the relatively large energy band gap of MoS\(_2\) [11-13], large on-off ratio of MoS\(_2\) TFT [11-14], low levels of flicker noise in MoS\(_2\) TFTs [15-17] and relatively high thermal conductivity of MoS\(_2\) thin films compared to thin films of other TMDs [18]. It was also shown that MoS\(_2\) TFT can be used as selective gas and chemical sensors [19, 20]. In this paper, we report on the experimental demonstration of MoS\(_2\) thin film transistors suitable for high temperature applications. The MoS\(_2\) TFTs are functional to temperatures of at least as high as 500 K and remain operational for at least after a month of aging. Using the voltage pulse measurements, we were able to show that the sub-linear and super-linear output characteristics of MoS\(_2\) TFT, frequently observed in the direct-current (DC) measurements, may result from the Joule heating and are associated with an interplay of the threshold voltage and mobility temperature dependences. We also report on a “memory step” effect in the form of a kink in the drain current-occurring at zero gate voltage irrespective of the threshold voltage value. This effect observed at temperatures above 450 K can be used for MoS\(_2\) thin film applications in high temperature sensors. The obtained results may lead to new applications for TFT implemented with MoS\(_2\) and other similar van der Waals materials in extreme-temperature electronics and sensors.
4.2 Material Characterization and Device Fabrication

For this study, thin films of MoS$_2$ were exfoliated from bulk crystals and transferred onto Si/SiO$_2$ substrates following the standard approach [5-8]. The thickness, H, of the exfoliated films ranged from a single layer to 18 layers. For the high-temperature experiments, we selected devices with the MoS$_2$ channel thickness $H = 9–12$ nm, which correspond to 15–18 layers of MoS$_2$ (the thickness of a single layer of MoS$_2$ is 0.65 nm). The relatively thick films were more thermally stable and demonstrated a higher mobility at elevated temperatures. The gating was still possible, although it required an application of a higher back-gate voltage. The thickness and quality of thin films were determined with the atomic force microscopy (AFM) and micro-Raman spectroscopy. Figure 4.1 (a) shows a representative scanning electron microscopy (SEM) image of the studied MoS$_2$ TFT. Micro-Raman spectroscopy (Renishaw InVia) was performed in the backscattering configuration under $\lambda = 488$ nm laser excitation laser using an optical microscope (Leica) with a 100× objective. The excitation laser power was limited to less than 0.5 mW to avoid local heating. In Figure 1(b), we present the informative bands at 383 cm$^{-1}$ ($E_{2g}^{1}$) and 406 cm$^{-1}$ ($A_{1g}$), consistent with the previous reports of the MoS$_2$ Raman spectra [21]. The Raman spectrum confirms that this sample is multilayer MoS$_2$ film. The latter follows from the frequency difference, $\Delta \omega$, between the $E_{2g}^{1}$ and the $A_{1g}$ peaks. The increase in the number of layers in MoS$_2$ films is accompanied by the red shift of the $E_{2g}^{1}$ and blue shift of the $A_{1g}$ peaks [21]. The inset shows the AFM image of a typical device. Devices with MoS$_2$ channels were fabricated using electron beam lithography (LEO SUPRA 55) for patterning of the source and drain electrodes and the electron-beam
Figure 4.1. Scanning electron microscopy image of a representative device (a). The pseudo-colors are used for clarity. Raman spectrum of MoS$_2$ thin film showing the $E_{2g}^1$ and the $A_{1g}$ peaks (b). The increase in the number of layers in MoS$_2$ films is accompanied by the red shift of the $E_{2g}^1$ and blue shift of the $A_{1g}$ peaks. The energy difference between $E_{2g}^1$ and the $A_{1g}$ peaks indicates that the given sample is a few-layer MoS$_2$ film. Inset shows AFM image and a line scan of a representative MoS$_2$ TFT. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); http://dx.doi.org/10.1063/1.4906496 with permission from AIP Publishing LLC.
evaporation (Temescal BJD-1800) for metal deposition. Conventional Si substrates with 300 nm thick SiO$_2$ layers were spin coated (Headway SCE) and baked consecutively with two positive resists: first, methyl methacrylate (MMA) and then, polymethyl methacrylate (PMMA). These devices consisted of MoS$_2$ thin-film channels with Au (100 nm) contacts. The heavily doped Si/SiO$_2$ wafer served as a back gate. The majority of the devices had a channel length, L, in the range from 1.3 µm to 3.5 µm, and the channel width, W, in the range from 0.5 µm to 2 µm.

4.3 DC Characteristics of MoS$_2$ TFTs

We investigated DC characteristics of a number of MoS$_2$ TFT with the channel thickness of 2–3 atomic layers and 15–18 atomic layers. The devices were also tested after a few days and two-month aging under ambient conditions. Figure 4.2 shows a comparison of the room temperature (RT) current-voltage (I-V) characteristics of the MoS$_2$ TFTs with the 2–3-layer and 15–18-layer thick channels. The effect of aging is also indicated. One can see that the MoS$_2$ TFTs with thicker channels are characterized by a higher threshold voltage, $V_{th}$, higher electron mobility, $\mu$, and smaller subthreshold slope. Figure 4.3 presents transfer characteristics of the MoS$_2$ TFTs for the temperature varying from RT to 500 K. The I-Vs were measured at the drain-source voltage $V_d$ = 0.1V. The temperature increase leads to the shift of the threshold voltage to more negative values is a characteristic kink in the transfer current-voltage characteristics at $T > 450$ K. It was well reproduced at several different temperatures above $T = 450$ K and during multiple measurements. This kink is seen at $V_g = 0$ for different temperatures and, therefore, for
Figure 4.2 Current-voltage characteristics of the fabricated MoS\(_2\) FET with different channel thickness at room temperature. Note that TFTs with thicker MoS\(_2\) channels are characterized by the higher threshold voltage, higher mobility, and smaller sub-threshold slope. The transfer current-voltage characteristics for the few-days and two-month aged devices are also shown for comparison. The drain voltage \(V_g = 0.1\) V. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); [http://dx.doi.org/10.1063/1.4906496](http://dx.doi.org/10.1063/1.4906496) with permission from AIP Publishing LLC.

different threshold voltages. A similar effect, which we called a “memory step,” was found earlier for graphene transistors at elevated temperatures [23]. In graphene, the “memory step” was negative, i.e., current decreased step-like when scanning the gate voltage from negative to positive values, while in MoS\(_2\) TFTs, the I-V characteristics
Figure 4.3 Temperature dependence of the transfer current-voltage characteristics at the drain-source voltage $V_d = 0.1$ V. The temperature increase leads to the shift of the threshold voltage to more negative values. Note a kink in the drain current—referred to as “memory step”—reproducibly appearing at $V_g = 0$ V for temperatures above $T = 450$ K. The intriguing phenomenon was previously observed for electronic glasses and graphene. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); http://dx.doi.org/10.1063/1.4906496 with permission from AIP Publishing LLC.

revealed a positive “memory step.” A similar memory effect (called the “memory dip”) was observed in electronic glasses [24-27]. Although the nature of this phenomenon is still a subject of debates, we can point out two common features in all three material systems: the onset of the effect at $V_g = 0$ V and presence of the slow relaxation processes [23, 24]. We discuss this effect in more details below. The effective mobility, $\mu$, was
Figure 4.4 Temperature dependences of the threshold voltage and mobility in the as fabricated MoS₂ TFT. The mobility and threshold temperature dependences have the opposite effect on the current-voltage characteristics. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); http://dx.doi.org/10.1063/1.4906496 with permission from AIP Publishing LLC.

calculated as [28]

$$\mu = \frac{L_g}{c_ox R_{ds}(V_g-V_{th})W}$$  \hspace{1cm} (1)

Here, $c_{OX} = \varepsilon_0 \varepsilon_r/d = 1.15 \times 10^4$ (F/m²) is the oxide capacitance, where $\varepsilon_0$ is the dielectric permittivity of free space, $\varepsilon_r$ is the dielectric constant, and $d$ is the oxide thickness. We used $\varepsilon_0 = 3.9$ and $d = 300$nm for the SiO₂ layer. Plotting the drain-to-source resistance, $R_{ds}$, vs. $1/(V_g - V_{th})$ and extrapolating this dependence to zero yielded
the estimate for the total contact resistance. The extracted data indicated that the contact resistance was negligible for all the samples at all temperatures. Figure 4.4 presents the evolution of the effective mobility and the threshold voltage with temperature. The threshold voltage, $V_{\text{th}}$, only weakly depends on temperature for $300 \text{K} < T < 370 \text{K}$. For $T > 370 \text{K}$, the mobility decreases rapidly indicating a high interface trap density.

In the linear regime, the drain-source current, $I_d$, is proportional to $\mu C_{\text{ox}} (V_g - V_{\text{th}}) V_d$. The dependences of the mobility and the threshold voltage on temperature have an opposite effect on current-voltage characteristics: The decrease of the mobility leads to the current decrease but decrease of threshold voltage leads to the current increase. As a result, current can either increase or decrease with the temperature increase depending on the specific shape of mobility and threshold voltage temperature dependences. For this reason, the sub-linear and super-linear output characteristics, often observed in DC measurements with MoS$_2$ TFTs at drain voltage exceeding 1–2V for the micron-size MoS$_2$ devices, can be attributed to Joule heating of the channel during the measurements and to the dominance of one or the other mechanism. Figure 4.5 shows the gate voltage dependence of the mobility at different temperatures. The weak gate voltage dependence of the mobility calculated assuming zero contact resistance is a piece of evidence suggesting a low contact resistance in the examined devices.

In this set of measurements, we established that MoS$_2$ TFTs are functional up to a temperature at least as high as 500 K. Since this is the first study of MoS$_2$ TFT performance at temperatures around 500 K, no direct comparison with other works [22, 29-31] is possible. However, there have been data reported for MoS$_2$ TFTs for
Figure 4.5 Gate-voltage dependence of the effective mobility in MoS$_2$TFT at different temperatures. The weak temperature dependence of the mobility suggests a low contact resistance. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); http://dx.doi.org/10.1063/1.4906496 with permission from AIP Publishing LLC.

temperatures around 350 K. In our devices (see Figure 4.4), the mobility decreased from 55 cm$^2$/Vs to 11 cm$^2$/Vs as temperature increases from RT to 500 K. The same trend was observed for CVD MoS$_2$ devices characterized at temperatures between 150K and 350 K [22]. Practical applications of MoS$_2$ TFT in control circuits or sensors require that they operate at least longer than 1 month. Figure 6 shows the temperature dependences of the threshold voltage and mobility for MoS$_2$ TFTs aged over a month.
Figure 4.6 Temperature dependences of the threshold voltage (a) and mobility (b) in four one-month aged MoS$_2$ TFTs. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); http://dx.doi.org/10.1063/1.4906496 with permission from AIP Publishing LLC.
under ambient conditions. The aged devices were characterized by a higher threshold voltage, lower mobility, and weaker temperature dependence of the mobility. As we pointed out already, the temperature dependence of the threshold voltage and mobility have an opposite effect on current voltage. To verify this assertion, we performed pulse measurements by sending microsecond pulses through MoS$_2$ TFTs to avoid Joule heating.

4.4 Pulse Characteristics of MoS$_2$ TFTs

In Figure 4.7(a), we show the output current-voltage characteristics of MoS$_2$ TFT measured in the pulse mode at T = 300 K and V$_g$ = 76 V. Figures 7(b) and 7(c) present the shape of the 10 µs voltage and current pulses. The maximum electric field achieved in these tests was 86.5 kV/cm with the maximum current density for 10-nm thick channel of 3×10$^5$ A/cm$^2$. One can see that the current-voltage characteristic is still linear at these voltage and current levels. The current rise time at 300 K is ~0.5 µs. A slight increase of the current on the top of the pulse, which is about 0.5%, is attributed to the minor heating of the device channel.

In order to observe the saturation in output current-voltage MoS$_2$ TFT characteristics, the pulse measurements were performed at elevated temperature when the threshold voltage shifts to smaller values. Figure 4.8(a) shows the output current-voltage characteristics measured in the pulse mode at the temperature T = 453 K and V$_g$ = 0. Figure 8(b) presents the shapes of the voltage and the current pulses at V$_g$ = 76 V. At 453 K, the characteristic current rise time is ~5 µs. The current saturation is clearly seen in Figure 8(a).
4.5 “Memory Step” Effects in MoS$_2$ TFTs

We now offer two possible origins of the “memory steps,” which we observed in this work in MoS$_2$ TFTs and, previously, in graphene devices [23]. The exact origin of the observed memory step effect in MoS$_2$ devices with different $V_{th}$ and the reasons for its intriguing appearance near $V_g = 0$ V are not clear. At the same time, it is difficult not to notice a similarity between the observed feature in MoS$_2$ thin films with those in graphene [23] and electron glasses [24-27]. The electron glasses demonstrated memory effects including the so called “memory dips,” i.e., irregularity, referred to as the “dip,” in the transfer I-V characteristics. Several mechanisms responsible for the “memory dip” have been discussed [24-27]. However, the underlying physics of the “memory dip” in the electronic glass is still under debates. In three different material systems — MoS$_2$ thin films, graphene and electron glasses — the current anomaly is found at $V_g = 0$ V. However, in contrast to MoS$_2$ thin films and graphene, the memory dips in electron glasses have been observed at cryogenic temperatures. In MoS$_2$ thin films and graphene, the effect is found at elevated temperatures. All three materials are characterized by slow relaxation processes. In graphene and MoS$_2$, these are processes of capture and release of free carries by deep levels. The concentration of these deep levels can be high and comparable with the concentration of free careers. We believe that when characteristic times of capture and release are similar and comparable with the sweep time, the condition for memory step is satisfied. The specific step observed in Figure 4.3 at $V_g = 0$ V can be explained by different mechanisms. The first proposed model is based on the following two assumptions: (i) the concentration of defects (deep traps) is comparable
Figure 4.7. Output current-voltage characteristics of MoS$_2$ TFT measured in the pulse mode for $V_g = 76$V at room temperature (a). The shapes of 10 µs voltage and current pulses are shown in the panels (b) and (c), respectively. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); [http://dx.doi.org/10.1063/1.4906496](http://dx.doi.org/10.1063/1.4906496) with permission from AIP Publishing LLC.
Figure 4.8 Output current-voltage characteristics of MoS$_2$ TFT measured in the pulse mode for V$_{g}$=0 V at the elevated temperature of T=453 K (a). The shapes of the voltage and current pulses at V$_{g}$ = 76 V is shown in the panel (b). The characteristic current rise time at 435 K is ~5 µs. Reprinted from C. Jiang, S. L. Rumyantsev, R. Samnakay, M. S. Shur and A. A. Balandin, J. Appl. Phys. 117, 064301 (2015); http://dx.doi.org/10.1063/1.4906496 with permission from AIP Publishing LLC.
with the concentration of free carriers; and (ii) the characteristic times of the charge carrier trapping by defects, de-trapping, and voltage sweep are of the same order of magnitude. In this case, when MoS$_2$ TFT stays for a long time at $V_g = 0$ V, there will be some number of free carriers and a large number of trapped carriers. During the voltage sweep, a negative gate voltage is applied and then swiped towards positive values. During this sweep, the concentration of free carriers is lower than the equilibrium owing to the long de-trapping time. This results in the lower than steady state current. Since gate voltage reached some vicinity around $V_g = 0$ V, the concentration of traps with electrons is below the equilibrium, which is compensated with the electrons from the contacts and step occurs. Given that the capture time is comparable with the voltage sweep time, the excess electrons ensure larger current above $V_g$ till certain voltage (about $V_g = 15$ V in Figure 4.3).

The second model is based on the assumption of different trapping and de-trapping times. At low temperatures (including RT for this material system), the trapping and detrapping times are very large. Therefore, the trap occupancy corresponds to that at the zero gate bias because the samples have been stored for long period of times (hours and days) with no gate bias applied. At all other biases, the steady-state trap occupancy is not achieved during the relatively fast sweep (minutes). At very high temperatures (around 450 K for given MoS$_2$ films), the de-trapping times become faster but trapping times remain about the same. Hence, when the Fermi level corresponds to the zero bias at high temperature, the traps can release additional charge resulting in the “memory step.”
Additional experiments and qualitative models are required to distinguish, which mechanism describes the observed phenomenon more accurately.

4.6 Conclusions

We investigated the high-temperature current-voltage characteristics of MoS$_2$ TFTs using DC and pulse measurements. The MoS$_2$ TFTs remained functional to temperatures of, at least, as high as 500 K. The temperature increase resulted in decreased threshold voltage and mobility, which have an opposite effect on the current-voltage characteristics. We established that the sub-linear and super-linear output characteristics of MoS$_2$ thin-films devices, frequently observed in DC measurements, may result from the Joule heating and interplay of the threshold voltage and mobility temperature dependences. The pulse measurements performed for the electric field of up to $\sim 87$ kV/cm at RT showed that the current-voltage characteristics are still linear. The current saturation in pulse measurements was achieved at $V_{SD}=6$V when the device temperature was elevated to 453 K. At temperatures above 450 K, we observed an intriguing phenomenon of a kink in the drain current that occurs at zero gate voltage, which we referred to as a memory step. The memory step effect was attributed to the slow relaxation processes in thin films of MoS$_2$ similar to those in graphene and electron glasses.
References


Chapter 5

Summary

In this dissertation, I described my research results on the phonon and electron properties and potential application of 2D van der Waals (VDW) materials. The focus of the studies was on the two different members of the Transition Metal Dichalcogenide (TMD) sub-class of VDW materials.

In first part of my dissertation, I reported on the phonon and thermal properties of thin films of tantalum diselenide (2H-TaSe$_2$) obtained via the “graphene-like” mechanical exfoliation of crystals grown by chemical vapor transport. The ratio of the intensities of the Raman peak from the Si substrate and the $E_{2g}$ peak of TaSe$_2$ presents a convenient metric for quantifying film thickness. The temperature coefficients for two main Raman peaks, $A_{1g}$ and $E_{2g}$, are -0.013 and -0.0097 cm$^{-1}$ / °C, respectively. The Raman optothermal measurements indicate that the room temperature thermal conductivity in these films decreases from its bulk value of $\sim$16 W/mK to $\sim$ 9 W/mK in 45 nm thick films. The measurement of electrical resistivity of the field-effect devices with TaSe$_2$ channels shows that heat conduction is dominated by acoustic phonons in these van der Waals films. The scaling of thermal conductivity with the film thickness suggests that the phonon scattering from the film boundaries is substantial despite the sharp interfaces of the mechanically cleaved samples. These results are important for understanding the thermal properties of thin films exfoliated from TaSe$_2$ and other metal dichalcogenides, as well as for evaluating self-heating effects in devices made from such materials.
In second part of my dissertation, I reported on fabrication of MoS$_2$ thin-film transistors (TFTs) and experimental investigations of their high-temperature current-voltage characteristics. The measurements show that MoS$_2$ devices remain functional to temperatures of at least as high as 500 K. The temperature increase results in decreased threshold voltage and mobility. The comparison of the direct current (DC) and pulse measurements shows that the direct current sub-linear and super-linear output characteristics of MoS$_2$ thin-films devices result from the Joule heating and the interplay of the threshold voltage and mobility temperature dependences. At temperatures above 450 K, a kink in the drain current occurs at zero gate voltage irrespective of the threshold voltage value. This intriguing phenomenon, referred to as a “memory step,” was attributed to the slow relaxation processes in thin films similar to those in graphene and electron glasses. The fabricated MoS$_2$ thin-film transistors demonstrated stable operation after two months of aging. The obtained results suggest new applications for MoS$_2$ thin-film transistors in extreme-temperature electronics and sensors.