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Exploring the Thermal Transport and Phase Nucleation Physics of Nanowires via
Suspended Microdevices

By

Lei Jin

A dissertation submitted in partial satisfaction of

the requirement of the degree of

Doctor of Philosophy

in

Applied Science and Technology

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Junqiao Wu, Chair

Professor Andrew Minor

Professor Christopher Dames

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Abstract

Exploring the Thermal Transport and Phase Nucleation Physics of Nanowires via Suspended Microdevices

by

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Doctor of Philosophy in Applied Science and Technology

University of California, Berkeley

Professor Junqiao Wu, Chair

The advance in nanofabrication and characterization methods enables researchers to study nanomaterials at small scales. Rich physics can emerge in nanomaterials due to their low-dimensional nature, such as boundary effect, quantum confinement effect etc. Also, nanomaterials usually have the most single-crystalline pristine qualities. This opens opportunities to study the intrinsic properties of many materials, which is hard to probe in bulk counterparts as the grain boundaries and defects in bulk samples can degrade their qualities. Combining the nanofabricated suspended microdevice and nanomaterials such as nanowires or nanoribbon, we can probe the intrinsic properties of materials which have interesting physics. Nanomaterials also have their unique structure and thermal physics properties which are very different from those of their bulk counterparts. In this dissertation, the author presents his work, in his pursuits of PhD degree at UC Berkeley, focused on exploring the thermal and transport physics of nanowire via transport measurement realized by using nanofabricated suspended microdevices.

Chapter 2 and 3 are focused on vanadium dioxide (VO_2), a strongly correlated materials with metal-to-insulator transition (MIT) occurring at temperature of 341 K. Although the first observation of the MIT of VO_2 was more than 60 years ago, the transition mechanism and the correlation physics of VO_2 is still under debate among theorists. Thanks to the advances in nanofabrication, measuring and modulating the MIT of single-crystalline VO_2 nanowires are made possible and accessible to experimentalist. This provides us an efficient tool to study the intrinsic properties of VO_2 and could help unveil its correlated nature. In chapter 2, a discovery of the recovery of Wiedemann-Franz (W-F) law in metallic VO_2 is reported. This recovery is realized by introducing point defects using energetic ion irradiation. The experimental measurements and theoretical explanations are demonstrated to explain this full restoration of otherwise violated W-F law in strongly correlated system. In chapter 3, a deeply supercooled intrinsic VO_2 metal is first realized by technique called irradiation shielding supported on suspended microdevices. Nucleation seeds created by ion surface milling are then introduced on nanowires' surface and the critical nucleation sizes of supercooled metallic VO_2 are measured for the first time. A model derived from classical nucleation theory is also presented.

In chapter 4, experimental observations of abnormal thermal transport behaviors of twisted layered GeS nanowires with a screw dislocation core in the center is reported. The thermal conductivity of twisted GeS nanowires is measured by using suspended microdevices, which increases by decreasing diameters of nanowires. This trend is against to the prediction from boundary scattering, which is commonly observed in nanowires such as silicon, silver etc. In contrast, the thermal conductivities of non-twisted layered GeS nanowires and GeS nanoribbon are also measured. Their thermal transport behaves the same as common nanowires, that is thinner wires have lower thermal conductivity. The abnormal increasement of thermal conductivity at smaller diameters of twisted nanowires must origin from either their dislocation cores or the twisting topology between layers. New thermal physics may arise in this type of materials as classical explanation of the measured results fails to give full explanations.

Table of Contents

Chapter 1 Introduction	1
1.1 Thermal conductivity	1
1.2 The suspended microdevice	2
Chapter 2 Exploring the restoration of Wiedemann-Franz law in defected VO₂ via thermal transportation measurement	6
2.1 Introduction	6
2.2 Experimental methods.....	7
2.2.1 VO ₂ growth and transfer	7
2.2.2 Platinum deposition to secure the thermal and electrical contact of as-transferred nanowire	9
2.2.3 Point defect generation	11
2.2.4 Transport measurement using suspended microdevice	15
2.2.5 Experiment procedure	16
2.3 Electrical conductivity	17
2.3.1 The metal-insulator phase transition of VO ₂	17
2.3.2 The effect of oxygen vacancies in VO ₂	19
2.3.3 The measured results of electrical conductivity of He-ion-irradiated VO ₂ ...	20
2.4 Thermal conductivity	23
2.4.1 The thermal conductivity of pristine VO ₂	23
2.4.2 The measured results of thermal conductivity of He-ion-irradiated VO ₂	24
2.5 The recovery of Wiedemann-Franz law	28
2.5.1 The evaluation of Lorenz number	28
2.5.2 Hydrodynamic model.....	30
2.5.3 Seebeck coefficient	33
2.6 Conclusion.....	34
Chapter 3 Probing the critical nucleation seeds in deeply supercooled VO₂	35
3.1 Introduction	35
3.2 The classical nucleation theory	36
3.2.1 Homogeneous nucleation	36
3.2.2 Heterogeneous nucleation	38

3.2.3	Probing the critical nucleation size	39
3.3	Achieving deeply supercooled VO ₂	39
3.3.1	T _{MIT} engineering of VO ₂ by helium ion irradiation	40
3.3.2	Irradiation shielding on suspended VO ₂ nanobeams	41
3.4	Finding the nucleation seeds	45
3.4.1	Nucleation seeds created on VO ₂ surfaces by Ga ion irradiation	45
3.4.2	Doping and etching effects of Ga ion irradiation	47
3.5	The critical nucleation sizes of metallic VO ₂	49
3.5.1	Experiment method	50
3.5.2	The classical nucleation theory model in supercooled M-phase VO ₂	51
3.5.3	Probing the interface energy of I-phase nucleus	54
3.6	Conclusions	56
Chapter 4 Abnormal thermal conduction in twisted GeS nanowire with a dislocation core		57
4.1	Introduction	57
4.2	The thermal transport measurements of GeS nanowires	59
4.2.1	The twisted GeS nanowires	59
4.2.2	The non-twisted GeS nanowires	62
4.2.3	The overall thermal conductivities	63
4.3	Theoretical efforts to explain the abnormal thermal transport in twisted GeS nanowire.....	66
4.3.1	Conductive core model	67
4.3.2	Spiral heat conduction model	70
4.4	Conclusions	74
Reference.....		75

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Chapter 1 Introduction

1.1 Thermal conductivity

The thermal conductivity κ is a measure of material's ability to transport heat, which can be expressed as Fourier law, that is $q = -\kappa \nabla T$, where q is the heat flow and ∇T is temperature gradient (I). In solid state materials, heat (or referred as thermal energy) can be carried by both electrons and phonons. In non-metallic material where the density of conduction electron is low or negligible, the thermal conductivity is mainly dominated by phonon transport process which is referred to as lattice thermal conductivity (κ_l), because phonon is a quantization of lattice vibrations (2). The electronic thermal conductivity (κ_e) is only comparable to that of phonon if electrical conductivity is high (usually above the order of 10^5 S/m, which is a typical conductivity of metals). Therefore, the total thermal conductivity $\kappa_{tot} = \kappa_e + \kappa_l$.

The electronic thermal conductivity can be determined by Wiedemann-Franz law (I), which is to be discussed on detail in section 2.1. The lattice thermal conductivity can be calculated as,

$$\kappa_l = \frac{1}{3} \sum C v_g \Lambda, \quad (1-1)$$

where C is the heat capacity of phonon, v_g is the group velocity of phonon and Λ is its mean free path (MFP). The summation includes all phonons. The C and v_g can be determined by the dispersion relation of phonons. The Λ is determined by the scattering process including phonon-phonon scattering (or so-called Umklapp scattering) Λ_{umkl} , phonon-impurity scattering Λ_{imp} and phonon-boundary scattering Λ_{bdy} . Using Matthiessen's rule, the effective MFP can be expressed as(2)

$$\Lambda_{eff}^{-1} = \Lambda_{umkl}^{-1} + \Lambda_{imp}^{-1} + \Lambda_{bdy}^{-1}, \quad (1-2)$$

with

$$\Lambda_{umkl}^{-1} = B_1 \omega^2 T \exp(-B_2/T) / v_g, \quad (1-3)$$

$$\Lambda_{imp}^{-1} = A_1 \omega^4 / v_g, \quad (1-4)$$

$$\Lambda_{bdy}^{-1} = D^{-1}, \quad (1-5)$$

where ω is the phonon frequencies, T is the temperature and D is the feature size such as diameter of nanowires. $A1$, $B1$ and $B2$ are fitting parameters. In bulk materials, the scattering is mainly dominated by Umklapp scattering and impurity scattering. In nanowires, as their feature sizes are small, boundary scattering is significant and can even be predominant at low temperatures where Umklapp scattering and impurity scattering is suppressed.

1.2 The suspended microdevice

The transport measurement of nanomaterials can be carried out by using suspended microdevice (3). Two silicon nitride (SiN_x) membranes of size of $40 \times 40 \mu\text{m}$ are suspended by several hundred- μm -long SiN_x beams. The microdevice is fabricated on silicon wafer with sequential steps of chemical vapor deposition of low stress SiN_x thin film, DC sputtering of platinum thin film, DUV lithography patterning, reactive ion etching and releasing of the micropads through wet silicon etching in TMAH hot bath (4). The detailed structure of the fabricated micropads is shown in figure 1.1. Each micropad has one serpentine platinum (Pt) coil and two Pt electrodes. The Pt coil functions as both resistive joule heater and a resistance thermometer to measure the temperatures of the micropad. The rectangular Pt electrode is used to measure voltage or inject electrical current into the sample.

In thermal transport measurement, one micropad is designated as heating pad while the other as sensing pad. Joule heating is induced on heating pad by applying a DC current through the Pt coil. The suspension maximumly reduces the thermal heat leakage to the substrate and a high vacuum atmosphere is used to reduce heat convection. Most of heat flow generated will pass through the sample, as the nanowire shown in figure 1.1 that bridges two micropads, from the heating pad to the sensing pad. This can cause a temperature rise on the sensing pads. The temperature of both heating and sensing pad, T_h and T_s respectively, can be measured by their Pt coils. The thermal conductance of SiN_x beams (G_b) and sample (G_s) can be calculated by solving their associated equivalent thermal circuit (3).

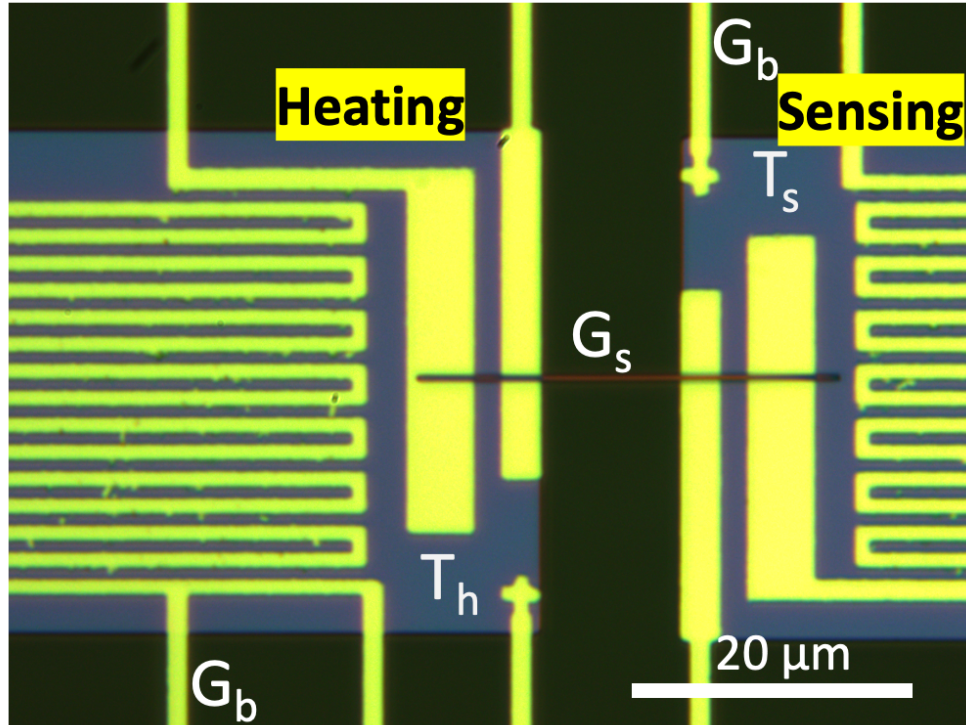


Figure 1.1. An optical image of suspended microdevice with a nanowire transferred bridging the gap. The temperature of heating and sensing pad, T_h and T_s respectively, can be measured by Pt coils. The thermal conductance of SiN_x beams (G_b) and sample (G_s) can be calculated by solving equivalent thermal circuit.

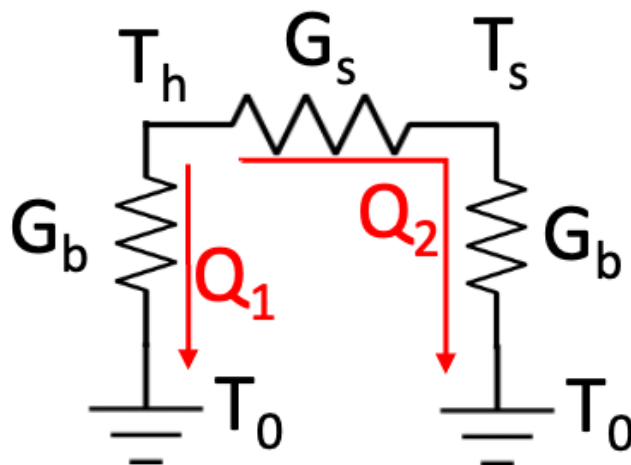


Figure 1.2. Equivalent thermal circuit of suspended microdevice.

Figure 1.2 shows the equivalent thermal circuit associated with the suspended microdevice shown in figure 1.1. The resistance joule heating can generate heat Q_h and Q_b at both the Pt coil on the heating pad and the Pt leads on the SiN_x beams, respectively. Therefore, we have

$$Q_h = I_h^2 R_h, \quad (1-4)$$

and

$$Q_b = I_b^2 R_b. \quad (1-5)$$

Half of the heat generated on SiN_x beams flows to the heating pads while the other half to the substrate. One portion of the heat generated on heating pad flows to the substrate through SiN_x beams (Q_1 in figure 1.2) while the other portion to the sensing pad through the sample (Q_2 in figure 1.2). Two equations can be rewritten by the fact that heat current is constant along a single path, that are

$$Q_1 = G_b \Delta T_h + Q_b, \quad (1-6)$$

$$Q_2 = G_b \Delta T_s = G_s (\Delta T_h - \Delta T_s), \quad (1-7)$$

where $\Delta T_h = T_h - T_0$, $\Delta T_s = T_s - T_0$ and T_0 is the environmental temperature of the substrate. And given the conservation of thermal energy, we can write

$$Q_1 + Q_2 = Q_h + 2Q_b, \quad (1-8)$$

by combining (1-6), (1-7) and (1-8), we can solve the three equations and have

$$G_b = \frac{Q_h + Q_b}{\Delta T_h + \Delta T_s}, \quad (1-9)$$

and

$$G_s = \frac{\Delta T_s (Q_h + Q_b)}{\Delta T_h^2 - \Delta T_s^2}. \quad (1-10)$$

Equation (1-10) is the total thermal conductance of the channel part of sample, the segment that bridging the gap between two micropads. After determining the thickness, width, and length of the channel, we can easily calculate its related thermal conductivity.

The electrical transport measurement is conducted by using four electrodes on the suspended microdevice in four-point configuration, with currents supplied from the two outer electrodes and voltages measured on the two inner electrodes. Meanwhile, if we measure the voltages on two electrodes with temperature bias applied between two micropads, Seebeck coefficient (I) can also be calculated. The most unique advantage of suspended microdevice is that it can measure thermal conductivity, electrical conductivity and Seebeck coefficient along the exact lattice direction of the sample. This is especially

important in some studies that requires the heat current and charge current to pass through the exact same lattice, such as a transport study in VO_2 to be shown in chapter 2. The second advantage is that the sample suspended is strain-free and not affected by substrate. This is especially important to materials that are sensitive to external elastic energy, such as VO_2 (5, 6). The suspension allows us to probe the most intrinsic transport properties.

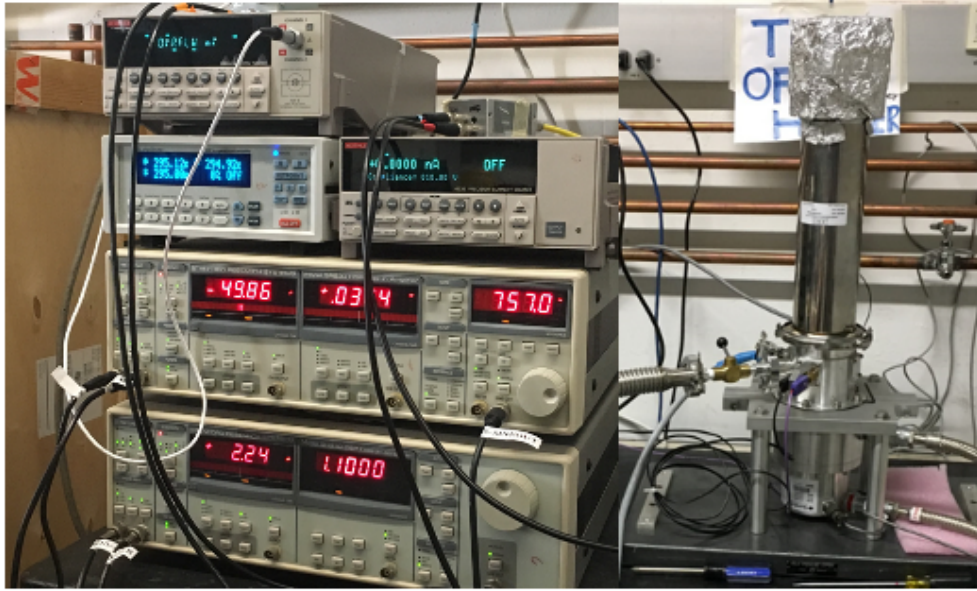


Figure 1.3. Experimental setup of the transport measurement using suspended microdevice.

The experimental setup of the transport measurement using suspended microdevice is shown in figure 1.3. The microdevice is mounted in a cryostat with high vacuum at a level of 10^{-6} Torr. A temperature controller is used to maintain the temperature ranging from 40 to 380 K with temperature variations about 10 mK. The temperature of the cryostat platform is controlled by balancing of helium compressor's cooling and resistive heater's heating. A current source supplies charge current through the sample. A voltage source reads the voltage difference between two ending points of the channel part of the sample. Two lock-in amplifiers are used to measure the temperatures of two micropads by reading the resistance of their associated Pt coils. A calibration of the relation between temperature and resistance of Pt coils are performed during the measurement as well.

Chapter 2 Exploring the restoration of Wiedemann-Franz law in defected VO₂ via thermal transportation measurement¹

2.1 Introduction

The Wiedemann-Franz (W-F) law basically states that the electronic thermal conductivity of a metal (κ_e) is proportional to its electrical conductivity (σ) and absolute temperature (T). The proportionality constant in this relation is called Lorenz number (L), which is equal to a universal constant, the Sommerfeld value, $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2$, where the k_B is the Boltzmann constant and e is the electron charge (I). The proportionally implying that electrons can carry both charge and heat in most of metals. The W-F law is well satisfied when the conducting charge carriers can be modeled as long-lived quasiparticles, where the elastic scatterings are predominant. This is the case in normal metals that are above their Debye temperature, where elastic scattering such as, the electron-phonon scattering and electron-impurity scattering are dominate. The violation of W-F law often implies the existence of non-negligible inelastic scattering process, such as small-angle electron-phonon scattering usually happens at low temperatures, electron-electron scattering via Columbic repulsion in the hydrodynamic regime; or a complete failure of the quasiparticle model to be applied in metals where non-Fermi-liquid physics must be considered (7-14).

One such examples is the so-called strongly correlated metals where the depiction of charge carrier is no longer long-lived quasiparticles nor can be referred as non-quasiparticles (15, 16). The strong inelastic electron-electron scattering and collective conduction mode of these correlated electrons gives a smaller Lorenz number compared to L_0 . This implies that the heat and charge transport of non-quasiparticles follow separate diffusive mode, where electrons can carry charge but not effectively heat. It seems that inelastic scattering is the key that makes the charge carriers deviates from the W-F law. Modulating the intensity of inelastic scattering may results in a modulation of the Lorenz number. The W-F law has been shown to be restored in Fermi liquids by adding elastic, electron-impurity scattering to suppress the originally dominating inelastic, electron-phonon scattering (17). This is consistent with the fact that to experimentally observe the breakdown of the W-F law in the hydrodynamic regime, samples must be ultra-pure with a negligible density of impurities. It is intriguing to extend this defect effect of quasiparticle transport to “bad”

¹ Reproduced in part with permission from Lei Jin et al., “Disorder recovers the Wiedemann-Franz Law in metallic phase of VO₂”, Phys. Rev. B Rapid Commun., 102, 041120(R) (2020).

metals with nonquasiparticle transport (10, 18). If the elastic scattering is enhanced to a sufficient level, the restoration of W-F law may be observed as the Lorenz number L being increased towards L_0 .

In this chapter, we report an observation of full restoration of W-F law by adding native point defects into metallic VO_2 . VO_2 is a correlated metal with metal to insulator transition (MIT) temperature (T_{MIT}) at 341 K. At temperature above T_{MIT} , VO_2 is in metallic phase with its Lorenz number be suppressed by about one order of magnitude below L_0 (8). The nonexistence of quasiparticle mode and strong inelastic electron-electron scattering due to electron correlations in VO_2 are attributed to this suppression. To enhancing elastic scattering of electrons in VO_2 , we introduced native point defects, such as vacancies, interstitials, and anti-sites, into crystalline VO_2 nanowires. The elastic electron-impurity scattering scales with the amount of point defects introduced into the otherwise perfect VO_2 lattice. With the thermal and electrical transport measurement of nanowires supported by suspended microdevices, we can extract the Lorenz number of VO_2 at different point defect levels. The restoration of Lorenz number can be therefore investigated.

2.2 Experimental methods

2.2.1 VO_2 growth and transfer

The VO_2 nanowires are prepared by using physical vapor transport (PVT) method (19, 20). A pile V_2O_5 powder about 20-30 mg is placed in a small quartz boat. As shown in figure 2.1, the boat is placed in the center of the furnace and a few unpolished quartz substrates are placed near the boat along downstream direction. We used pure argon (Ar) gaseous flow to drive the evaporate VO_x droplets which will condensed on the downstream quartz substrates and develop the growth of VO_2 nanowires. The Ar flow is supplied at flow rate of 6.8 sccm with atmospheric pressure controlled around 4 Torr. The growth temperatures are set in a range of 850-950 °C. The duration of heating process is 2 hrs. The overall growth process is followed by a natural cooling process.

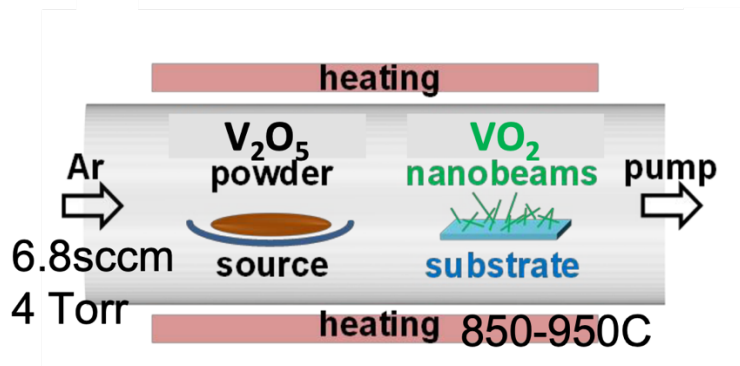


Figure 2.1. Schematics summarizing the PVT growth of VO_2 nanowires using tube furnace. (Figure adapted from Lee et al., J. Am. Chem. Soc. 2013, 135, 4850–4855 (2013)).

The nanowires grown have thickness distribution from tens of nanometers to a few micrometers. The lengths of VO_2 nanowires range from tens of micrometers to hundreds of micrometers. The density of nanowires is also high as shown in figure 2.2. Due to the rough surface of unpolished quartz surfaces, all VO_2 nanowires are tilted and free-standing. This makes them transferrable, unlike the polished smooth surface where all VO_2 nanowires grown are clamped into the substrate.

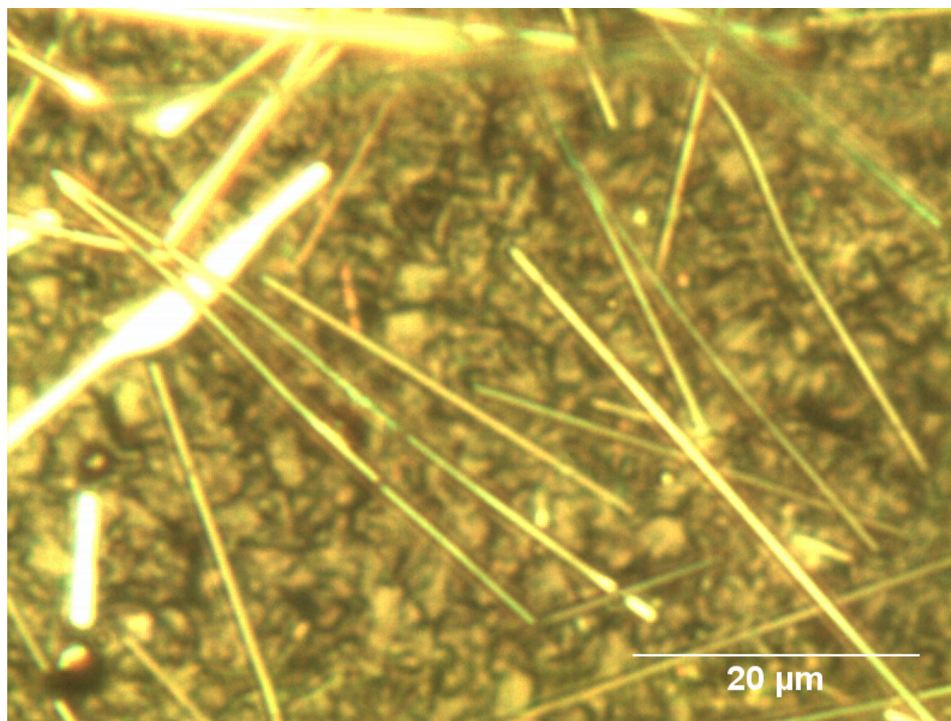


Figure 2.2. An optical image of as-grown VO_2 nanowires on the unpolished quartz surface.

The transfer of these VO_2 nanowires from the as-grown substrates to suspended microdevices can be achieved by using tungsten (W) needle via a probe station (as shown in figure 2.3). The electric static forces between needles and nanowires facilitate the picking-up process. A secondary needle can be applied to adjust the orientation of the as-picked-up nanowire to place it down onto the designated suspended microdevice. Because the static force between pad surface (line contact) is larger than that of the needle (point contact), the as-picked-up nanowire can be detached from the needles and placed as a thermal bridge between two pads.

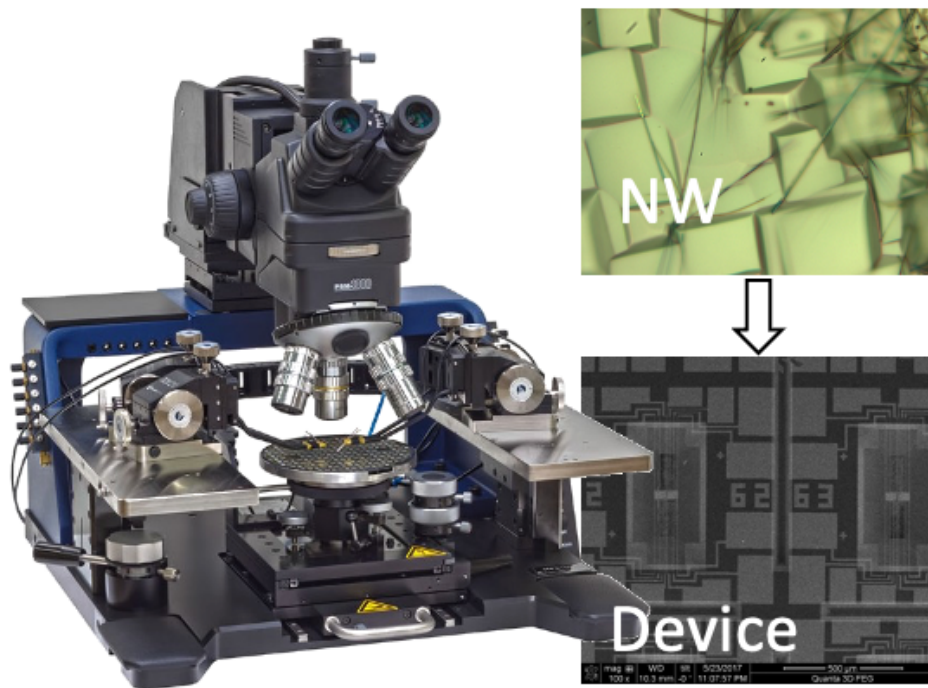


Figure 2.3. Dry transfer process of VO_2 nanowires from as-grown substrate to suspended microdevice using probe station. The probe station, as-grown substrate and chip with suspended microdevices are demonstrated.

2.2.2 Platinum deposition to secure the thermal and electrical contact of as-transferred nanowire

In transport measurement, it is important to minimize the contact resistance to ensure the measured thermal/electrical resistance is dominated in the measurement. This is especially important for thermal measurement, as we can only measure the thermal resistance in a two-point configuration. Therefore, the total resistance includes the contact resistance between nanowire and the electrodes on the suspended pads. To overcome this issue, we deposited Pt metal induced by focused ion beam (FIB) (21) by to secure the nanowire on each suspended pad and reduced both the thermal and electrical contact resistance to negligible levels (22). The energetic Ga ion beam induces the condensation of Pt on the irradiated surface from its gaseous compounds, which forms solid Pt metal blocks in ion irradiated areas. The Figure 2.4 shows a VO_2 nanowire is bonded onto two suspended pads with FIB-induced Pt depositions on the 4 electrodes, respectively.

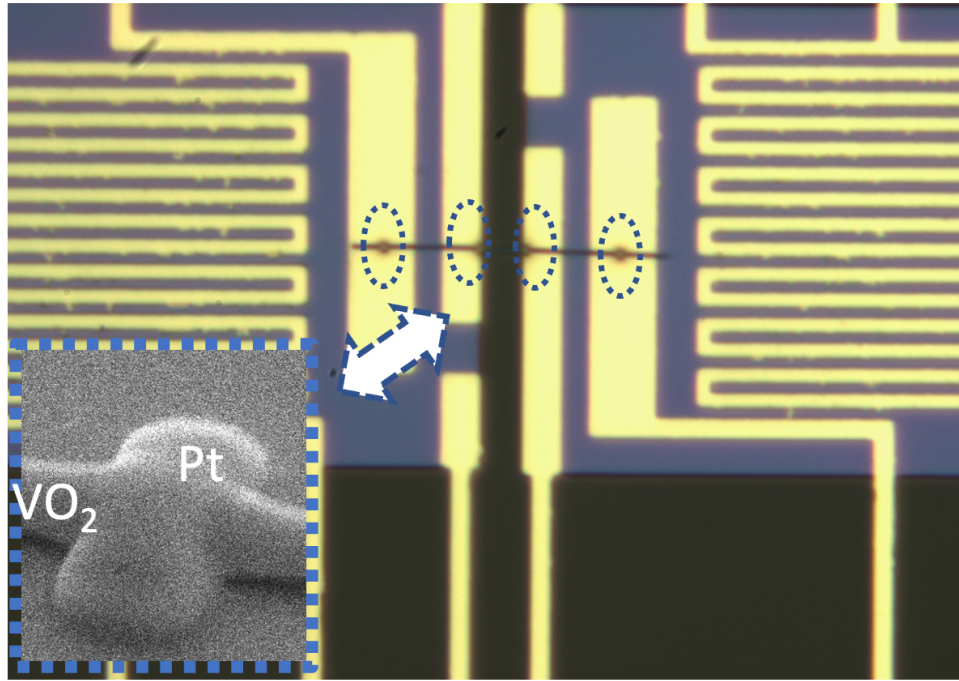


Figure 2.4. A SEM image showing VO_2 nanowire is bonded to the suspended pads via FIB-induced Pt deposition. (Insert) A detailed high-resolution SEM of one bond made by Pt deposition. (Figure adapted from Phys. Rev. B Rapid Commun., 102, 041120(R) (2020)).

However, as Ga ion irradiation can significantly damage the VO_2 quality by doping and cause lattice defects (23, 24), the Ga ion beam current level must be controlled under a certain level. Also, we need to avoid exposing the suspended part of VO_2 nanowire which is the channel part to be measured. To reduce as much deposition time as possible, we first deposited two pillars on each side of the nanowire and then cover the top surface of the nanowire together with the as-deposited pillars (insert of figure 2.4). This is the most efficient and protective way to make a good contact by using FIB. As Pt gaseous

compounds do not wet VO_2 surface, a direct Pt deposition on VO_2 cannot surround the two sidewall surfaces of the nanowire. If the nanowire is thicker than 100 nm, the directly deposited Pt cannot contact the electrodes but piling upwards on the top surface of the VO_2 nanowire.

The thermal/electrical contact resistances are negligible after Pt deposition. This is proved by comparing the measured resistance of nanowire with Pt one bond and with multiple bonds on the same electrode. An exact same resistance measured from both situations proves that the measured resistance is indeed dominated by the nanowire channel and contact resistance is negligible. The constancy between both measurements further proves that Pt deposition does not damage the measured nanowire channel, as the resistance would be different if the quality of VO_2 is degraded. High sample quality can also be confirmed in the measured electrical conductivity results (shown in section 2.3) as the conductivity jump between metallic and insulating phases of VO_2 at MIT is abrupt and high.

2.2.3 Point defect generation

Native point defects are 1D atomic imperfections in crystal lattice without any extrinsic atoms involved. There are three types of native point defects: vacancies, interstitials and anti-sites (as shown in figure 2.5) (25, 26). These point defects are always present in materials according to thermal dynamic laws. They may donate or trap charge carriers, which can affect the carrier density and light emission in semiconductor (27). They can also elastically scatter electrons and phonons, which is adopted in this work to enhance elastic scattering of electron in correlated VO_2 metal. To avoid complication of associated effects from extrinsic atoms such as their doping effects in VO_2 , we require these point defects to be only consists of native atoms (V and O) and their vacancies.

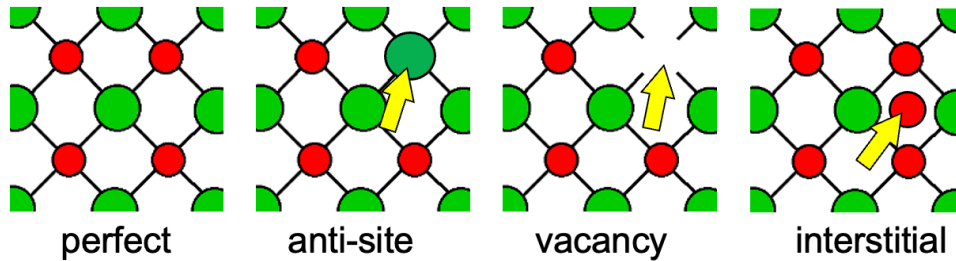


Figure 2.5. Schematics of three types of native point defects in an artificial lattice: anti-sites, vacancies, and interstitials.

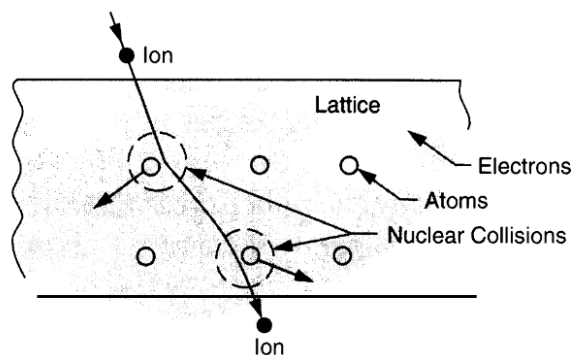


Figure 2.6. Schematics of ion irradiation penetrating through a nanowire. The ion changes its trajectory by nuclear collision while leaving point defects created in the lattice. (Figure taken from Michael Nastasi, Chapter 5 of *Ion-Solid Interactions Fundamentals and Applications*, Cambridge University Press, 1996).

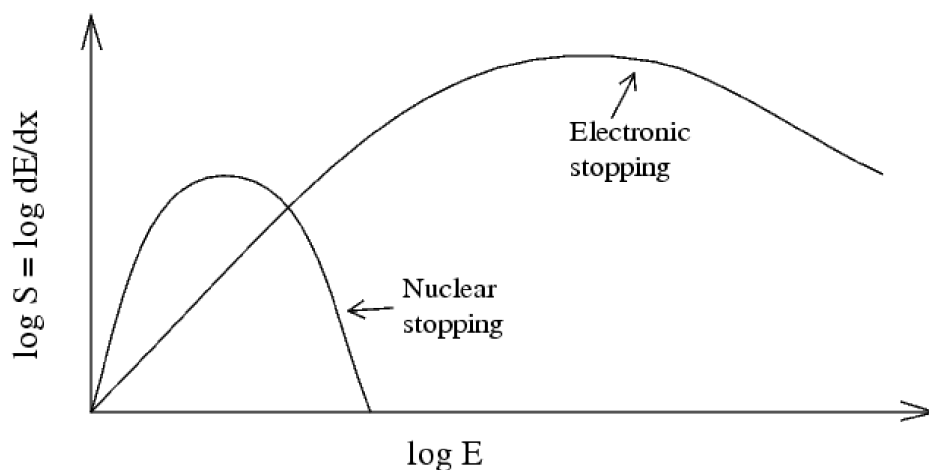


Figure 2.7. Schematics the loss of incident ion energy per propagating distance (dE/dx) in both nuclear and electronic stopping process with respect to the total energy of incident ions E . (Figure taken from beam.helsinki.fi/~knordlun/mdh/rangetext.html).

To introduce point defects into VO_2 , we designed helium (He) ion irradiation on VO_2 . Figure 2.6 shows that a He ion penetrating through VO_2 nanowires while leaving native point defects along its trajectory. In the energetic ion-solid interaction, the incoming injected ion can loss its energy to both electrons and ion cores in the lattice, which is referred to as electronic stopping and nuclear stopping of incident ion respectively (28-30). As shown in figure 2.7, the electronic stopping process is dominant when the incident ion has high energy, while the nuclear stopping is dominant when the incident ions have low

energy. In electronic stopping process, the electrons in the valence band absorb the energy from the ion and get excited to higher energy state. These excited electrons are then quickly thermalized back to their valence band by releasing phonons or photons. During electronic stopping, the lattice is heated but not damaged by ion irradiation. In the contrast, in nuclear stopping, the ionic cores at the lattice sites are knocked out of their original positions by incident ions and cannot be restored naturally. Point defects are generated via nuclear stopping during ion irradiation. Therefore, in this work, we need to control the ion energy with certain low levels to have significant nuclear stopping process while to allow them fully penetrating through the entire nanowires without being trapped inside nanowires.

Here, we used helium ion irradiation supported by helium ion microscope (Zeiss ORION NanoFab) to generate native point defects (31, 32). The acceleration energy of He ion is set at 30 kV. The projected range of the He ions of 30 keV in VO₂ is 160 nm, as predicted by Monte Carlo simulations, the Stopping and Range of Ions in Matter (SRIM) program (33). The simulation also ignores channeling effects (34), which allows ions penetrate with a deeper distance if they travel along the direction of crystalline lattice channels. Therefore, He ion can be considered as fully penetrating through VO₂ nanowires if their thickness is smaller than 160 nm. Native point defects can be thus introduced into VO₂ lattice. As shown in Figure 2.8, the He ion irradiation is defined by the green box fully covering the nanowire channel across two suspended pads. The arrow in the green box defines the direction of raster of ion beam. The raster line of helium ion beam is perpendicular to the nanowire axial direction. This can avoid heat accumulating on the nanowire as in the scanning of each line, there is enough cooling time for the nanowire before the ion beam recontact the nanowire in the next raster line.

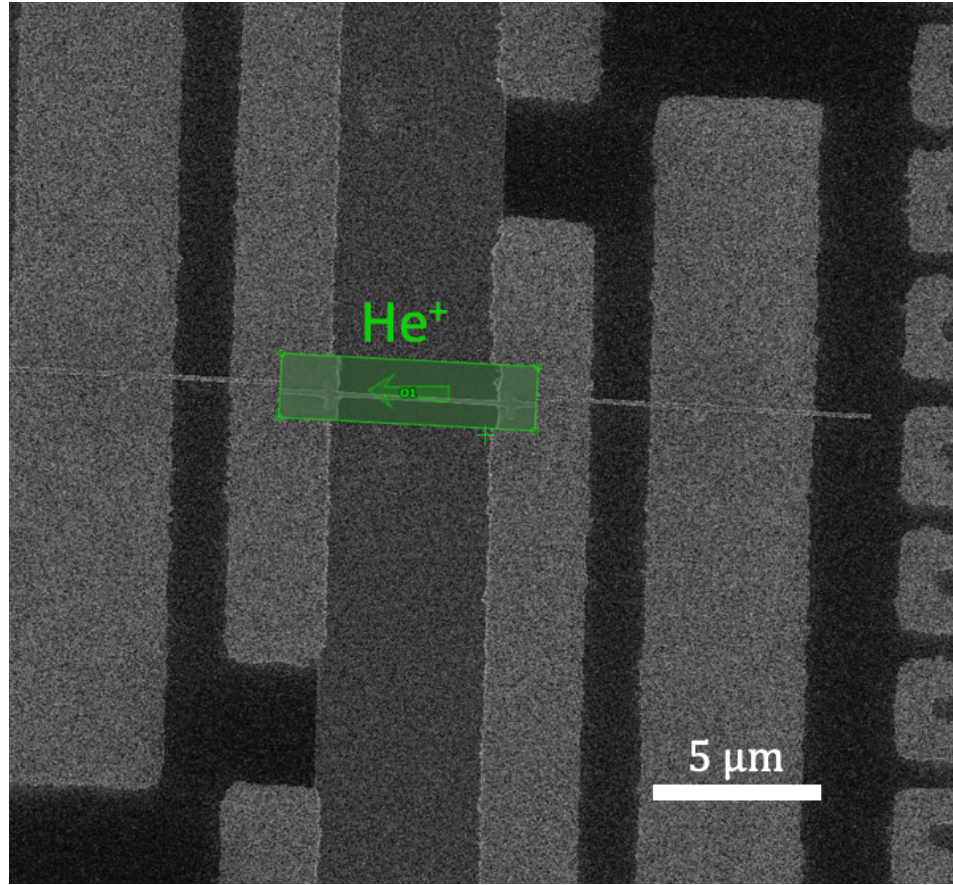


Figure 2.8 Helium ion image of irradiated VO₂ nanowire. The He ion irradiation is defined by the green box.

Another advantage of using helium ion to introduce native point defects is that helium ion irradiation does not degrade the crystallinity of VO₂. The small atomic mass of He ions can avoid damaging the VO₂ lattice severely. After irradiation, the VO₂ nanowires remain fully crystalline without any signature of amorphization and their metal to insulator phase transition still exists. We examined the crystallinity of He-ion-irradiated VO₂ using an FEI ThemIS transmission electron microscope (TEM) operated at 300 kV. Figure 2.9 (a) is a low-resolution TEM image a VO₂ nanowire with two regions marked top and bottom that were irradiated by He ion at dose of 5×10^{16} and 1×10^{15} ions/cm², respectively. The highest dose corresponds to the maximum irradiation dose investigated and the central part of nanowire is unirradiated. Figure 2.9 (b)-(c) are the selected area electron diffraction (SAED) patterns of VO₂ at regions with different doses corresponding to the regions shown in Figure 2.9 (a). The SAED results show constantly sharp and clear patterns in all doses, implying that the defected VO₂ nanowires are fully single-crystalline for all the He ion dose applied in this study. This confirms that the light weighted He ion does not generate extended defects (35) or cause amorphization. The single crystallinity is also essential for us to study point defect physics in VO₂.

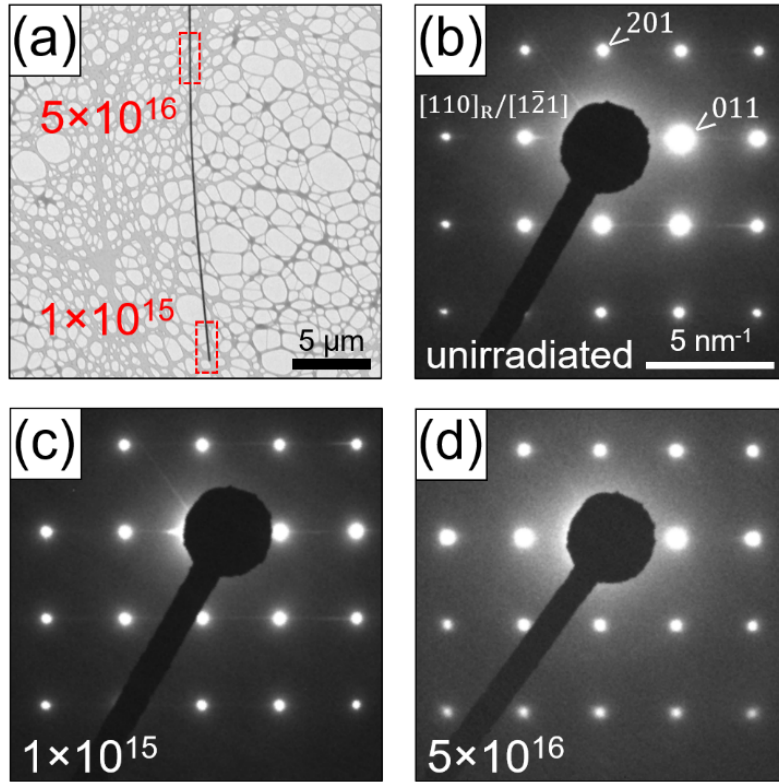


Figure 2.9. (a) Low resolution TEM image showing a VO_2 nanowire irradiated with He ions to doses of 1×10^{15} and 5×10^{16} ions/ cm^2 in the regions marked at the bottom and top, respectively. The central region remains pristine. SAED patterns are shown for the (b) pristine, (c) 1×10^{15} ions/ cm^2 irradiated and (d) 5×10^{16} ions/ cm^2 irradiated regions of the VO_2 nanowire. The survival of the sharp SAED pattern to the highest irradiation dose indicates that the He ion irradiation of VO_2 damages the lattice by generating point defects, without degrading the crystallinity. (Figures adapted from Phys. Rev. B Rapid Commun., 102, 041120(R) (2020)).

2.2.4 Transport measurement using suspended microdevice

The thermal conductivity of VO_2 nanowire is measured by suspended microdevice. As shown in figure 2.4, a VO_2 nanowire is transferred between two suspended pads forming a

thermal channel/bridge. When the heating pads is heated by its resistance coil, heat flows from heating pads to the sensing pads via VO_2 nanowires. Once we know the heat that passes through the nanowire and the temperatures at both end of the nanowire, the thermal conductance can be calculated. The temperature is calculated by measuring the resistance of the Pt resistance coils on both pads functioning as platinum resistance thermometers (PRTs) (36). The relation of resistance and temperature of both PRTs can be calibrated by background temperature controlled by temperature controller with temperature fluctuation small than 10 mK during the measurement. The suspension of pads and nanowires and high vacuum atmosphere (pressure less than 10^{-6} Torr) prevent extensive thermal leakage to the environment. Also, the contact resistance between nanowire and pads are reduced by Pt deposition to be in a negligible level compared with the resistance of the nanowire. Therefore, an equivalent thermal circuit can be defined and the heat flow that pass through the nanowires can be calculated by solving the equivalent circuit. After measuring the width, thickness and length of measured nanowire channel, the final thermal conductivity can be calculated.

The electrical conductivity of VO_2 nanowire is measured by the four electrodes on the micropads forming a 4-point configuration. The current is supplied by a current source through two outer electrodes and the voltage is measured by a voltage meter through two inner electrodes. The contact resistance is not measured in 4-point configuration. Therefore, the electrical conductivity can be measured. Furthermore, as we can measure both the voltage and temperature at two ends of the nanowire channel, the Seebeck coefficient can also be calculated. The detailed descriptions of the transport measurement methods can be found in section 1.2.

2.2.5 Experiment procedure

After the nanowires are grown using PVT method and are transferred to micropads (section 2.2.1), Pt deposition is performed by using FIB to bond nanowires onto the four electrodes of suspended pads (section 2.2.2). Then, the thermal and electrical conductivity of pristine VO_2 is measured. Next, He ion irradiation is performed on the measured VO_2 nanowire and followed by remeasurements of its thermal/electrical conductivity. It is important to maximally minimize the exposure time of the VO_2 nanowire to the air especially after irradiation. The defected VO_2 nanowires are more vulnerable to oxidation than pristine VO_2 . After irradiation, the transport measurements are conducted immediately. The last step is to repeat irradiation and measurement on the same VO_2 nanowire iteratively to collect a systematic data of conductivity change with respect to different accumulative native point defect levels (proportional to the He ion irradiation doses).

2.3 Electrical conductivity

2.3.1 The metal-insulator phase transition of VO₂

The metal to insulator transition of VO₂ was first discovered by F. J. Morin et al in 1959 (figure 2.10) (37). VO₂ transits from metallic (M) phase to insulating (I) phase when temperature drops below 341 K, the metal insulator transition temperature (T_{MIT}) (38, 39). As shown in figure 2.11, the electrical conductivity change is also accompanied by crystal lattice structure phase transition. The M phase VO₂ adopts a tetragonal rutile (R phase) structure with space group $P4_2/mnm$ and lattice constants $a = b = 4.55 \text{ \AA}$ and $c = 2.85 \text{ \AA}$. The crystal lattice of I phase VO₂ is monoclinic (M1 phase) with space group $P2_1/c$ and lattice constants $a = 5.75 \text{ \AA}$, $b = 4.53 \text{ \AA}$, $c = 5.38 \text{ \AA}$ and $\beta = 122.6^\circ$. The unit cell volume is double in M1 phase compared to R phase. Zig-zag chains of V are formed by V-V dimer in M1 phase.

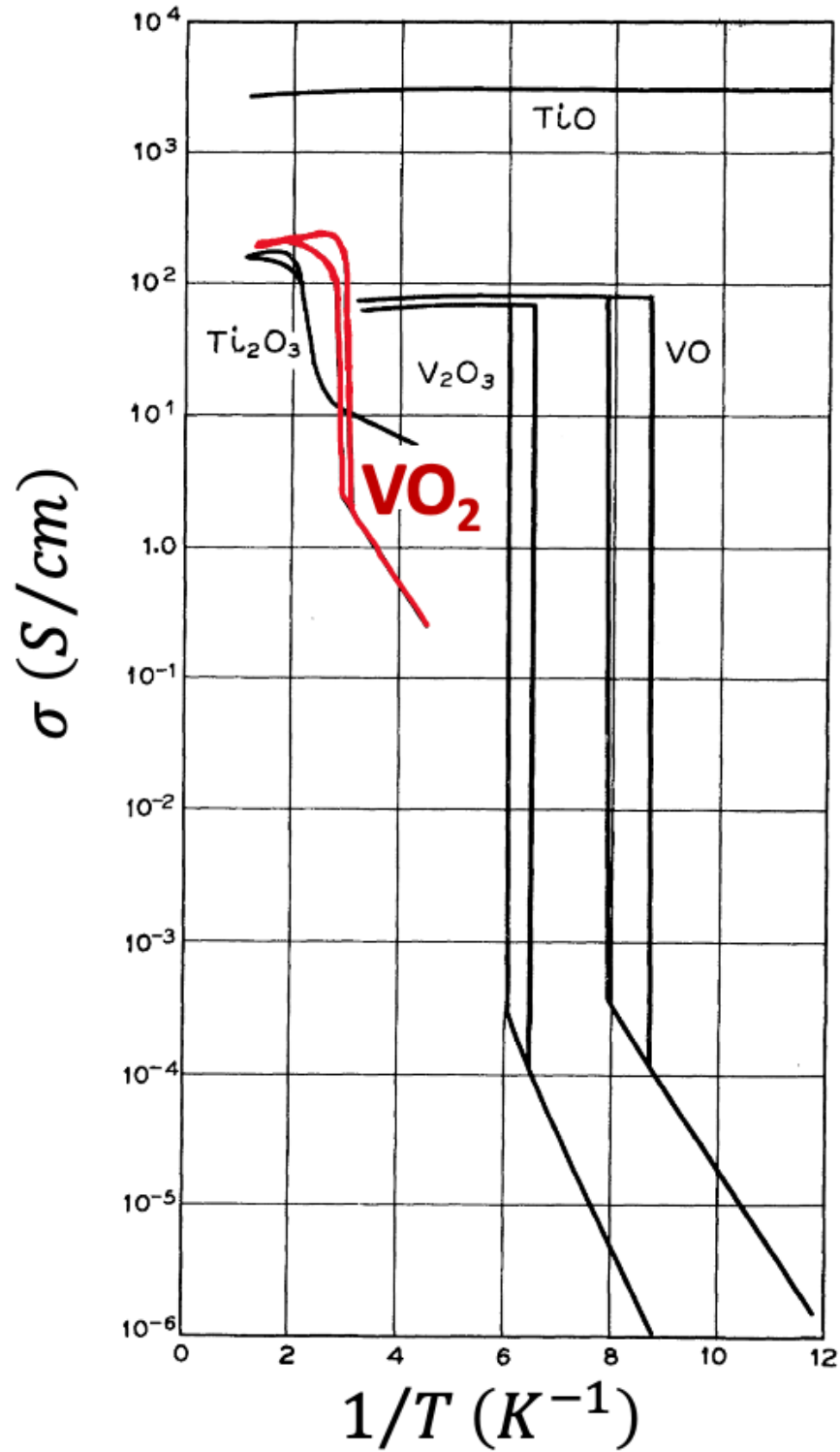


Figure 2.10. The electrical conductivity of VO_2 during its metal insulator phase transition. The phase transition is observed as an abrupt change of the electrical conductivity around 341 K. (Figure adapted from F. J. Morin et al, Phys. Rev. Lett. 3, 34 (1959)).

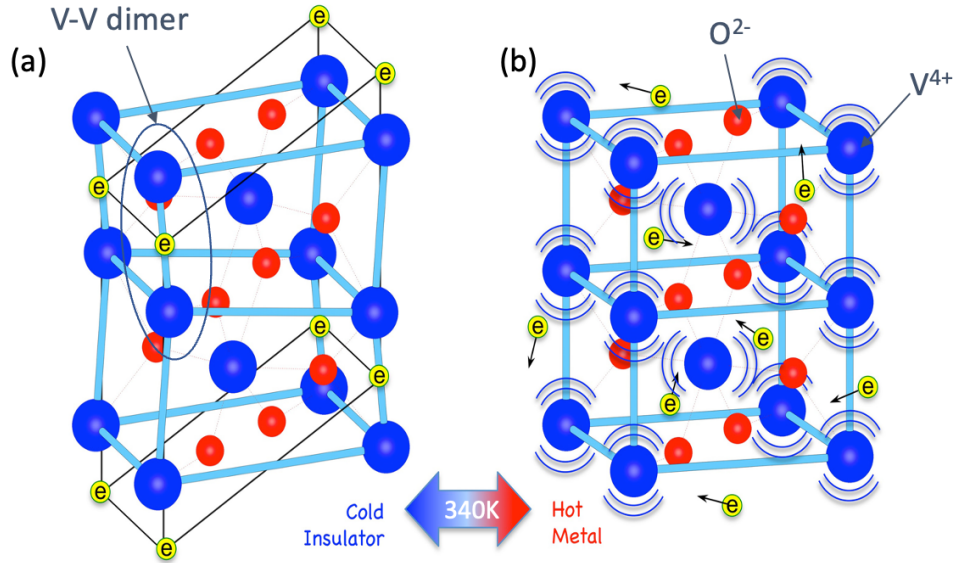


Figure 2.11. Schematics of crystal lattice of VO_2 at different phases. The crystal structural transits from monoclinic (M1) phase to tetragonal rutile (R) phase when VO_2 changes from insulating state to metallic states across T_{MIT} of 341 K. (Figure adapted from <https://phys.org/news/2015-04-insulator-to-metal-transition-vanadium-dioxide.html>).

2.3.2 The effect of oxygen vacancies in VO_2

As mentioned in section 2.2.3, point defects are created by He ion irradiation. These point defects can take forms of vacancies, interstitials and anti-sites of both vanadium and oxygen atoms in VO_2 crystal lattice. Many evidence has been shown that the oxygen vacancies are easier to be generated in VO_2 as oxygen can escape VO_2 and make VO_2 materials oxygen deficient. Cui et al has shown that oxygen vacancies have the lowest formation energy in VO_2 among all the other types of point defects (26). Oxygen vacancies are expected to be electron donors in VO_2 . As creating oxygen vacancies is effectively removing negatively charged oxygen ions, to balance charge neutrality, extra electrons must be supplied to the lattice. This makes oxygen vacancies as effective electron donors (40). One work to study the effects of oxygen vacancies is conducted by Fan et al (41). The number of oxygen vacancies is controlled by the oxygen partial pressure supplied during the growth of VO_2 thin films. Their work shows that in VO_2 thin film with oxygen vacancies, a drop of resistance of is clearly observed in the I phase VO_2 thin films at

temperatures lower than T_{MIT} . This is because the increase of electron density in oxygen deficient VO_2 thin films enhances their electrical conductivity by increasing the number of charge carriers.

Another effect of oxygen vacancies in VO_2 is to reduce the T_{MIT} to about room temperature. This opens many opportunities to utilize the properties of MIT in VO_2 in daily life applications. Zhang et al reports a drop of T_{MIT} in VO_2 nanowire after exposure it under high energetic electron beam in TEM (42). In their work, the center of one suspended VO_2 nanowire was irradiated by electron beams in TEM at room temperature. Oxygen vacancies were observed in the region of electron beam irradiation. The M phase of VO_2 is observed at a temperature of 56 °C (329 K) which is about 10 K below its normal T_{MIT} (341 K). Another example is from a VO_2 thin film irradiated by oxygen ions reported by Ramirez et al (43). In their work, a VO_2 thin film with thickness about 100 nm is irradiated by energetic oxygen ions at doses of 2×10^{14} , 5×10^{14} , 1×10^{15} and 2×10^{15} ions/cm² respectively. Oxygen vacancies are generated during the irradiation. A lowering of resistivity of I phase VO_2 and a reduction of T_{MIT} by increasing oxygen ion doses are observed. In addition, increases of electrical resistivities of irradiated VO_2 are observed when VO_2 is metallic in this work. This is the opposite trend compared to I-phase VO_2 . The electron-impurities scattering introduced by oxygen vacancies reduces the mobility of electrons in M phase VO_2 . Although the electron doping effects can help reduce the resistivity, the number of electrons donated by oxygen vacancies is negligible compared to the intrinsic conduction electrons in M phase VO_2 . Therefore, the overall effect is increasing the electrical resistivity of M-phase VO_2 after oxygen ion irradiation.

2.3.3 The measured results of electrical conductivity of He-ion-irradiated VO_2

As mentioned in section 2.3.2, the oxygen vacancies are more likely to be created in VO_2 due to their low formation energy and the fact that the oxygen can escape through VO_2 surface. In our experiment, the He ion irradiation can also create point defects forms mainly of oxygen vacancies. The changes of electrical conductivity in He-ion-irradiated VO_2 resembles the previous work, which has three key features: 1) an increase of electrical conductivity of I-phase VO_2 ; 2) a reduction of T_{MIT} and 3) a decrease of electrical conductivity of M-phase VO_2 . Figure 2.12 shows the measurement of electrical conductivity of three He-ion-irradiated VO_2 nanowires with their diameters of 130, 140 and 160 nm at various He ion irradiation doses, respectively. The diameters of the measured VO_2 nanowires are all below 160 nm, allowing He ions to fully penetrate through the entire nanowires during irradiation. These single-crystalline VO_2 nanowires are firstly measured in their pristine quality before irradiation. Both heating and cooling process are measured. The sharp and abrupt jumps in electrical conductivity are observed at 341 K implying good qualities of these VO_2 nanowires. Then, He ion irradiation is performed in a He ion microscope with irradiation area covering the entire nanowire channel on the

suspended pads. Below the He ion dose of 1×10^{15} ions/cm², there is no clear change of electrical conductivity of irradiated VO₂, which means the point defects created is too few to induce any effect in VO₂. At the dose ranging from 1×10^{15} to 1.5×10^{16} ions/cm², the shift of $\sigma(T)$ curves with irradiation agrees with the effect of oxygen vacancies on VO₂ reported in all the previous works mentioned in section 2.3.2. The MIT persists in VO₂ even after the dose of irradiation at 1.5×10^{16} ions/cm², although the sharpness of the MIT and conductivity ratio between the metallic and insulating phases are reduced. The T_{MIT} is reduced from 341 K of the pristine quality to near 300 K for the heavily irradiated state.

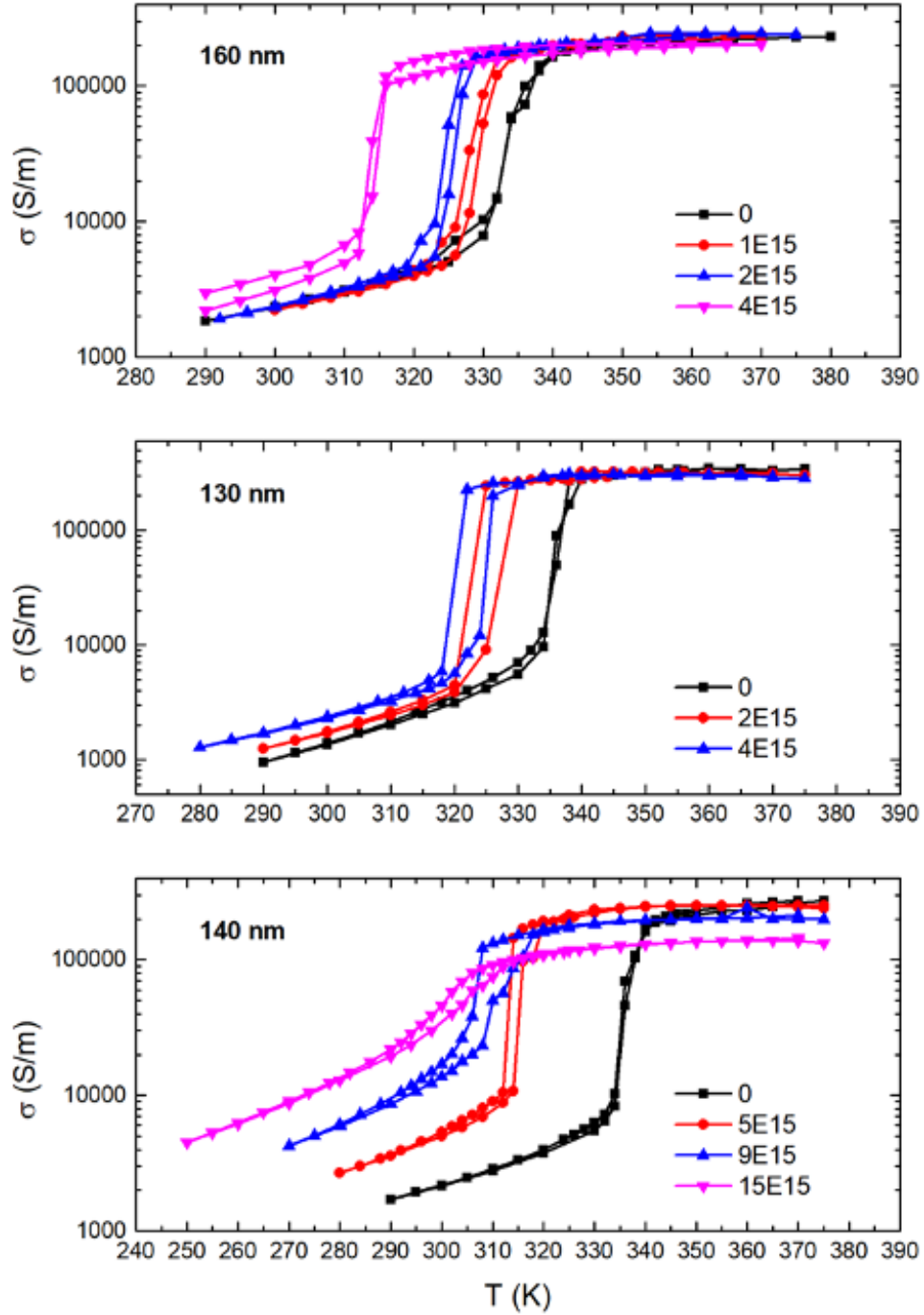


Figure 2.12. Electrical conductivities of VO_2 nanowires across the metal-insulator transition of three VO_2 nanowire with thickness of 160, 130 and 140 nm respectively. The VO_2 nanowires are irradiated with He ions at accumulated doses ranging from 1×10^{15} to 1.5×10^{16} ions/cm².

2.4 Thermal conductivity

2.4.1 The thermal conductivity of pristine VO₂

In normal semiconductors, the thermal conductivity consists of two parts: the lattice contribution and the electronic contribution. The former describes the heat transport carried by phonons while the latter describes that carried by charge carriers (electrons or holes). In most non-metallic materials, the electronic contribution to thermal conductivity is negligible compared to its lattice counterparts. This is predicted by Wiedemann-Franz (W-F) law (*I*), which states the electronic thermal conductivity $\kappa_e = L_0 \sigma T$, where the Sommerfeld value $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$, σ is the electrical conductivity and T is the temperature. Take $\sigma = 10^3 \text{ S/m}$, a typical value of semiconductor such as doped silicon at $T = 300 \text{ K}$, its corresponding electronic thermal conductivity is $\kappa_e \approx 7 \times 10^{-3} \text{ W/mK}$, which is three or four orders of magnitude smaller compared to its lattice thermal conductivity κ_l (on order of ones or tens of W/mK at room temperature). To make κ_e comparable to κ_l , the σ needs to be on order of 10^5 S/m , which is a typical value of metals or heavily doped degenerate semiconductors. Therefore, one should expect the thermal conductivity of M-phase VO₂ consists of both κ_e and κ_l , while that of I-phase VO₂ only consists of κ_l .

However, as it is discussed in section 2.1, metallic VO₂ is a strongly correlated metal or “bad” metals, where its inelastic electron-electron scatterings from Coulombic repulsion are not negligible due to electron correlations. The resistivity of VO₂ also exceeds the Mott-Ioffe-Regel (MIR) limit (*44*), which is derived from the Heisenberg uncertainty principle for momentum and position (*45*). The surpassing of MIR limits means that the mean free path of electrons in VO₂ is small than its lattice constants. This is not allowed in classical Drude model (*I*), where the resistivity of charge carriers arises from collisions with lattice imperfections such as impurities or dopants. The violation of MIR limits implies strong electron-electron interactions or a complete failure or long-lived quasiparticle descriptions. The W-F law is also violated in such cases with its Lorenz number smaller than the Sommerfeld value (*9*).

The first systematic study on the thermal conductivity of VO₂ across the metal-insulator transition was reported by Lee et al (*8*). In their work, κ_e is determined by subtracting κ_l obtained by combining both the first principles calculations and x-ray scattering measurements, from the measured total thermal conductivity (κ_{tot}). The measured κ_{tot} exhibits small change across the MIT. The difference between the total thermal conductivity of metallic phase ($\kappa_{\text{tot}}^{\text{M}}$) and that of insulating phase ($\kappa_{\text{tot}}^{\text{I}}$) is about 0.2 W/mK. Let us assume that both M and I phase VO₂ obey the W-F law, that is $L = L_0$. The σ in their work rises from $\sigma^{\text{I}} = 4.6 \times 10^3 \text{ S/m}$ (I phase) to $\sigma^{\text{M}} = 8.0 \times 10^5 \text{ S/m}$ (M phase). This

predicts that κ_e exhibits an abrupt jump from nearly zero to 6.9 W/mK. The measured difference of κ_{tot} between I and M phase is less than 3% of κ_e in the M phase (κ_e^{M}). Considering that κ_e^{M} predicted by W-F law alone is already larger than the measured κ_{tot} . Applying W-F law results a negative κ_l in the M phase, which is unphysical and implies that the W-F law is violated.

To extract the value of κ_e from the measured κ_{tot} in phase VO₂, the κ_l needs to be calculated. The phonon dispersion relation is first calculated using density functional theory. The phonon scattering rates are obtained from energy- and momentum- resolved inelastic x-ray scattering (IXS). In this calculation (8), at T_{MIT} , the bulk value of lattice thermal conductivity of the I-phase VO₂ is $\kappa_l^{\text{I,bulk}} = 6.46$ W/mK while that of the M-phase VO₂ is $\kappa_l^{\text{M,bulk}} = 5.72$ W/mK. The difference between $\kappa_l^{\text{I,bulk}}$ and $\kappa_l^{\text{M,bulk}}$ of bulk VO₂ materials is about 13%. The bulk value of κ_l includes Umklapp scattering, electron-phonon scattering and all other possible scattering of phonons in bulk defect-free VO₂. In VO₂ nanowire, using the Matthiessen's rule, we can combine the bulk scattering together with boundary and impurity scattering. In this case, the difference between $\kappa_l^{\text{I,NW}}$ and $\kappa_l^{\text{M,NW}}$ is even smaller. Therefore, one can assume that the lattice thermal conductivity is almost equal between M and I phase VO₂ nanowires at T_{MIT} .

After κ_l is calculated, the electronic thermal conductivity can be determined as $\kappa_e = \kappa_{\text{tot}} - \kappa_l$. In the I-phase VO₂, the charge carrier density is too low to contribute to the thermal conduction. Therefore the $\kappa_l^{\text{I}} \approx \kappa_{\text{tot}}^{\text{I}}$ and $\kappa_l^{\text{M}} \approx 0$. In M-phase VO₂, the $\kappa_e^{\text{M}} = \kappa_{\text{tot}}^{\text{M}} - \kappa_l^{\text{M}} \approx \kappa_{\text{tot}}^{\text{M}} - \kappa_{\text{tot}}^{\text{I}}$, which is 0.72 W/mK at T_{MIT} . Therefore, the Lorenz number $L = (\kappa_e^{\text{M}}/L_0\sigma^{\text{M}}T) \cdot L_0 = 0.11L_0$, indicating a strong suppression of Lorenz number by nearly an order of magnitude.

2.4.2 The measured results of thermal conductivity of He-ion-irradiated VO₂

Point defects serves as impurities in materials can scatters phonons. The thermal conductivity is reduced due to the induced phonon-impurity scattering (46) in both I and M phases of VO₂ from point defects. Figure 2.13 is the thermal conductivity of three VO₂ nanowires at different irradiation doses, which are the same nanowires and He doses measured in electrical transport as shown in section 2.3.3. The T_{MIT} is also reduced with increased He ion doses. The T_{MIT} determined from thermal transport is the same as that determined in electrical transport. This indicates that the metal insulator transition and crystal lattice structure transition occur simultaneously.

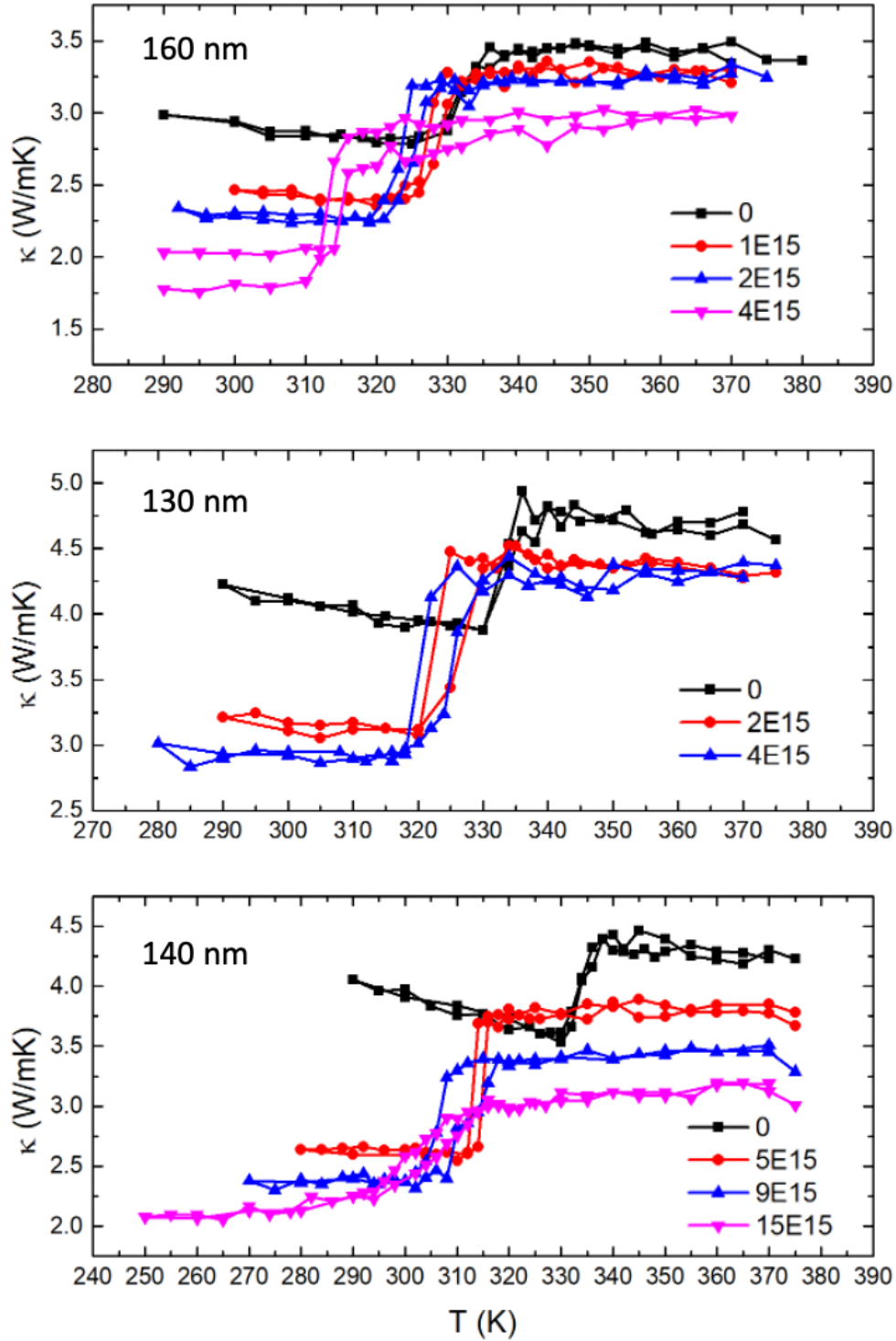


Figure 2.13. Thermal conductivities of VO₂ nanowires across the metal-insulator transition of three VO₂ nanowire with thickness of 160, 130 and 140 nm respectively. The VO₂ nanowires are irradiated with He ions at accumulated doses ranging from 1×10^{15} to 1.5×10^{16} ions/cm².

Impurity scattering from point defects in defected VO₂ can also be revealed in the T -dependent slope of thermal conductivity at I phase. As electronic thermal conductivity can be ignored in insulating VO₂, the thermal conductivity is mainly lattice thermal conductivity. In figure 2.14, we extract the slope of thermal conductivity with respect to temperature in insulating VO₂ ($d\kappa_1/dT$) under different He ion irradiation doses. In unirradiated pristine VO₂, $d\kappa_1/dT$ is negative. This decreasing trend of $\kappa_1(T)$ indicates that Umklapp scattering dominates phonon scattering. After irradiation, $d\kappa_1/dT$ increases and switches sign from negative to positive, which implies different scattering mechanisms arises after irradiation. Phonon relaxation time (τ) in insulating VO₂ nanowires can be expressed as $\tau^{-1} = \tau_{umkl}^{-1} + \tau_{imp}^{-1} + \tau_{bdy}^{-1}$ in Matthiessen's rule (section 1.1), with Umklapp scattering ($\tau_{umkl} \propto T^{-1}$), impurity scattering (τ_{imp}) and boundary scattering ($\tau_{bdy} \propto T^0$) considered. The Klemens' expression ($\tau_{imp}^{-1} \propto \omega^4$) can be employed here to determine electrons scattering with point defects (46, 47), where ω is the phonon frequency. τ_{imp} implicitly depends on temperature on high order as phonon distribution changes with temperature in Bose-Einstein statistics. Compare to Umklapp scattering, phonon-impurity scattering rate is almost T -independent especially when temperature is above Debye temperature. From DFT calculation the upper energy limit of acoustic phonon in insulating VO₂ is around 20 meV(8). In our temperature range (280-360 K, $k_B T \sim 24$ -31 meV), acoustic phonon modes should be well excited. The average frequency (ω) of acoustic phonon is insensitive to temperature rise. $d\kappa_1/dT$ gradually shifts towards zero implies more and more impurity scattering are introduced in VO₂ by increasing ion irradiation dose. Meanwhile, phonon density also increases with temperature. At high irradiation dose where impurity scattering overcomes Umklapp scattering, positive $d\kappa_1/dT$ is also observed because more phonons are involved in thermal transport.

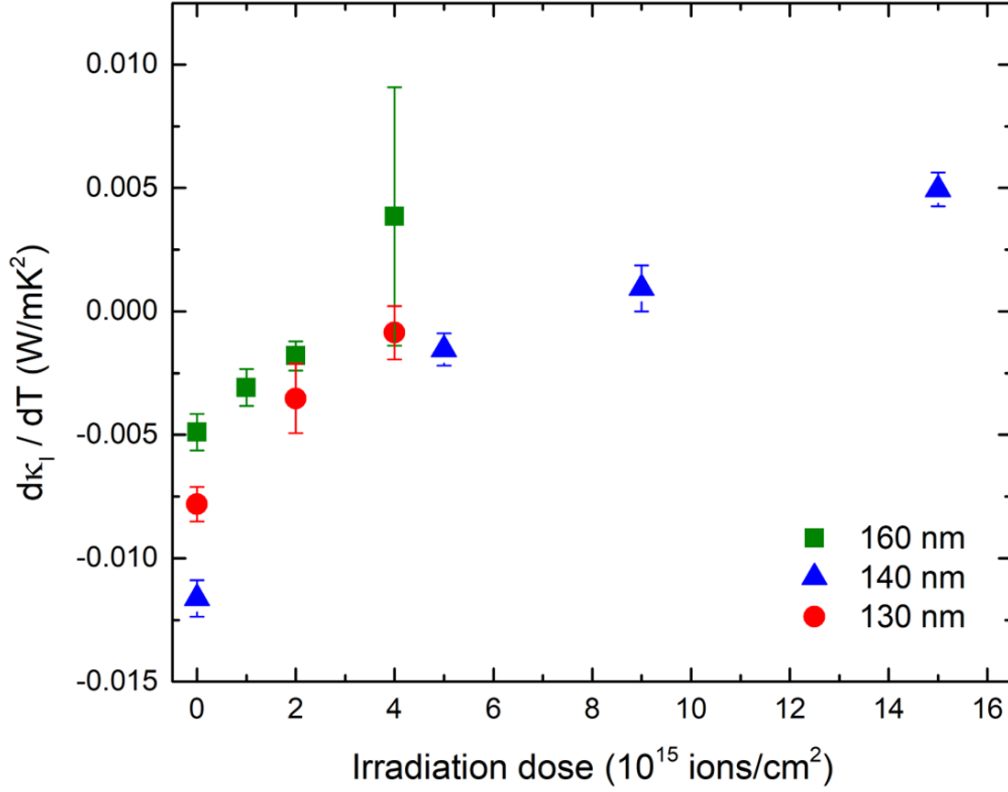


Figure 2.14. Effects of impurity scattering in irradiated VO₂. The temperature coefficient of I-phase thermal conductivity becomes less negative with irradiation and even switches sign, indicating progressively stronger phonon scattering by impurities rather than by other phonons.

To probe the validity of W-F law in irradiated VO₂, we calculated the electronic thermal conductivity predicated by the W-F law that is $\kappa_e^0 = L_0 \sigma T$. In figure 2.15, we shifted the κ_e^0 by an offset to match the κ_I^I at T_{MIT} . This effectively adds the lattice thermal conductivity κ_I^I into the κ_e^0 , which is $\kappa_{e_offset}^0 = \kappa_e^0 + \kappa_I^I$. For pristine VO₂, the $\kappa_{e_offset}^0$ is even larger than the measured κ_{tot} , which is consistent with previous work. With He ion irradiation dose increases, the jump of measured κ_{tot} increases and starts to approach that of $\kappa_{e_offset}^0$. At the He ion dose at 1.5×10^{16} ions/cm², the $\kappa_{e_offset}^0$ and κ_{tot} matches with each other, indicating a full recovery of W-F law.

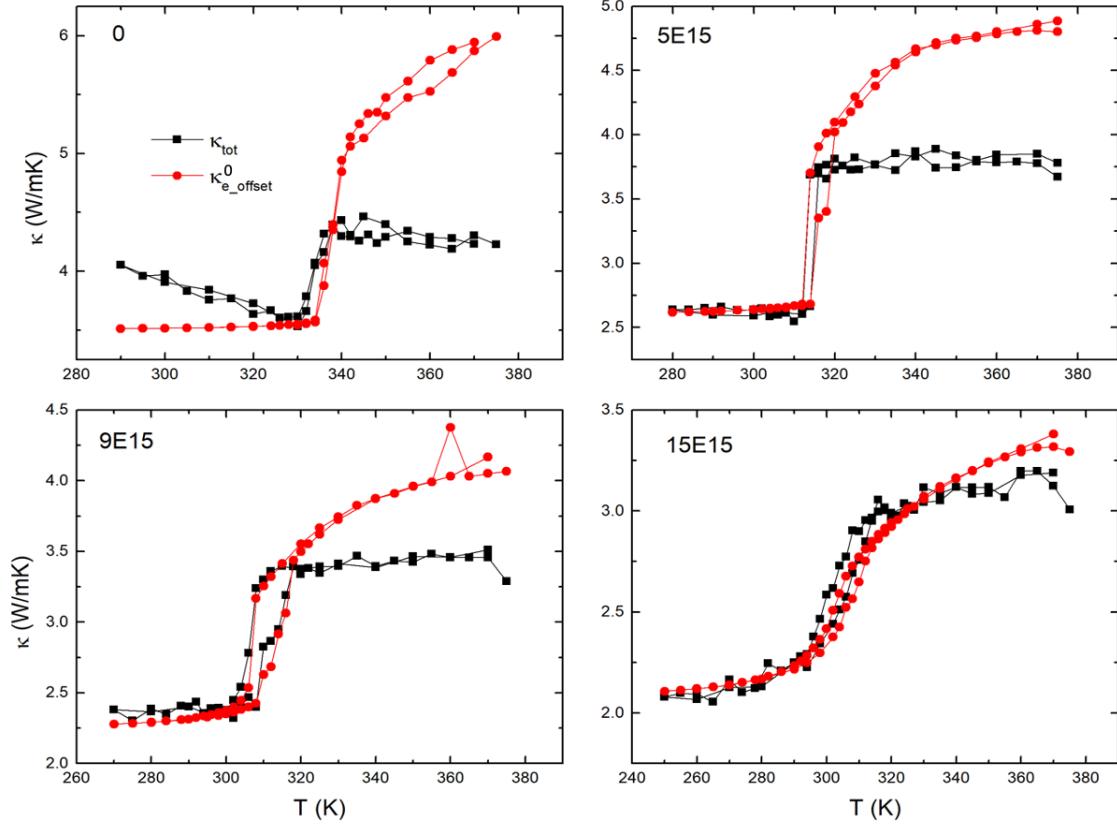


Figure 2.15. Comparisons between total thermal conductivity κ_{tot} and electronic thermal conductivity predicted by W-F law κ_e^0 at He ion doses at 0, 5, 9 and 15×10^{15} ions/cm².

2.5 The recovery of Wiedemann-Franz law

2.5.1 The evaluation of Lorenz number

In section 2.4.1, combining using inelastic x-ray scattering and first-principles calculation, Lee *et al.* showed that the lattice thermal conductivity (κ_l) for VO₂ remains almost the same when VO₂ transitions between the I and the M phase at the transition temperature (8). This means that $\kappa_l^I \approx \kappa_l^M$ near T_{MIT} . The M phase has a more anharmonic lattice (48) which results shorter phonon mean free path for low energy phonon modes (smaller than 10 meV). On the other hand, the I phase has many more optical phonon modes with low group velocities because its unit cell is double in monoclinic structure compared to rutile (38).

This can lower the MFPs. As a result, the average mean free path (MFP) for the M and I phase is very close to each other, which is 5.18 and 5.86 nm, respectively. If the boundary and impurity scattering of phonons are included via the Matthiessen's rule, The approximation that $\kappa_l^I \approx \kappa_l^M$ improves further, because such scattering of thermal phonons is not much different in the M and I phase. This provides a convenient method to evaluate the Lorenz number for the M phase of VO₂, because according to $\kappa = \kappa_l + \kappa_e$ and the fact that κ_e is nearly zero in the I phase, κ_e^M at T_{MIT} can be estimated by $\kappa_e^M = \kappa^M - \kappa_l^M \approx \kappa^M - \kappa^I$. That is, the jump across T_{MIT} in the measured total thermal conductivity is mainly attributed by the electronic thermal conductivity gained in the M phase. We will adopt this method to estimate κ_e^M in all the VO₂ samples, and use it to evaluate the Lorenz number near T_{MIT} according to

$$\frac{L}{L_0} = \frac{\kappa_e^M}{L_0 \sigma^{M.T}} \approx \frac{\kappa^M - \kappa^I}{L_0 \sigma^{M.T}}. \quad (2-1)$$

One of the advantages of using suspended microdevices measuring transport in nanowires is that the thermal and electrical conductivity are measured along the exact same lattice direction. The Lorenz number calculated does not has any errors results from different lattice orientations in both transport measurements. Figure 2.16 shows the normalized Lorenz number L/L_0 at the respective T_{MIT} from three different VO₂ nanowires, each of which was irradiated with a dose ranging from zero to 1.5×10^{16} ions/cm². Two data points are shown for each measurement, calculated for data collected in the heating and cooling step, respectively. L/L_0 all increase as a function of irradiation dose for all the nanowires. Moreover, plotting L/L_0 as a function of T_{MIT} reveals a universal trend for all the data, regardless of the different samples and different doses. L/L_0 approaches 1, namely, the W-F law is fully recovered with $L = L_0$, at the dose of 1.5×10^{16} ions/cm². Interestingly, this dose is also the maximum dose under which the MIT can survive: irradiation at higher doses completely destroys the MIT.

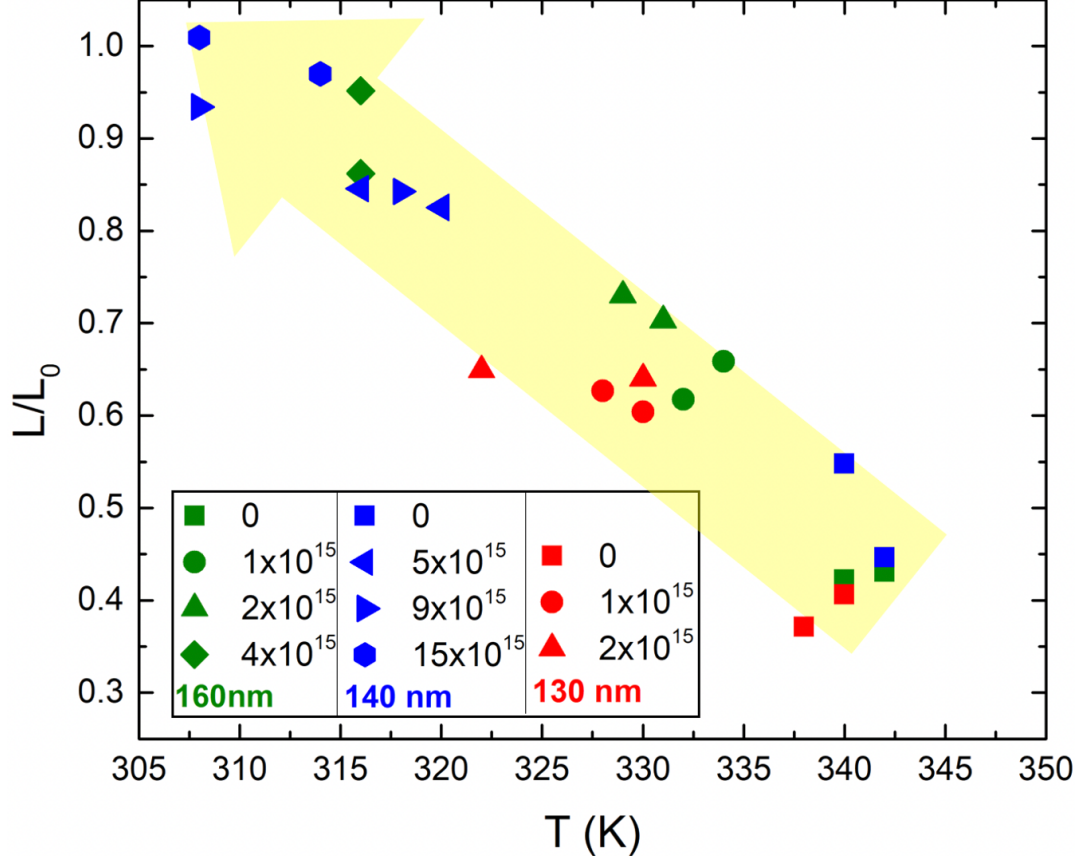


Figure 2.16. Normalized Lorenz number (defined as $(\kappa_M - \kappa_I)/\kappa_e^0$ at T_{MIT}) of three VO₂ nanowires with different thicknesses (labeled) and at different irradiation doses (in units of ions/cm²), showing the recovery of L upon introduction of defects to the Sommerfeld value ($L_0 = 2.44 \times 10^8 \text{ W}\Omega\text{K}^{-2}$) of a normal metal.

2.5.2 Hydrodynamic model

In quasiparticle transport, charge currents can only be degraded in momentum-nonconserving scattering processes of charge carriers, whereas electronic heat currents can also be degraded by energy-nonconserving (*i.e.*, inelastic) scattering of charge carriers (11, 49). This is because that charge flow only transports momentum, but heat flow transports both momentum and energy. Therefore, the W-F law can be violated at low temperatures where inelastic electron-phonon scattering becomes significant (49) and $L/L_0 < 1$. Another example is the breakdown of the W-F law in quasiparticle transport of hydrodynamic Fermi liquids (11, 18). In the hydrodynamic regime, electron-electron

interactions dominate, and the Lorenz number is lowered. This is because the charge current is not relaxed by the electron-electron interactions as they are momentum-conserving. However, the heat current can be relaxed because this scattering can be inelastic. In both two scenarios of quasiparticle transport where $L < L_0$ (low temperature or hydrodynamic regime), it has been shown that disorder raises L toward L_0 and restores the W-F law (11, 18, 49). The MFP of both charge and heat transport are simultaneously and proportionally degraded by the additional, momentum-nonconserving, impurity scattering of electrons. The full recovery of W-F law is also proved to be possible if elastic scattering dominates.

However, similar theory of disorder effects in nonquasiparticle transport has not been established. Despite many fundamental differences, strong electron-electron interactions exist in both quasiparticle transport of hydrodynamic Fermi liquids and nonquasiparticle transport of non-Fermi liquids. We thus “borrow” the results obtained when treating disorder in hydrodynamic Fermi liquids (18) to discuss defect scattering in nonquasiparticle transport. In this case, it has been shown that the Lorenz ratio is approximated by

$$\frac{L}{L_0} \approx \frac{\Gamma}{\Gamma + \gamma}, \quad (2-2)$$

where γ is the electron-electron scattering rate, and Γ is the electron-defect scattering rate. We also adopt the relaxation time approximation and relate the scattering rate to electrical conductivity as $\sigma^M \propto \tau$, where τ is the relaxation time and is the reciprocal of the scattering rate. It is straightforward to show that

$$\frac{L}{L_0} \approx 1 - \frac{\sigma^M}{\sigma_{pure}^M}, \quad (2-3)$$

where σ_{pure}^M is the ideal electrical conductivity in defect-free samples. As shown in Figure 2.17, L/L_0 has a nearly linear dependence on σ^M consistent with equation 2-3. Therefore, strong elastic scattering from the disorder indeed restores the W-F law, and L/L_0 can be viewed as a measure of the fraction of disorder scattering in this “bad” metal.

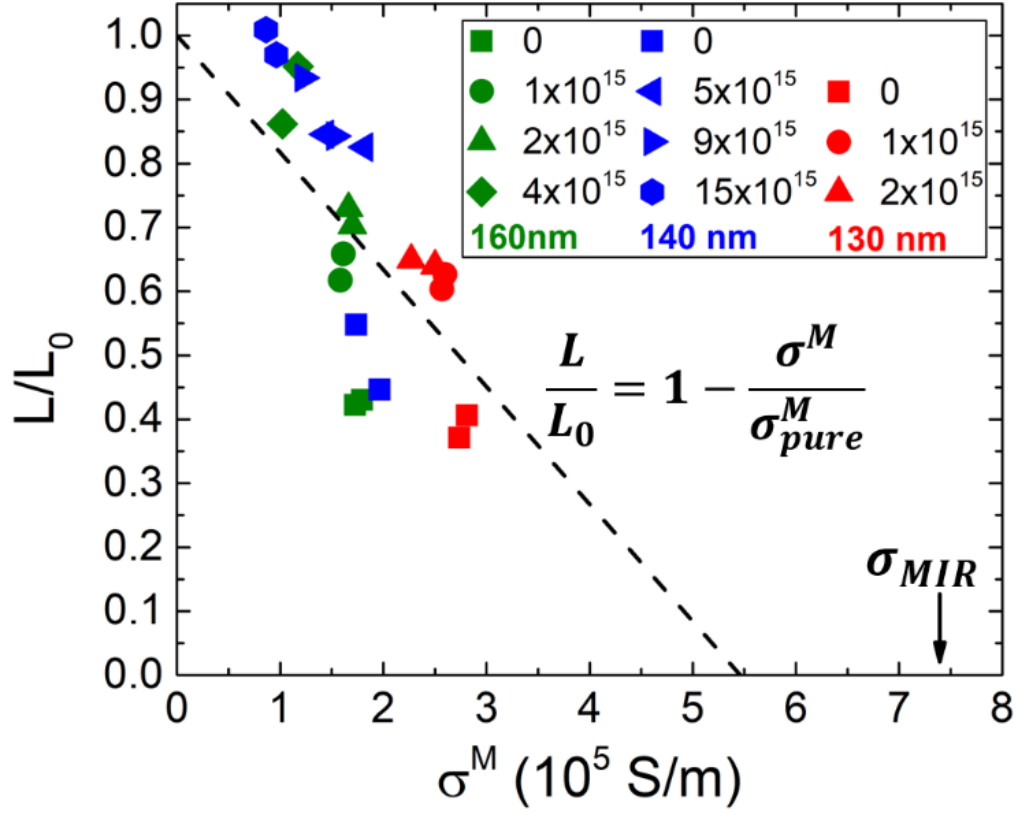


Figure 2.17. Normalized Lorenz number L/L_0 (as defined in equation 2-1) for three VO_2 nanowires of different thicknesses (labeled) for different irradiation doses (in units of ions/ cm^2) as a function of σ for the M phase just above the MIT, showing the recovery of L upon introduction of defects toward the Sommerfeld value ($L_0 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$) of a normal metal. The error range of the L/L_0 data points is about ± 0.1 . The MIR limit of σ is indicated with an arrow, proving that all data exceed the σ_{MIR} . (Figure adapted from Phys. Rev. B Rapid Commun., 102, 041120(R) (2020)).

It is noted that the average separation between neighboring point defects from the He ion irradiation is about a few nm according to simulations using the SRIM program. This is much longer than the MFP of charge carriers in the M phase of pristine VO_2 , which is about 1~2 Å estimated assuming the Drude model. It is surprising that such sparsely distributed point defects can significantly reduce σ of M-phase VO_2 , by more than 50% (figure 2.17). The MFP resulting from defect scattering is inversely proportional to not only the density of defects, but also to the scattering cross section. It has been reported that atomic impurities show a larger scattering cross section area in “bad” metals than in normal metals (50). The unusually large electron-defect scattering cross section in a “bad” metal may only be explained by the correlated nature of the interacting electrons (51). Consequently, the significant reduction in σ^M by irradiation implies anomalously strong electron-defect interactions in the M phase of VO_2 .

2.5.3 Seebeck coefficient

The Seebeck coefficient (S) of VO_2 can be measured simultaneously with thermal and electrical conductivity. Another parameter that indicates the lack of quasiparticle transport is that the dimensionless electronic figure of merit, $S^2/L = S^2\sigma^M T/\kappa_e^M$, is unusually large. The parameter S^2/L is theorized to be very low for quasiparticle transport in a Fermi liquid, as S is suppressed by the factor $k_B T/E_F$. Indeed, it is on the order of 10^{-4} for conventional metals such as Cu. In contrast, in the metallic phase of VO_2 , values of S^2/L are all between 10^{-2} and 10^{-1} , as shown in Figure 2.18 (a).

Further evidence of significant change in the electron scattering mechanism by defects is the behavior of the Seebeck coefficient. Derived from the linearized Boltzmann transport equation for parabolic bands, the Seebeck coefficient of a metallic system can be written as:

$$|S| = \frac{k_B}{e} \frac{\pi^2}{3} \frac{k_B T}{E_F} \left(\frac{3}{2} + r \right), \quad (2-4)$$

where a power law energy dependence for the relaxation time is assumed: $\tau(E) \propto E^r$, and r is the power index (52-54). For elastic scattering, r varies from $-1/2$ for acoustic phonon scattering to $3/2$ for ionized impurity scattering. For inelastic scattering (53), the power law energy dependence of τ fails and r is not a constant. As figure 2.18 (b) shows, the values of S agree very well with Lee *et al.* for pristine VO_2 , but increase for irradiated samples while retaining the linear dependence on T . This is in stark contrast to the behavior of S for W-doped VO_2 measured by Lee *et al.* In the latter case, S collapses onto the same T dependence as that of the pristine VO_2 , suggesting that W dopants do not change the electron scattering mechanism in VO_2 . In the absence of a defect theory for nonquasiparticle transport, we discuss the behavior of S in the framework of Eq. (4) in the relaxation time approximation. In figure 2.18 (b), the overall upward shifting in $S(T)$ after irradiation implies higher r values, which is consistent with the increased importance of defects to provide more ionized impurity scattering in the electron scattering process.

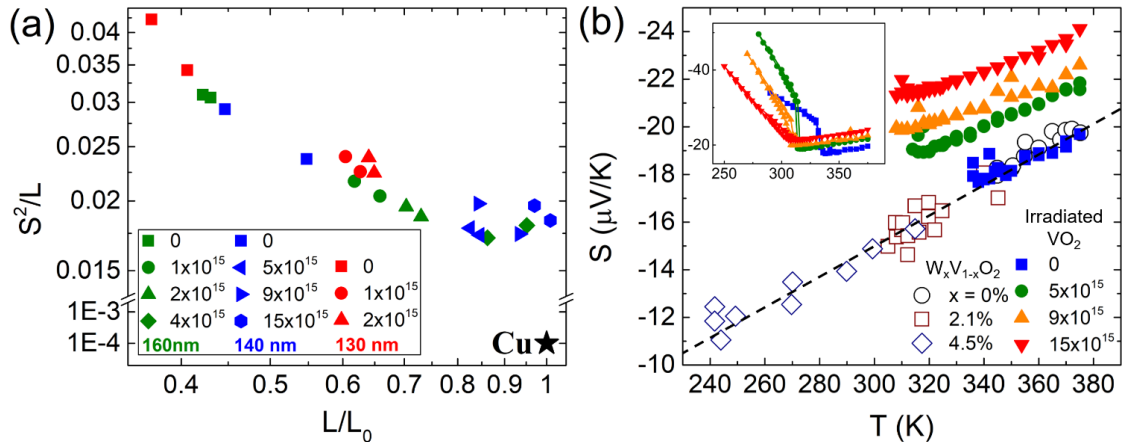


Figure 2.18. Effects of impurity scattering in irradiated VO₂. (a) The electronic figure of merit (S^2/L) at T_{MIT} decreases with L/L_0 . The nonquasiparticle transport in the M phase of VO₂ manifests in both the unusually high S^2/L value as well as the lower-than-unity L/L_0 value, in contrast to normal metals such as Cu. (b) M-phase Seebeck coefficient of a 140 nm-thick VO₂ nanowire after irradiation to different doses, compared with that of W-doped VO₂ nanowires adopted from Lee *et al.* The upward shift in the Seebeck coefficient upon irradiation reflects increasingly stronger scattering of itinerant electrons by ionized impurities. (Figures adapted from Phys. Rev. B Rapid Commun., 102, 041120(R) (2020)).

2.6 Conclusion

In conclusion, we show empirical validity of a quasiparticle transport model in a system where long-lived quasiparticles are clearly absent. The evidence is restoration of the electronic thermal conductivity to the quasiparticle value in a metallic system where it is originally suppressed by the absence of quasiparticles. We introduce atomic-level point defects as elastic scattering centers for conduction electrons using energetic particle irradiation. The increased weight of elastic scattering fully recovers the Wiedemann-Franz law at high defect densities. This finding bridges the decoupled electro-thermal transport in the nonquasiparticle regime to a coupled one in the more conventional, quasiparticle regime. In addition, ion irradiation is shown to be an effective tool for not only modulating the conductivities, but also controlling the conduction mechanism of electronic and thermal currents.

Chapter 3 Probing the critical nucleation seeds in deeply supercooled VO₂

3.1 Introduction

Nucleation is the initial step to form a new thermodynamic phase of a crystal that can monotonously grow into a larger sized nucleus from a metastable parent phase (55, 56). For nearly a century, it has been assumed that forming a growing new phase requires the size of nucleus to exceeds critical nucleation sizes according to classical nucleation theory (CNT) (57, 58). There has been no direction evidence for the existence of such nucleation sizes due to their transient and nanoscopic nature for a long time. Recently, Guoying et al. show that graphene oxide nanosheets of controlled sizes can have a notable impact on ice nucleation in water droplets only above a certain size that varies with the degree of supercooling of the droplets (59). The existence of critical nucleation sizes is thus observed and their experimental measurements agree with the classical nucleation theory. Although such nucleation process in common materials (e.g., H₂O) is well understood theoretically, in some strongly correlated materials, such as vanadium dioxide (VO₂), the nature of metal-insulator transition (MIT) is still under debate. Whether there exist critical nucleation sizes and how well the CNT model can predict the nucleation behavior in strongly corelated system are also unknown and lack experimental evidence. Although the MIT of VO₂ has been widely studied and used in many applications, the fundamental nucleation physics such as the critical nucleation size in VO₂ has not yet been investigated. Therefore, it is very interesting to probe the nucleation nature in VO₂.

In this work, we studied the critical nucleation sizes in the cooling process of the MIT of VO₂. First, we realized a deeply supercooled VO₂ domain on a suspended VO₂ nanobeam by using the so-called irradiation shielding created by helium ion irradiation at a certain dose. The suspension of VO₂ provided by suspended microdevice is to fully release strain along the supported VO₂ nanobeam (6) to allow us to probe its intrinsic phase transition properties. Next, we introduced nucleation seeds onto VO₂ surface, which has controlled sizes and circular shapes. Then, we probed the critical nucleation sizes in the metallic (M) phase to insulating (I) phase transition of VO₂ by cooling the VO₂ nanobeam from temperatures above 341 K (metal insulator transition temperature, T_{MIT}) down to room temperature. The relation between critical nucleation sizes and nucleation temperatures are measured by recording the I phase nucleation temperatures (T_{nuc}) with the corresponding

nucleation seeds with given diameters. To differentiate these two phases of VO₂, we used optical color contrast between M and I phase using an optical microscope. The insulating phase usually has brighter optical color, such as red and green, which depends on the diameter of the nanobeam. The metallic phase usually has dimmer brown color. We experimentally proved the existence of such critical nucleation sizes in the MIT of VO₂ and compared the measured results with CNT predictions. Our results could provide some insights into the MIT of VO₂, whose mechanism is still under debating and not fully understood.

3.2 The classical nucleation theory

The classical nucleation theory is a commonly used theoretical model to describe the kinetics of a nucleation process. The nucleation process has two different types: homogeneous nucleation (60) and heterogeneous nucleation (61, 62), which is determined by whether or not the nucleation is triggered by favorable nucleation sites such as surfaces, defects or foreign particles. The critical nucleation sizes can be calculated by minimizing the total Gibbs free energy of the system, which consists of a volume free energy and interface free energy between the new phase and parent phase.

3.2.1 Homogeneous nucleation

Homogeneous nucleation is process where nucleation is occurring without any preferential nucleation site. Compared to heterogeneous nucleation, homogeneous nucleation is much rarer because initiating the nucleation requires much higher energy to overcome the potential barrier of phase transition. Also, it is very difficult to have a natural ultrapure material without any imperfection unless deliberately controlled under lab conditions. However, homogeneous nucleation is much simpler and easier to understand than heterogeneous nucleation in terms of theoretical calculation. To understand heterogeneous nucleation, it is easier to begin with homogeneous nucleation. In common lab conditions, the phase transition is under constant temperatures and pressures. The Gibbs energy (G) is a thermodynamic potential that is minimized when a system reaches equilibrium under constant pressure and temperature. Assuming a microscopic spherical nucleus of new phase with a radius r is created in a parent phase, the change in the total Gibbs free ΔG can be expressed as,

$$\Delta G = \frac{4}{3}\pi r^3 \cdot \Delta g_V + 4\pi r^2 \cdot \sigma_s, \quad (3-1)$$

The first term is the volume term of free energy change, where Δg_V is the difference in free energy per unit of volume between the new phase that nucleates and the parent phase that

nucleation is occurring in. Δg_V is always negative as the nucleation process always progresses in a direction to lower the system thermodynamic potential G . The second term comes from the free energy gained by creating an interface between the nucleus and the parent phase, where σ_s is the surface energy of the interface. The surface energy is always positive.

Figure 3.1 shows the schematics of ΔG with respect to the radius r of a nucleus in homogeneous nucleation. The green curve is the total Gibbs free energy as a function of radius. The first bulk free energy term is plotted in red. It scales with the volume of nucleus ($\sim r^3$) and is always negative. The second interface free energy term is plotted in black. It is always positive and scales with surface area ($\sim r^2$). This gives rise of a free energy barrier and a corresponding critical nucleation size.

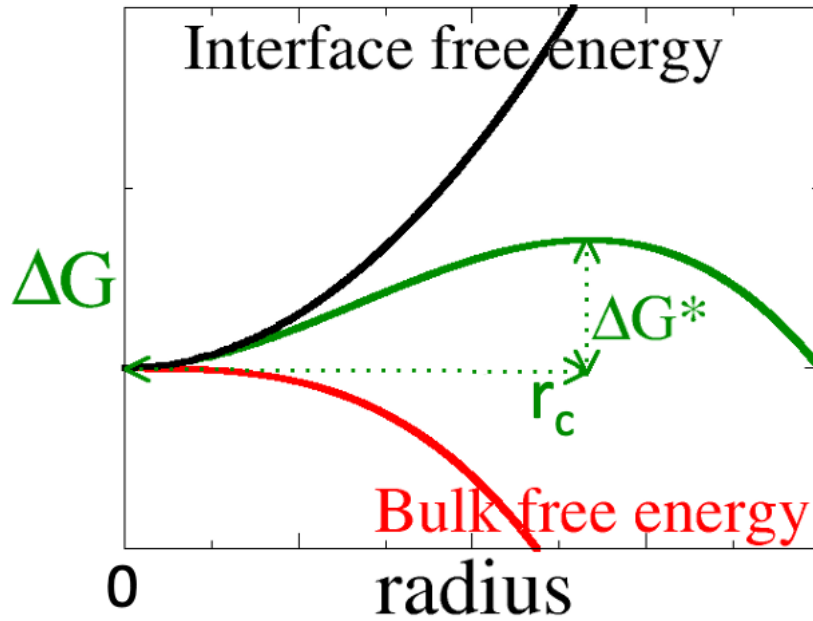


Figure 3.1. Schematics of ΔG with the radius r of a nucleus in homogeneous nucleation. The green curve is the change of the total Gibbs free energy, which consists of a bulk free energy term (red curves) and an interface free energy (black curve). A free energy barrier ΔG^* and a critical nucleation radius r_c can be determined by the maximum of ΔG . (Figure adapted from https://en.wikipedia.org/wiki/Classical_nucleation_theory).

To find the maximum of ΔG , we let $\frac{d\Delta G}{dr} = 0$, which gives a critical nucleation radius as

$$r_c = \frac{2\sigma_s}{|\Delta g_V|}, \quad (3-2)$$

and a free energy barrier of the phase transition as

$$\Delta G^* = \frac{16\pi\sigma_s^3}{3|\Delta g_V|^2}, \quad (3-3)$$

For a nucleus with $r < r_c$, the r of nucleus tends to decrease to minimize the free energy ΔG . The nucleus will eventually disappear and the nucleation is prohibited. If the nucleus has gained enough energy to overcome the free energy barrier ΔG^* and has a radius $r > r_c$, to decrease ΔG , the nucleus should increase its size which can eventually be developed into a new phase formation. Therefore, the r_c is the critical radius, the radius r of nucleus needs to surpass r_c to trigger new phase nucleation. This is the origin of the critical nucleation sizes in CNT.

3.2.2 Heterogeneous nucleation

Unlike homogeneous nucleation, heterogeneous nucleation occurs on preferential nucleation sites such as surfaces or impurities. It is much more common than homogeneous nucleation. This is because the free energy barrier of nucleation is greatly reduced by the nucleation seeds. The interface energy of nucleated new phase with respect to the nucleation seeds is much lower compared to that with respect to the parent phase. Therefore, the second interfacial term in equation 3-1 is greatly reduced, which promotes the nucleation of new phase on the nucleation seeds. Figure 3.2 schematically shows the lowered free energy barrier in heterogeneous nucleation compared the homogeneous nucleation assuming the interface energy between the new phase nucleus and nucleation seeds is zero. The complete consideration of ΔG should include the interface energy of nucleus by nucleation seeds and the interface energy with parent phase, where the critical radius r_c may change compared to that given by the homogeneous model.

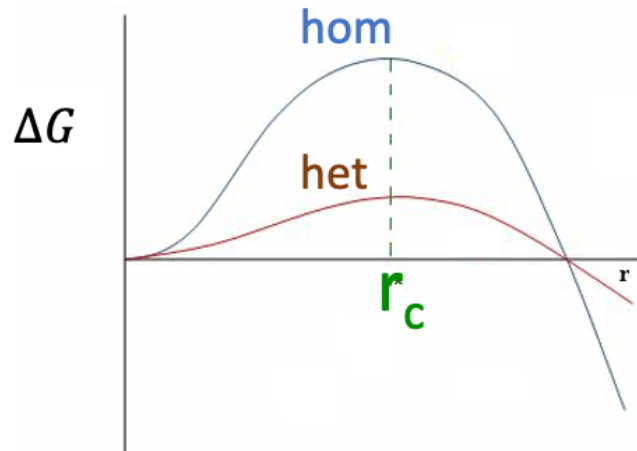


Figure 3.2. Schematics of the change of total Gibbs free energy ΔG in nucleation showing that the free energy barrier is lowered by nucleation seeds in heterogeneous nucleation (red curve) compared to that in homogeneous nucleation (blue curve). (Figure taken from https://en.wikipedia.org/wiki/Classical_nucleation_theory).

3.2.3 Probing the critical nucleation size

It is almost impossible to directly measure the critical nucleation sizes during the nucleation process due to its nanoscale and transient nature. However, one can introduce nucleation seeds with controlled sizes and observe whether the nucleation occurs at certain temperatures or not to probe the critical nucleation sizes. This is because, as shown in figure 3.3, if the sizes of nucleation seeds (L) are larger than the critical nucleation sizes ($2r_c$), the nucleation process will be promoted as the nucleus can easily have a radius r that exceed the critical radius r_c . The nucleus can grow and eventually form a new phase. On the contrary, if $L < 2r_c$, the nucleation seed does not support a nucleus to have its radius r larger than r_c , and thus the nucleation is not promoted from this nucleation seed.

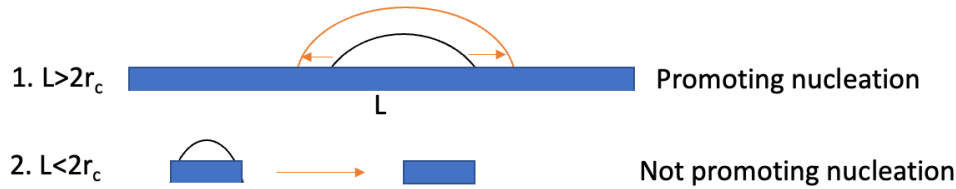


Figure 3.3. Schematics showing nucleation seeds (blue plate) promoting or not promoting nucleation with its size larger or smaller than the critical nucleation size respectively.

Therefore, we can conclude that at the nucleation temperature T_{nuc} , the $L \approx 2r_c$. Generally, there are two major experimental challenges, one is to achieve a pure and deeply supercooled or superheated system; the other is to introduce nucleation seeds with controlled sizes, which will be introduced and discussed in section 3.3 and 3.4 respectively.

3.3 Achieving deeply supercooled VO_2

3.3.1 T_{MIT} engineering of VO_2 by helium ion irradiation

As discussed in section 2.3.2, the oxygen vacancies generated in VO_2 can induce T_{MIT} decreasing. Also, as shown in both electrical conductivity measurements (figure 2.12) and thermal conductivity measurements (figure 2.13), the drop of T_{MIT} is observed in the helium-ion-irradiated VO_2 . Figure 3.4 shows the T_{MIT} reductions at different the helium ion irradiation dose extracted from electrical and thermal transport measurement as shown in chapter 2. VO_2 nanobeams are uniformly irradiated by He^+ from a dose of 1×10^{15} ions/ cm^2 to nearly 1×10^{16} ions/ cm^2 . The MIT of VO_2 is not affected by helium (He) ion dose below this range. Also, the MIT is not sharp and eventually disappear for He ion doses that are higher than 1×10^{16} ions/ cm^2 . Therefore, the tunable range of T_{MIT} is from 341 K (the T_{MIT} of pristine VO_2) down to temperatures around 310 K (the reduced T_{MIT} at the highest dose). The maximum reduction of T_{MIT} is around 30 K and the T_{MIT} can be easily controlled with the He ion doses.

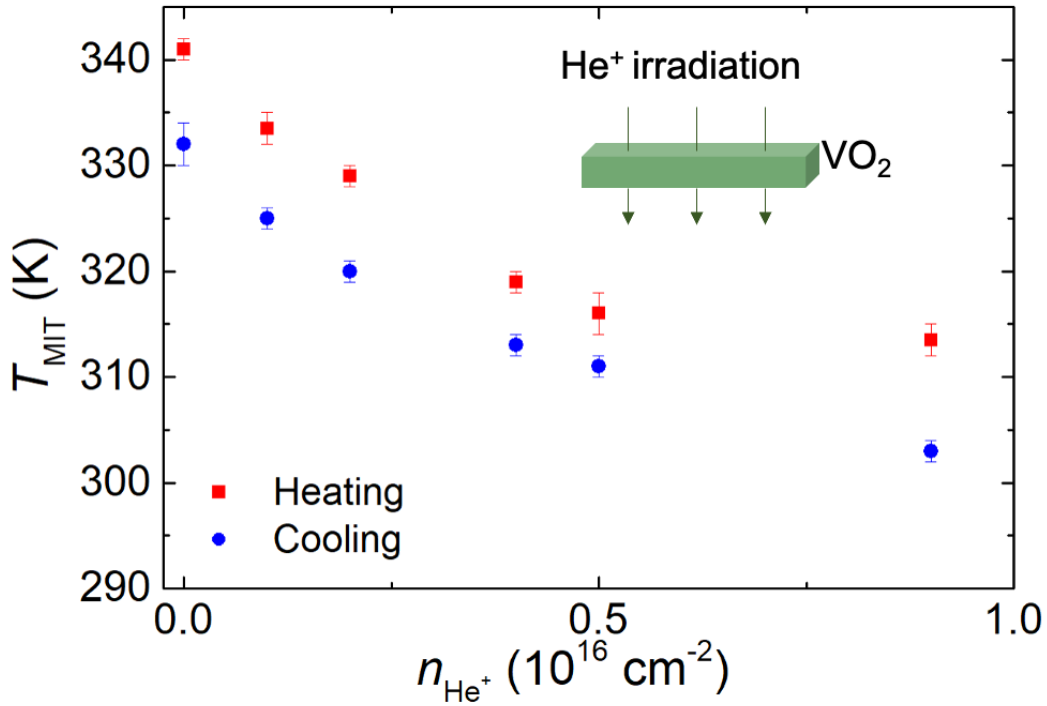


Figure 3.4. The metal-insulator transition (MIT) temperature (T_{MIT}) of VO_2 nanobeams as a function of dose of He ion irradiation. T_{MIT} is determined from transport measurements. The Inset shows schematically a VO_2 nanobeam uniformly irradiated by He^+ ions before Pt bonding for electrical measurements.

In addition to reduced T_{MIT} , the single crystallinity of VO_2 is well preserved in He ion irradiation whatever doses used in this study as discussed in section 2.2.3. There is no extended defects or imperfection in irradiated VO_2 which is important to achieve supercooled VO_2 via irradiation shielding, which is discussed in section 3.3.2.

3.3.2 Irradiation shielding on suspended VO_2 nanobeams

To probe the critical nucleation sizes of M phase VO_2 , we need the I-phase nucleation to be triggered completely by the introduced nucleation seeds. To achieve this, any nucleation seeds other than the designed ones must be excluded. The experimental proof of such exclusion of nucleation seeds is to observe the supercooling of M phase VO_2 , that is VO_2 remains in metallic phase to temperatures below T_{MIT} during the cooling process. Although the most thermodynamically stable state of VO_2 is its insulating phase, the phase transition from M to I phase cannot occur due to the large free energy barrier (as discussed in section 3.2.1), which prevents the kinetic transition process of I phase nucleation. The free energy barrier cannot be overcome by thermal energy fluctuation but can be overcome by lowering the free energy barrier by using heterogenous nucleation process (as discussed in section 3.2.2). Nucleation seeds can lower the interfacial free energy of the nucleation seeds, which promote the kinetic process of MIT and induce I phase nucleation.

Nucleation seeds that can trigger I phase nucleation in VO_2 includes grain boundary, rough surfaces or boundaries and M-I domain walls etc. Therefore, we choose VO_2 nanobeams as platform due to its smooth surface and single crystallinity (compared to VO_2 thin films, which is polycrystal with their grain boundaries about a few hundreds of nanometers). In literature, supercooled VO_2 nanobeams have been achieved by either using substrate strain (63) or by graded tungsten doping (6). However, the strained VO_2 is affected by extrinsic elastic energy and graded W-doped VO_2 is not pure VO_2 where the MIT is affected. To probe the critical nucleation sizes, pure and strain free VO_2 nanobeams are required. In our experiment setup, the strain along the VO_2 nanobeam can be fully released by suspension (6). As shown in figure 3.5 (a), we placed a VO_2 nanobeam bridging two suspended micropads. The VO_2 nanobeam is bonded to electrodes on both micropads by FIB-induced Pt deposition to secure its both physical and thermal contacts to corresponding electrodes. The long SiN_x beams ensure the high flexibility of two micropads and releases any strain along the mounted VO_2 nanobeam. The smooth and clean surfaces of transferred VO_2 nanobeams as shown in figure 3.5 (b) is necessary to achieve deep supercooling of M-phase VO_2 to avoid nucleation from any surface imperfection.

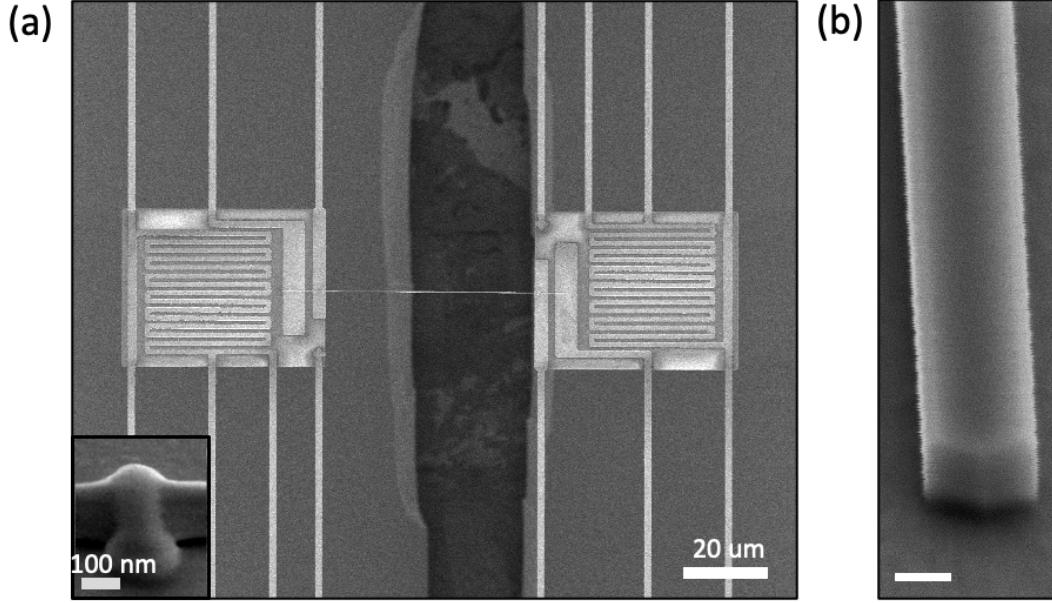


Figure 3.5. (a) Scanning electron microscope (SEM) image of a VO_2 nanobeam supported by two suspended micropads. Scale bar is $20\ \mu\text{m}$. (Insert) SEM image of FIB-deposited Pt bonding with the underlying electrode to minimize electrical/thermal contact resistance. Scale bar is $100\ \text{nm}$. (b) SEM image of a VO_2 nanobeam showing rectangular cross section with smooth surfaces. Scale bar is $100\ \text{nm}$.

After one VO_2 nanobeam is transferred onto the suspended device, we used He ion irradiation to create two irradiated segments on the suspended VO_2 nanobeam to shield the center pristine VO_2 segments by irradiation. The left schematic in figure 3.6 shows a typical irradiation arrangement to achieve deep supercooling. The FIB deposited Pt bonds (yellow blocks) used to secure electrical and thermal contacts are also shown. The bonding can prevent the bending of nanobeams caused by the interface strain between M and I phase VO_2 segments. In the M to I phase transitions (cooling process), the He-ion-irradiated segments stay metallic when T is above their reduced T_{MIT} , which is usually a few tens of kelvin below $341\ \text{K}$ (normal T_{MIT}). In this temperature range, these two metallic He-ion-irradiated segments function as shields to prevent any nucleation seeds, especially M-I domain walls, which can promote I phase nucleation, to contact the sandwiched unirradiated pristine VO_2 segment. Therefore, we name the unirradiated pristine VO_2 segment as shielded segment while the irradiated segment as shielding. The functionality of this shielding-to-shielded-to-shielding arrangement of segments is therefore referred to as irradiation shielding. At $T \leq \text{reduced } T_{\text{MIT}}$, the shielding segments transit from M to I phase. The M-I phase domain walls outside of the irradiation shielding unit can propagate through the shielding segments via their MIT. Therefore, the lowest T limit of supercooled shielded VO_2 segment to remain metallic (T_{sc}) is determined by the reduced T_{MIT} of shielding segments, that is T_{sc} is equal to the reduced T_{MIT} of shielding segments. A normal suspended

VO₂ nanobeam without irradiation shielding is also shown as the right schematic in figure 3.6 as comparisons, where a normal MIT at temperature of 341 K is observed.

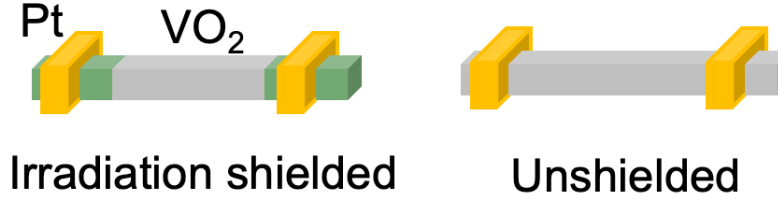


Figure 3.6. Schematics of He⁺ irradiation for nucleation shielding in a single VO₂ nanobeam. The middle, pristine VO₂ segment (grey) is shielded against influence from the Pt contacts (yellow blocks) by two end VO₂ segments locally He⁺-irradiated (green).

The supercooling of VO₂ achieved by irradiation shielding can be clearly revealed in electrical transport measurements using suspended microdevice. In cooling process, the electrical conductivity (σ) of VO₂ in the designed irradiation shielding unit (green solid curve in figure 1c) stays at a metallic level until a temperature of 310 K, which is the reduced T_{MIT} of shielding segments. The He ion dose applied is 5×10^{15} ion/cm². A large supercooling is thus confirmed by the transport measurement. As a comparison, the MIT of an unshielded VO₂ nanobeam (black dotted curve) occurs at 341 K for both heating and cooling process with small hysteresis. The supercooling cannot happen as the M-I domain wall that origins from either the ends of VO₂ nanobeams or the Pt bonding contacts can freely progress through the entire VO₂ nanobeam and promote I phase nucleation at its thermodynamical temperature (T_{td} , the highest temperature at which I phase is thermodynamically more stable than M phase).

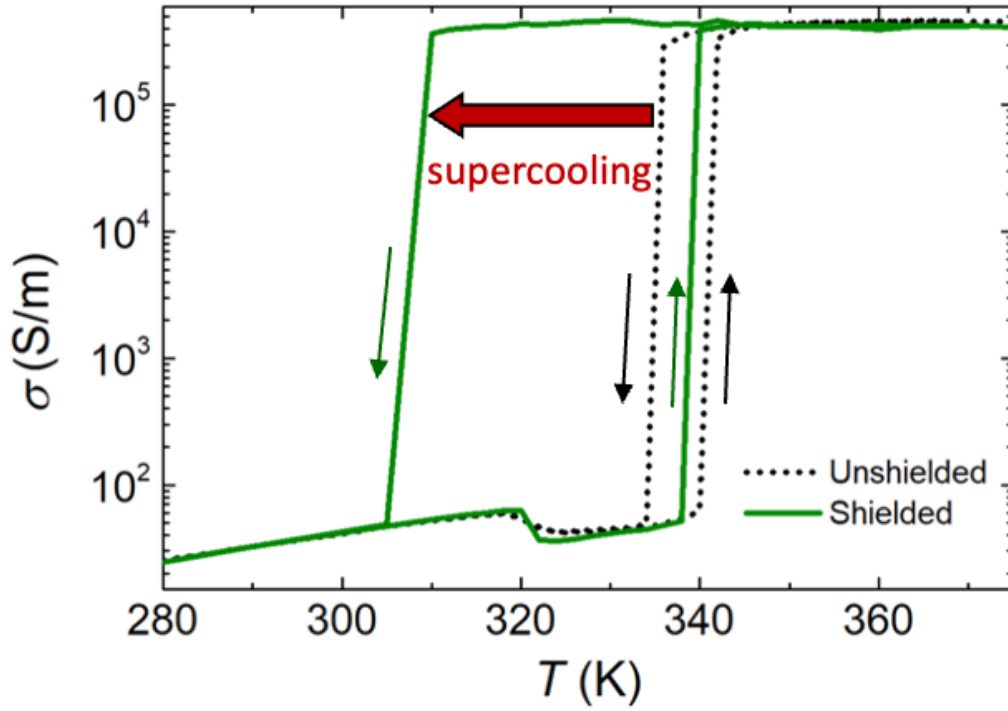


Figure 3.7. Electrical conductivity of VO₂ nanobeams with or without He⁺ irradiation shielding. Deep supercooling of the M phase up to 300 K is observed in the VO₂ shielded by two segments, each with 5×10^{15} He⁺ cm⁻² irradiation.

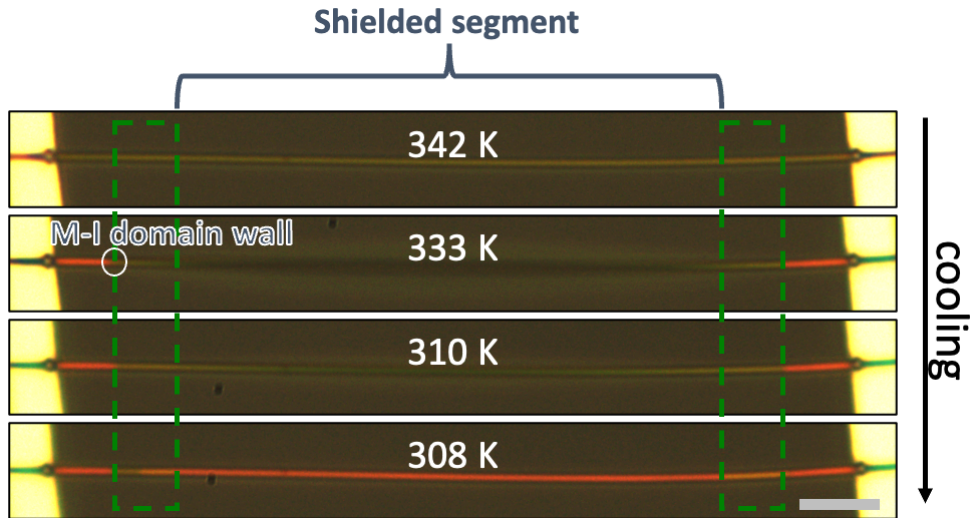


Figure 3.8. Optical images of the deeply supercooled, shielded VO₂ nanobeam. A 30 μm -long VO₂ segment is shielded by two 4 μm -long He⁺-irradiated segments (indicated by green dashed boxes, at a dose of 5×10^{15} He⁺ cm⁻²). The M phase (dark yellow) of the shielded, pristine VO₂ is

supercooled and transforms to the I phase (bright red) at 308 K, which is close to the natural reduced T_{MIT} of the irradiated shielding zones. Scale bar is 5 μm .

Another method to confirm supercooling of irradiation shielded VO_2 is by observing its optical color by using optical microscope. The suspended VO_2 nanobeams show a good color contrast between M and I phase under optical microscope. The M phase VO_2 has dimmer color while I phase has brighter one. The optical color also depends on the diameter of VO_2 nanobeams. For example, in I-phase VO_2 , the nanobeams with green color has diameter from about 100 to 160 nm and the nanobeams with red color has diameters around 200 to 300 nm. Figure 3.8 shows the cooling process of one suspended VO_2 nanobeam with irradiation shielding near both ends of the suspended VO_2 . The He ion irradiated region is indicated by the green dashed boxes. Two shielding segments about 4 μm long are irradiated by He ions at a dose of $5 \times 10^{15} \text{ cm}^{-2}$. The shielded pristine VO_2 segment in the center is about 30 μm long. At first, the whole VO_2 nanobeam is fully metallic at T that is larger than T_{td} , the natural T_{MIT} that is determined by the thermodynamic laws. Two segments outside of irradiation shielding (near the edges of micropads) transit from M to I phase once T is lower than T_{td} (333 K). The heterogeneous nucleation stems from Pt bonds and trigger the MIT in these segments which are not shielded by irradiation. On the contrast, the shielded VO_2 segment stays metallic until T reaches T_{sc} (310 K), where the shielding segments transit from M to I phase. A deeply supercooled VO_2 segment is clearly observed by the changes of its optical color. Therefore, combining irradiation shielding, suspension from floating micropads and strain-free and single-crystalline VO_2 nanobeams with smooth surfaces, pristine VO_2 can be maximumly supercooled down to a designed temperature (T_{sc}), which can be engineered by the He ion irradiation doses applied in the shielding segments. The fabrication of such supercooled VO_2 device is highly repeatable and of very high success rate.

3.4 Finding the nucleation seeds

3.4.1 Nucleation seeds created on VO_2 surfaces by Ga ion irradiation

To probe the critical nucleation sizes in heterogeneous nucleation, the nucleation seeds must have well-defined sizes with small size distribution. In our preliminary experiments, it turns out that commercially available metallic nanoparticles such as Pt nanoparticles in aqueous dispersion cannot sufficiently lower the free energy barrier to trigger I-phase

nucleation by attaching them to supercooled M-phase VO_2 surfaces. This is further proved by depositing a large block of Pt metal using electron beam on top of VO_2 nanobeam where no I-phase nucleation can be found. However, if we use gallium (Ga) ion beam to induce Pt deposition on VO_2 , the nucleation can be observed in supercooled VO_2 nanobeams. This implies that Ga ion can damages the VO_2 top surfaces and make the damaged regions as nucleation seeds. Also, we can precisely control the shape and size of areas with Ga ion irradiation, which satisfies the requirements of size control on nucleation seeds in this study.

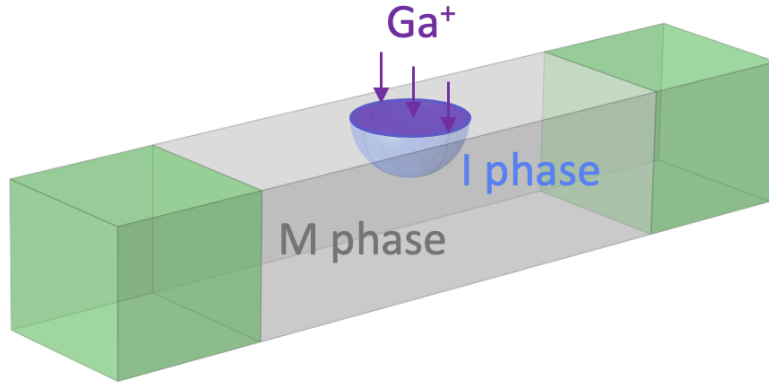


Figure 3.9. A schematic showing a disk-shaped nucleation seed (purple) on the pristine VO_2 surface created by Ga ion irradiation. The Ga ion penetration depth is ~ 15 nm, very shallow compared to the diameter of the irradiated area, hence the nucleation can be approximated as a disk shape. The green segments are He^+ -irradiated shields to ensure the deep supercooling of the sandwiched pristine VO_2 segment (gray).

As shown by the schematics in figure 3.9, a circular-shaped area on the top surface of VO_2 nanobeam is irradiated by Ga ions in one shielded VO_2 segments (gray domain) sandwiched by two shielding segments (green domains). The Ga ion irradiation is performed by using focus ion beams (FIB) with ion current of 1.5pA and with acceleration energy of 30 keV. The doses are limit below $8.8 \times 10^{16} \text{ cm}^{-2}$ to avoid significant surfacing milling, which is controlled by Ga ion irradiation time. To avoid exposing most parts of VO_2 nanobeams, we linked electron beam and gallium beam in a SEM/FIB dual beams system. The electron beam is used to locate the sample and irradiation locations. The Ga beam is operated in a reduced view on single exposure to maximumly reduce any side effect from Ga beam exposure. The duration of Ga ion irradiation is usually within 1 s and no extensive heating effect resulted from irradiation is observed. The distribution of the designed Ga irradiation doses and the sizes of irradiated areas are shown in figure 3.10. The diameter of irradiated area ranges from 10 to 240 nm. The Ga ion irradiation dose ranges from 1.1 to $8.8 \times 10^{16} \text{ ions/cm}^2$. The corresponding I phase nucleation temperature (T_{nuc}) from these nucleation seeds can cover the entire temperature range of supercooling of the supercooled M-phase VO_2 , which is from the thermodynamic temperature (T_{id} , which

normal T_{MIT} of unshielded pristine VO_2 , 341 K) to the supercooling temperature (T_{sc} , which is determined by the reduced T_{MIT} of He ion irradiated shielding segments).

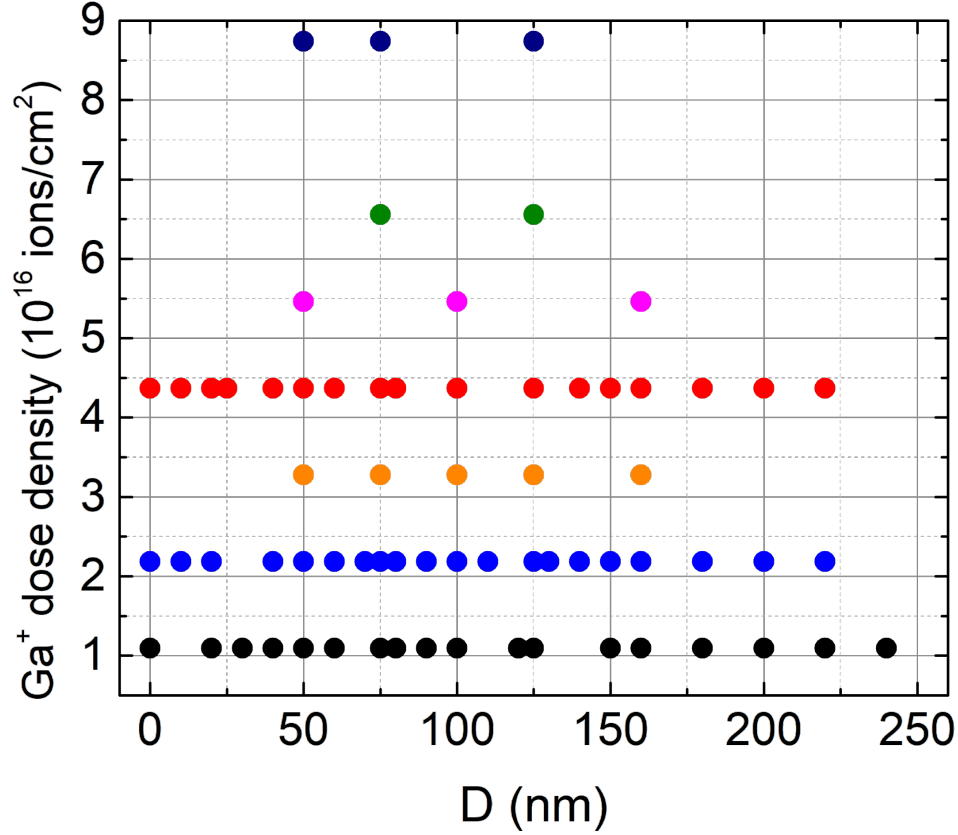


Figure 3.10. The distribution of Ga ion irradiation dose and the diameter of irradiated circular area on the top surface of VO_2 nanobeams.

3.4.2 Doping and etching effects of Ga ion irradiation

There are two major effects of Ga ion irradiation on VO_2 that may contribute to lowering the interface energy of nucleus, that is Ga doping and surface milling.

From Stopping and Range of Ions in Matter (SRIM) simulation (33), the penetration depth of Ga ions in VO_2 is estimated as 15 nm at their acceleration energy of 30 keV. This means that a 15 nm-thick Ga-doped VO_2 layer is formed at the irradiated surfaces. Given the order of magnitude of irradiation dose is of 10^{16} ions/cm², the density of Ga is about 10^{22} ions/cm³. On the contrast, the carrier concentration of M-phase VO_2 is on order of 10^{23} cm⁻³. This indicates that the nucleation seeds are heavily Ga-doped VO_2 . And this may further imply

that the quality of Ga irradiated VO₂ is not pristine and may even be amorphous. In literature, the Ga-doped VO₂ is reported to have a T_{MIT} higher than that of pure VO₂ (64). This favors I phase nucleation as the increase of T_{MIT} implying easier I phase nucleation and the composition of nucleation seeds can be I phase Ga-doped VO₂ at temperatures from T_{td} to T_{sc} .

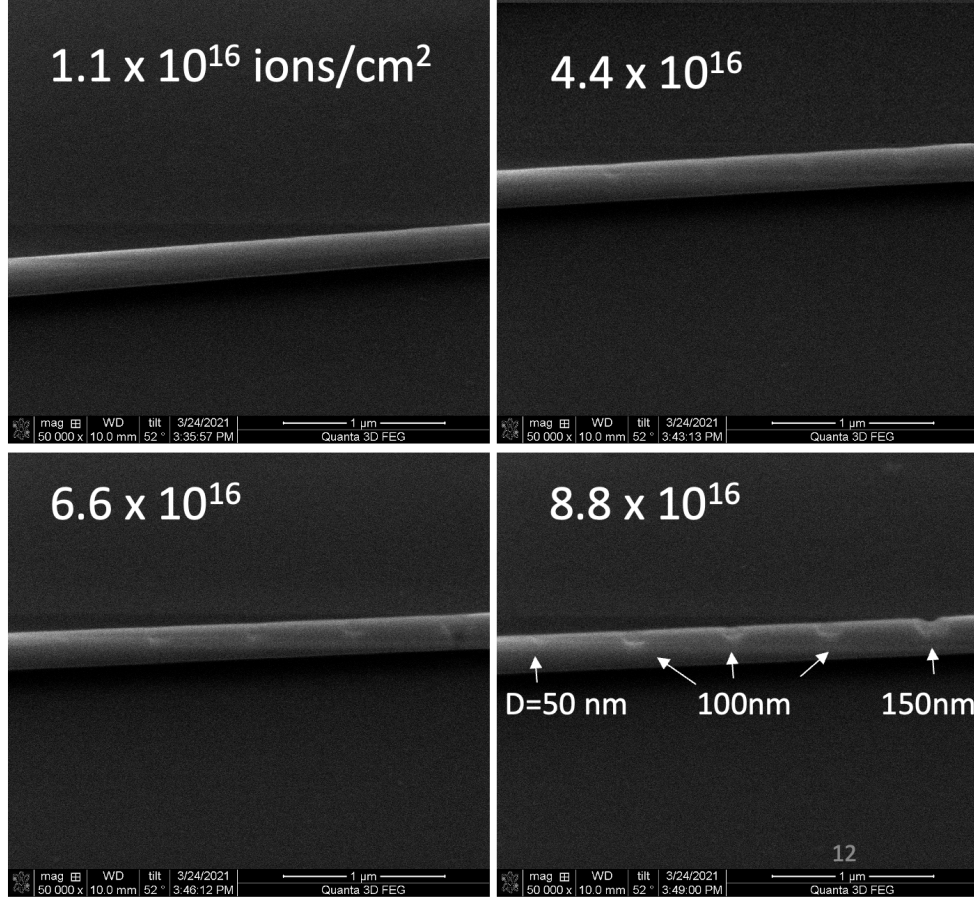


Figure 3.11. SEM images of VO₂ surfaces irradiated by Ga ion beams in circular shapes. The diameters of five irradiated circles are 50, 100, 100, 100 and 150 nm from left to right, respectively. The Ga ion irradiation doses are set as 1.1, 4.4, 6.6 and 8.8 x 10¹⁶ ions/cm², as indicated in each image.

The original purpose of Ga ion irradiation is milling surfaces or cutting samples as Ga ion is a heavy atom and can cause a lot of defects through its collisions with lattice (65). Figure 3.11 shows SEM images displaying the Ga ion irradiation made with different diameters and at four different Ga ion doses. The surface is slightly etched down by a few nanometers which is later determined by atomic force microscope (AFM). Figure 3.12 shows the results of AFM measurements of Ga ion milling effect on VO₂. The etching depth of Ga ions on VO₂ nanobeam is positively related to the diameters of the irradiation shapes. The depths

also increase with Ga ion doses. The maximum milling depth is 7 nm which is created using the highest irradiation dose (8.8×10^{16} ions/cm²) and with nanobeam's diameter of 150 nm. The AFM confirms that there is no extensive surface etching pit shown on VO₂ nanobeams. However, as shown in figure 3.11 the surface milling can add more surface roughness and imperfection, which can further lower the interface free energy between I-phase VO₂ nucleus and nucleation seeds.

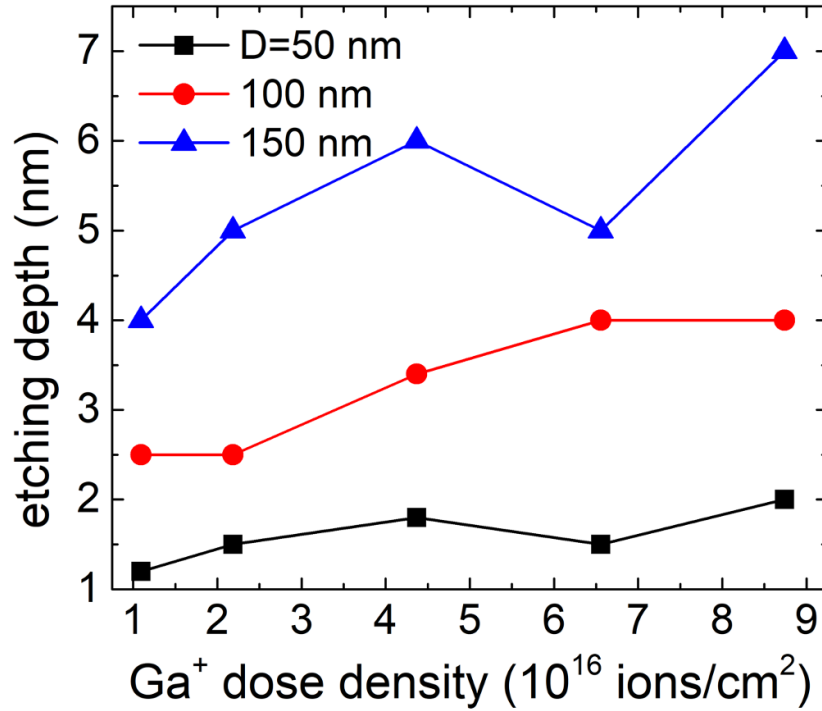


Figure 3.12. The etching depth of Ga irradiated surface of VO₂ nanobeams measured by AFM. The irradiation patterns have circular shape with diameters of 50, 100 and 150 nm respectively.

Therefore, a circular-shaped nucleation seed is created on the surface of VO₂ nanobeam, whose diameters (D) and Ga ion doses (n_{Ga^+}) can be controlled by Ga ion irradiation using FIB.

3.5 The critical nucleation sizes of metallic VO₂

3.5.1 Experiment method

To probe I phase nucleation by FIB-induced nucleation seeds of different D and n_{Ga^+} , multiply shielding and shielded segments are arranged alternately along each VO_2 nanobeam. The supercooling process of one such VO_2 nanobeam are shown in figure 3.13. Each segment is 3 μm long and the gap between two floating micropads is 50 μm wide. A total of eight independent supercooled VO_2 segments with irradiation shielding are created. Nucleation seeds are introduced to each as with one nucleation seed in one shielded segment. A supercooled segment free of nucleation seed is reserved as control sample to measure T_{sc} , which is the lowest temperature that supercooling could be maintained with irradiation shielding. A small segment outside of irradiation shield (near the left end in figure 3.13) is also reserved to measure T_{td} , which is the T_{MIT} of pure pristine VO_2 determined thermodynamic laws. In the VO_2 nanobeam shown in figure 3.13, the n_{Ga^+} of all nucleation seeds is fixed at $2.2 \times 10^{16} \text{ cm}^{-2}$ while their D varies from 10 to 180 nm. The T_{td} can be determined as 332 K by the I-phase nucleation temperature of the reserved segment near the Pt bonding on the left micropad. This is lower than 341 K, which is observed in T_{MIT} during cooling process. Such small hysteresis between heating and cooling processes is almost always observed in pristine VO_2 nanobeams. Also, at $T = T_{\text{td}}$, I phase nucleation happens in two supercooled segments, where D of the corresponding nucleation seeds is 140 and 180 nm, respectively. This implies full suppression of VO_2 supercooling is observed, that is the I-phase nucleates at T_{td} . At $T = 317 \text{ K}$, the nucleation seed with D of 100 nm induces I phase nucleation. Its T_{nuc} is between two limits. At $T = T_{\text{sc}}$ (308 K), all shielded segments transit to I phase as shielding segments changing from M to I phase and the M-I domain wall can contact supercooled segments.

The kinetic behavior of supercooling in VO_2 is also observed. The I phase nucleation is observed as a sudden and abrupt process. The I phase occupation of the whole shielded segment domain is instant. The device in figure 3.13 also demonstrates that the range of nucleation temperature probed can fully cover the temperature range of supercooling, that is from T_{td} to T_{sc} . All cooling speed is limited at 2.5 K/min. A temperature controller is used to ensure the temperature of nanobeams follows closely with that of the heater.

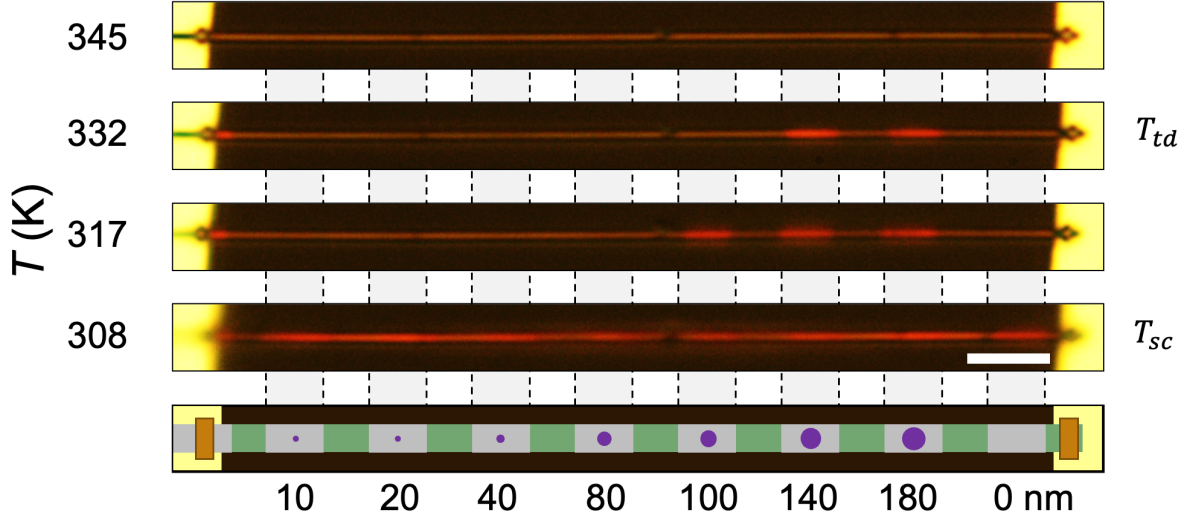


Figure 3.13. Optical images of the I phase nucleation process along a long, suspended VO₂ nanobeam. The nanobeam is divided into eight pristine segments, each shielded by two segments He⁺ irradiated at a dose of $5 \times 10^{15} \text{ He}^+ \text{ cm}^{-2}$; then a nucleation seed is introduced on the surface of each of the pristine segments by Ga⁺ irradiation at a dose of $2.2 \times 10^{16} \text{ cm}^{-2}$, but with different diameters. The lowest panel shows the schematic where the diameter of disk-shaped nucleation seed (D) increases from 10 to 180 nm. Scale bar is 5 μm .

3.5.2 The classical nucleation theory model in supercooled M-phase VO₂

As the strongly correlated materials have not been fully understand and the nucleation theory of strongly correlated material is lacking, we adopt the modeling method from CNT (57) to predict the critical nucleation sizes $2r_c$ as a function of T_{nuc} in VO₂. According to CNT, the total Gibbs free energy ΔG of forming a new I phase in supercooled M phase VO₂ can be expressed as

$$\Delta G = \frac{2}{3}\pi r^3 \cdot \Delta g_v + 2\pi r^2 \cdot \sigma_s + \pi r^2 \cdot \gamma, \quad (3-4)$$

where r is the radius of the I phase nucleus (assumed as hemisphere, as shown in figure 3.14 a), Δg_v is the difference of volume Gibbs free energy between I and M phases, σ_s is the interface energy between I phase and M phase VO₂ and γ is that between I phase VO₂ and FIB-induced nucleation seeds. The shape of I phase nucleus is assumed to be hemisphere as an approximation to general situations. Let $d\Delta G/dr = 0$, and the critical radius can be derived as

$$r_c = \frac{2(\sigma_s + \gamma/2)}{|\Delta g_v|}. \quad (3-5)$$

Also,

$$\Delta g_v = \frac{\Delta h_f(T_{td} - T_{nuc})}{T_{td}}, \quad (3-6)$$

where Δh_f is the volume enthalpy of formation. Therefore,

$$r_c = \left| \frac{2(\sigma_s + \gamma/2)}{\Delta h_f} \right| \left(\frac{1}{1 - T_{nuc}/T_{td}} \right), \quad (3-7)$$

and

$$T_{nuc} = T_{td} \cdot \left[1 - \left| \frac{2(\sigma_s + \gamma/2)}{\Delta h_f} \right| \left(\frac{1}{r_c} \right) \right]. \quad (3-8)$$

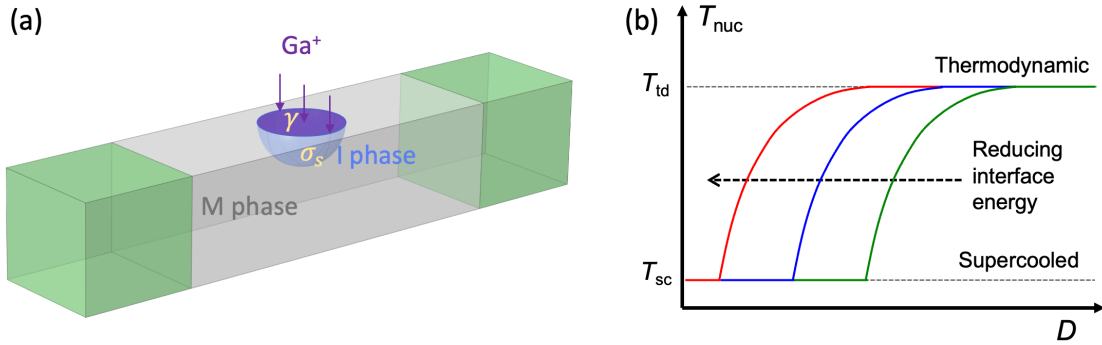


Figure 3.14. (a) The CNT model in irradiation shielded VO₂ segment: the I-phase nucleus is assumed to a hemisphere with its interface energy with parent M-phase VO₂ as σ_s and interface energy with FIB-created nucleation seed as γ . (b) Schematics of the dependence of I phase nucleation temperature (T_{nuc}) on D , as predicted by the classical nucleation theory. T_{nuc} is limited by the thermodynamic MIT temperature (T_{td}) and the supercooled temperature (T_{sc}) of the shielded VO₂. With reduced interface energy, smaller D is needed for the nucleation at a given temperature.

The $T_{nuc}(r_c)$ predicted by CNT is shown schematically in figure 3.14 b, which is the results of equation (3-9) and combined with the properties of VO₂ with irradiation shielding. At $T_{sc} < T_{nuc} < T_{td}$, the I-phase nucleation can be triggered by FIB-induced nucleation seeds once D is larger than or equal to $2r_c$. A monotonously increasing trend of $T_{nuc}(D)$ can be qualitatively assumed with a given n_{Ga+} between the thermodynamic and supercooled limits. Beyond these two limits, the I phase nucleation is not involved with nucleation seeds but

is governed by irradiation shielding (lower limit) and thermodynamics of VO₂ (upper limit). Therefore, T_{nuc} is constant and not changes with D . The Ga ion dose can also modulate γ in our CNT model. Higher disordered surfaces are easier to promote nucleation by further lowering down interface energy of nucleus. This indicates that increasing n_{Ga^+} can reduce γ . Given equation (3-8), a decrease in γ can lead to an increase in T_{nuc} at a given r_c . A shift to smaller D of $T_{\text{nuc}}(D)$ curves by increasing n_{Ga^+} is also indicated in figure 3.14b.

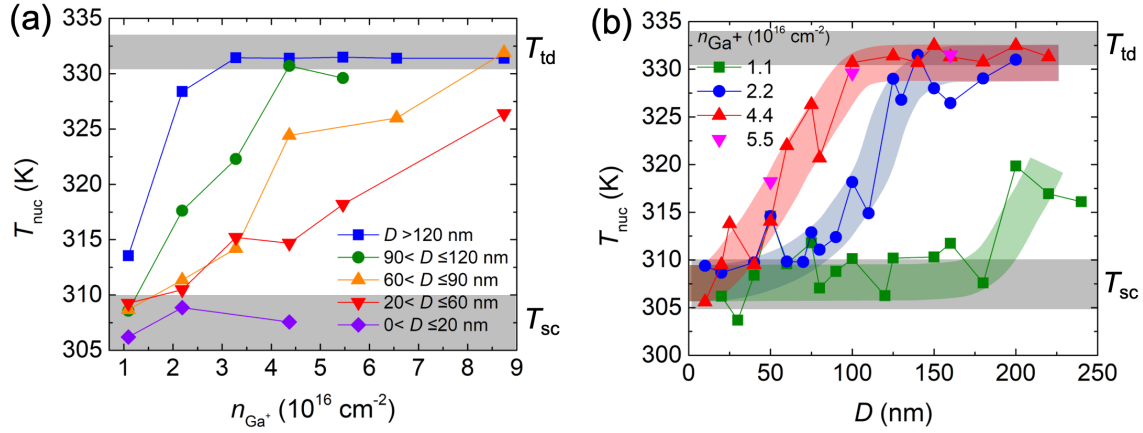


Figure 3.15. (a) Measured dependence of T_{nuc} on Ga⁺ irradiation dose (n_{Ga^+}) in the seed at different D intervals. Heavier dose in seed promotes the I phase nucleation as shown by the increased T_{nuc} . (b) Measured dependence of T_{nuc} as a function of D at different doses. The thick curves are a guide to the eye. The critical sizes of nucleus can be determined from the rise above the supercooled limit. T_{nuc} for nucleation seeds with large D and high doses is found to reach the thermodynamic limit. T_{nuc} saturates with nucleation seeds at Ga⁺ doses above $4.4 \times 10^{16} \text{ cm}^{-2}$. T_{td} and T_{sc} are marked by the gray shaded areas in (a) and (b).

After collecting a systematic data of (D , T_{nuc} and n_{Ga^+}), we can analysis our data with respect to the prediction of CNT model. In our measurements, the sizes of VO₂ nanobeams range from 200 to 270 nm. The D of nucleation seeds ranges from 10 to 220 nm. The n_{Ga^+} of nucleation seeds range from 1.1 to $8.8 \times 10^{16} \text{ cm}^{-2}$. Figure 3.15 (a) shows the averaged T_{nuc} with respect to n_{Ga^+} with D kept in the same interval for each curve. A monotonous increasing trend of T_{nuc} is observed with D between 20 and 120 nm. This proves that nucleation seeds with higher n_{Ga^+} can promote nucleation by reducing the interface energy of nucleus. If D is larger than 120 nm and n_{Ga^+} higher than $3.3 \times 10^{16} \text{ cm}^{-2}$, a saturation of T_{nuc} at T_{td} can be observed. This proves that the deep supercooling of M-phase VO₂ can be fully suppressed when D exceeds the critical nucleation size at T_{MIT} . If D is smaller than 20 nm, T_{nuc} saturates at the lowest supercooled limit, that is T_{sc} . D is smaller than critical nucleation size and no I phase nucleation can be triggered until the shielding segments transit from M to I phase. Figure 3.15 (b) shows the T_{nuc} with respect to D with constant n_{Ga^+} . Both limits, T_{td} and T_{sc} , and the monotonously increasing dependence between them

are observed as predicted by CNT model (shown as figure 3.14 (b)). The shift of $T_{\text{nuc}}(D)$ with larger n_{Ga^+} to smaller D is also observed.

3.5.3 Probing the interface energy of I-phase nucleus

After obtaining curves of $T_{\text{nuc}}(D)$ shown in figure 3.15 (b), we can use equation 3-8 to fit the unknown interface energy term, $\sigma_s + \gamma/2$. The value of the enthalpy of formation of VO_2 is obtained from literature, as $\Delta h_f = 1025 \text{ cal/mole}$ (39, 64, 66). The $r_c (= D/2)$ and T_{td} can be obtained from measured experimental results. The fitting results is shown in figure 3.16. The total interface free energy of I-phase nucleus can be estimated as 0.8280, 0.3930 and 0.2284 J/m^2 at Ga ion doses of 1.1, 2.2 and 4.4 10^{16} cm^{-2} , respectively. This also agrees with the density functional theory study of the surface energies of rutile VO_2 (67).

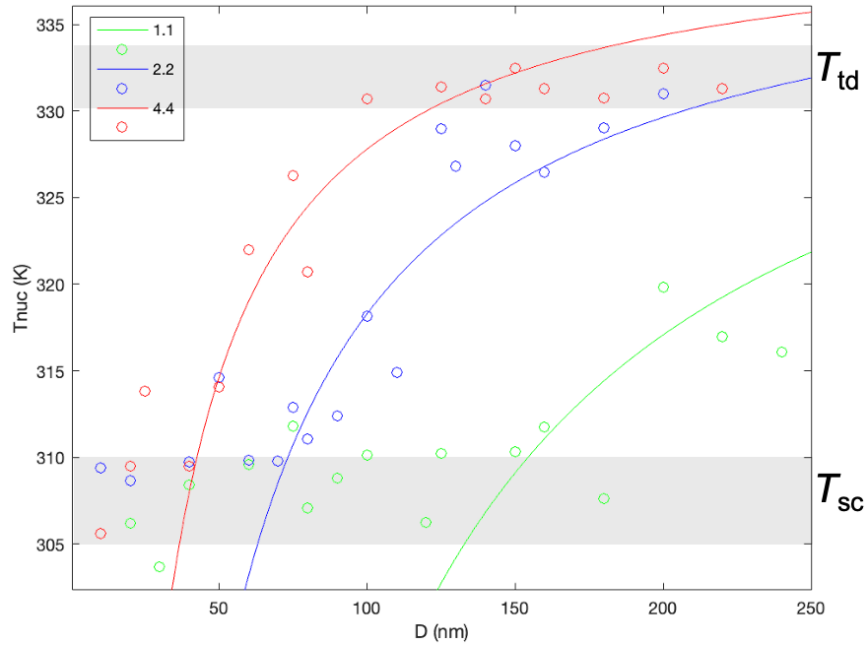


Figure 3.16. The fitting of $T_{\text{nuc}}(D)$ at Ga ion doses of 1.1, 2.2 and 4.4 10^{16} cm^{-2} , respectively. The solid curves are fitted results of experimental data (open circles) between two T limits. The CNT model shows good predictions of T between T_{td} and T_{sc} .

Furthermore, from equation [4] or [5], the interface energy can be expressed as

$$\sigma_s + \gamma/2 = \frac{|\Delta h_f|}{2T_{td}} r_c (T_{td} - T_{nuc}). \quad (3-9)$$

At $T_{sc} < T < T_{td}$, $D \approx 2r_c$. Given Δh_f and T_{td} are constant, we can derive that $D\Delta T \propto \sigma_s + \gamma/2$, where $\Delta T = T_{td} - T_{nuc}$. Therefore, the interface energy of nucleated I phase domain can be probed by measuring T_{nuc} and D . In figure 3.17, the colored symbols represent data with I phase nucleation occurring between thermodynamic and supercooled limit. A linear fitting of $D\Delta T$ with respect to $(n_{Ga^+})^{-1}$ (black solid line) can be applied to our measured results. This implies that the interface energy of nucleated I phase domain could be inversely proportional to n_{Ga^+} of nucleation seeds within a certain dose range. This also explains that nucleation seeds with higher n_{Ga^+} can induce I phase nucleation at higher temperature due to lower interface energy required for I phase nucleation. In the thermodynamic and supercooled limit, the relation $D \approx 2r_c$ is no longer valid and $D\Delta T$ has no direct relation with interface energy. Data with T_{nuc} equals to T_{sc} (open black circle) and T_{td} (black cross) are also shown in figure 3.17. Some results show negative $D\Delta T$ at the thermodynamic limit. This can occur especially with nucleation seeds have large D or high n_{Ga^+} . The highly disorder VO_2 surface after Ga ion irradiation with high dose reduces the natural hysteresis in pristine VO_2 and leads to a negative ΔT .

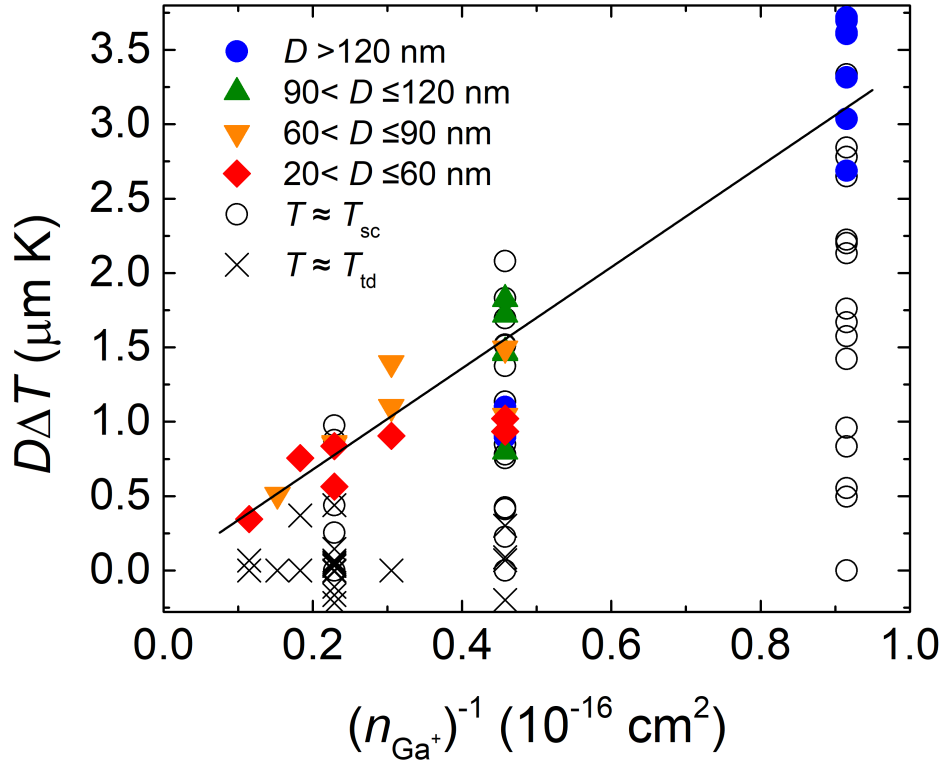


Figure 3.17. Measured $D\Delta T$ of all nucleation seeds with different diameters as a function of reciprocal of Ga^+ dose density. The black cross hairs and black open circles are $D\Delta T$ data measured from the nucleation seeds that drive the VO_2 to thermodynamic and supercooled limits, respectively. Between these two limits (colored symbols), T_{nuc} depends on D and dose of

the nucleation seeds. A linear fitting of all colored symbols (black solid line) indicates that the interface energy ($\propto D\Delta T$) of the nucleation seeds is inversely proportional to their Ga^+ irradiation dose density n_{Ga^+} .

3.6 Conclusions

In conclusion, we experimentally show that the critical nucleation size in VO_2 follows the trend predicated by CNT for the first time in strongly correlated materials. A supercooled VO_2 platform is created by using irradiation shielding and suspension from the floating micropads. The nucleation seeds are the disordered surface on VO_2 nanobeams that are irradiated by energetic Ga ion, which can be tuned by their diameter and Ga ion dose applied. The existence of critical nucleation size in VO_2 can help to unveil the mechanism of MIT VO_2 . The method of achieving deep supercooling in VO_2 can also be applied to other research and applications involving the phase transition of VO_2 .

Chapter 4 Abnormal thermal conduction in twisted GeS nanowire with a dislocation core

4.1 Introduction

Screw dislocation is a one-dimensional chiral topological defect of a crystal lattice. The lattice plane shifts by one layer or more along the dislocation line and forms a spiral staircase like structure. The ability of introducing twisting topology into van der Waals nanowires opens more opportunities to manipulate the optical, electrical, and thermal properties of materials (68-72). Recently, Yin et al demonstrated the growth of twisted germanium sulfide (GeS) nanowires derived by a screw dislocation core (73). The axial screw dislocations are firstly introduced into nanowires growing along cross-plane directions (74-76). The twist rate of this van der Waals nanowires is determined by the Eshelby twist $\alpha = \frac{b}{\pi R^2}$, where $\mathbf{b}$ is the Burgers vector, which represents the magnitude and direction of the lattice distortion resulted from a dislocation in a crystal lattice, where R is the radius of the nanowires (75, 77, 78). The Eshelby twist of nanowires can reduce the elastic energy induced by the screw dislocation core. Figure 4.1 shows schematics of a nanowire with perfect lattice, screw dislocation core and screw dislocation core accompanied by a Eshelby twist (79), respectively. In layered van der Waals nanowires, the twisting can be continuous from layer to layer with its overall twisting rate determined by the Eshelby twist (73).

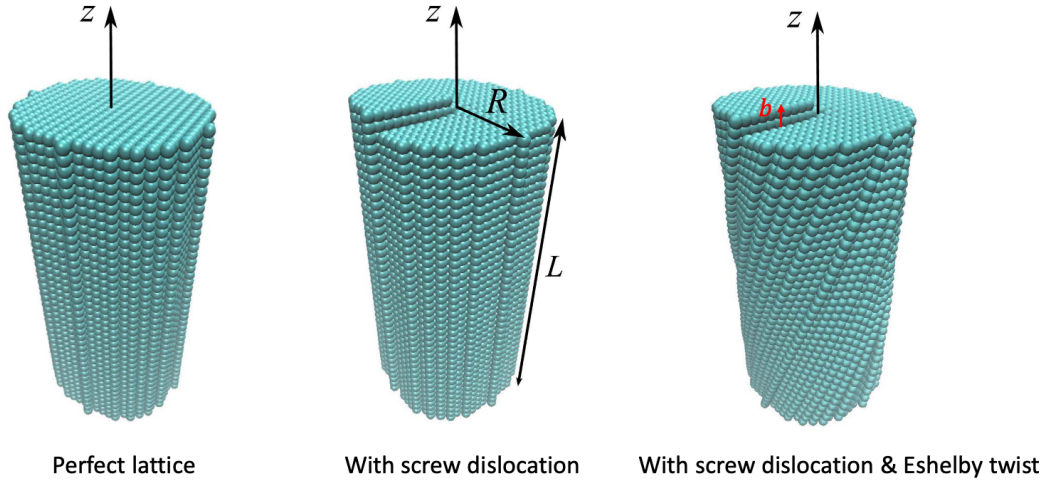


Figure 4.1. Comparisons of nanowires with perfect lattice and with screw dislocation core. The Eshelby twist is also shown in the rightest image, which is proportional to the magnitude of Burgers vector $\mathbf{b}$ and inversely proportional to the square of radius R^2 . (Figures adapted from Baimuratov, A. S. et al. Sci. Rep. 5, 14712 (2015)).

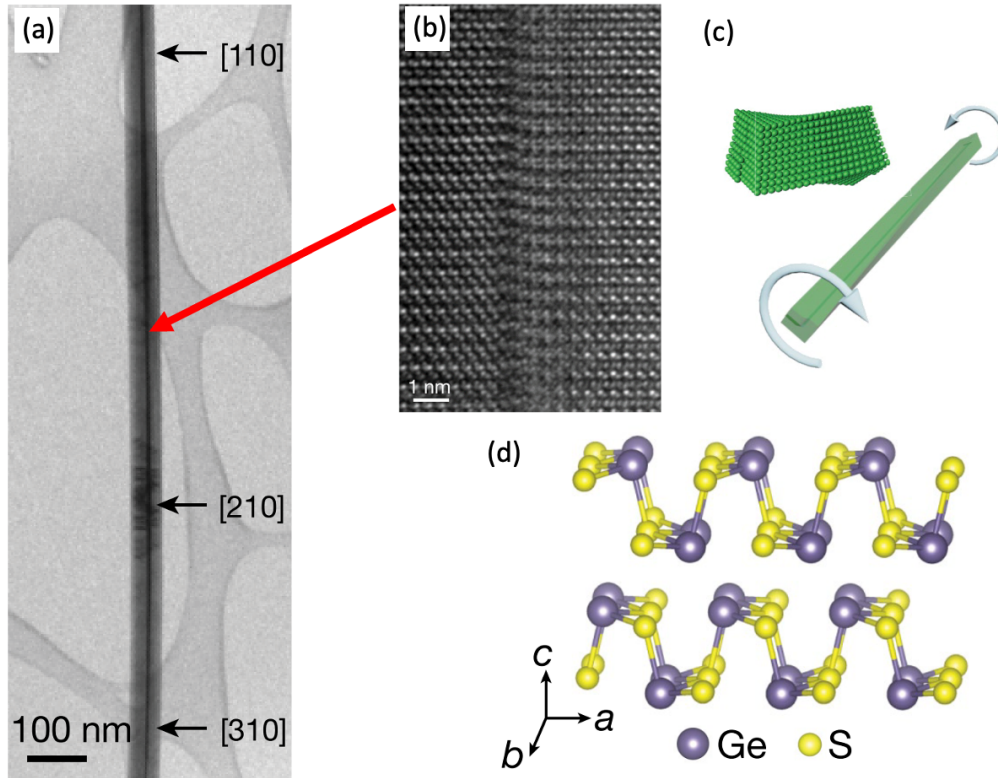


Figure 4.2. (a) TEM image of a GeS nanowire with Eshelby twist; (b) high-resolution TEM image of the dislocation core; (c) schematics showing the

growth of nanowire with Eshelby twist. The inset shows a schematic of the atomic structure of the Eshelby twist. (d) The lattice structure of layered GeS. (Figures adapted from Y. Liu et. al. Nature, 570, 358-362 (2019)).

Figure 4.2 shows the lattice structure of twisted GeS nanowire with a screw dislocation core (73). A single dislocation core structure can be clearly observed in a TEM image (figure 4.2 (a)) shown as a black line in the center of the GeS nanowire. The high-resolution TEM image of the core shows the displacement of the atomic layers around it. The twisting angle between layers is very small, which is on the order 10^{-4} rad per layer.

In this chapter, we present the thermal transport of twisted GeS nanowire with screw dislocation core. An abnormal thermal conductivity behavior is observed. The thermal conductivity increases by decreasing diameters (D) of nanowires, which opposes to the trend predicted by boundary scattering that is commonly dominate in nanowires such as Si. The possible causes of the enhancement on thermal conductivity at small diameters may from the screw dislocation core or from the spiral topology of the twisting between layers. As comparisons, the thermal conductivity of non-twisted GeS nanowires and GeS nanoribbon is also measured, which shows thermal transport behaviors as normal semiconductors.

4.2 The thermal transport measurements of GeS nanowires

The thermal transport measurement is carried out by suspended microdevices as mentioned in section 2.2.2 and 2.2.4. We first identify the diameters and the twisting of as-grown GeS nanowires by using TEM images. Then, the nanowires are transferred from the TEM grids to suspended microdevice. Due to the softness of van der Waals materials, instead of using Ga beam in FIB, we used electron beam to induce Pt deposition for making bonds between GeS nanowires and suspended micropads. This can prevent heavy lattice damages to GeS nanowires which can be caused by the ion beams. The thermal transport measurements are carried out from 60 to 375 K with temperature step at 10 K. T -dependent thermal conductivities $\kappa(T)$ of GeS nanowires with different diameters are measured.

4.2.1 The twisted GeS nanowires

Figure 4.3 shows two of the twisted nanowires used in this study. Screw dislocation core is observed as a thin black line in the center of nanowire in TEM images. The wrinkle-like patterns are caused by the strain field induced by the dislocation core. The van der Waals

layers with twisting can form a spiral staircase like structure along the screw dislocation core. Also, instead of van der Waals bonding, the atomic interactions in the core region are covalent. Therefore, the transport properties in twist GeS nanowires can be affected by both the core and the van der Waals layers.

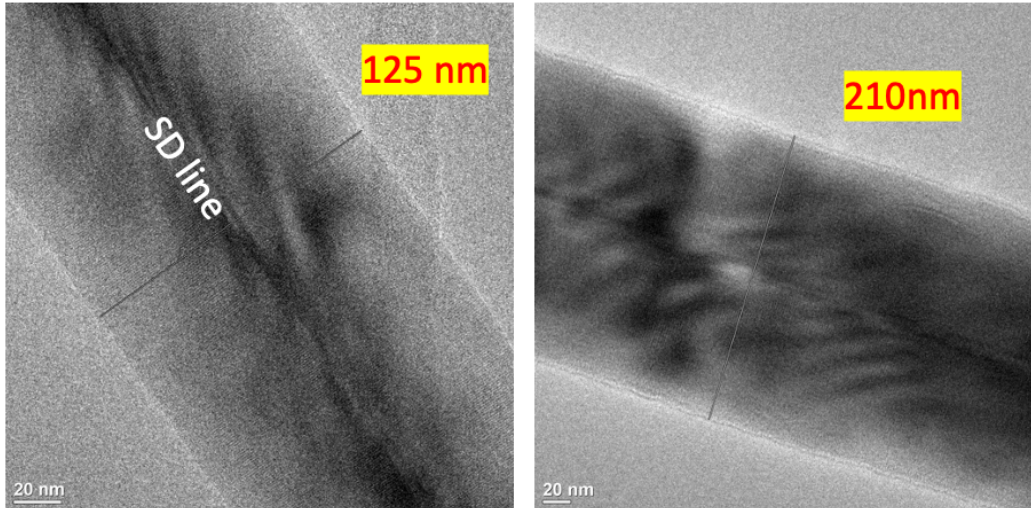


Figure 4.3. The TEM images of two twisted GeS nanowires with diameters of 125 and 210 nm, respectively. The screw dislocation core in the center can be observed as a black line and the wrinkle-like patterns on the nanowires are resulted from the strain field induced by the core.

First, let us consider all the possible effects from the core that affect phonon. The rigid covalent bonding in the core region could largely enhance the thermal conductivity compared to the loose van der Waals bonding between atomic layers. Previous simulation of multilayer graphite with a screw dislocation core also shows the enhanced thermal conductivity by the covalent bonding in the core region compared to pure van der Waals layers without a core (80). In addition, the strain field caused by the core can reduce thermal conductivity. Although the classical calculation predicts no phonon-core scattering if phonons transport along the dislocation core (47, 81-83), the recent molecule dynamic (MD) simulations indicate that scatterings between phonon and core can still occur along the core direction (84-86). This is because the anharmonicity in the interatomic potential caused by the strain can enhance phonon-phonon scattering, while the classical theory only considers the phonon scattering from the strain field. Also, as gold (Au) is catalyst in GeS nanowires' growth, Au may diffuse into the dislocation core and make a conductive core (73). This can also enhance thermal transport in GeS nanowire.

Next, we should investigate the effect of the twisting topology that is associated with screw dislocation core. The spiral staircase-like layers in twisted GeS nanowires could provide additional phonon conduction channels along in-plane directions. The spiral heat flow can make extra contribution to enhance the total thermal conductivity in addition to the heat

flow that conducts along the cross-plane direction (80). The in-plane thermal conductivity with covalent bonds is higher than that of cross-plane direction with van der Waals bonds. The contributions from the spiral heat flow cannot be ignored without investigation. In addition, twisting between van der Waals layers can reduce the heat flow that conducts through layers. The twisting makes the thermal conduction resembles one-dimensional glass-like thermal transport, where additional phonon scatterings come from the distortedness of layers rotations. This has been experimentally proven in MoS₂ thin films at large-angled layer rotations (87). However, the layer rotation angles in twisted nanowire are on the order of 10⁻⁴ rad per layer (73). It is highly probably that the thermal conduction reduction effect from layer twisting is negligible in GeS nanowires.

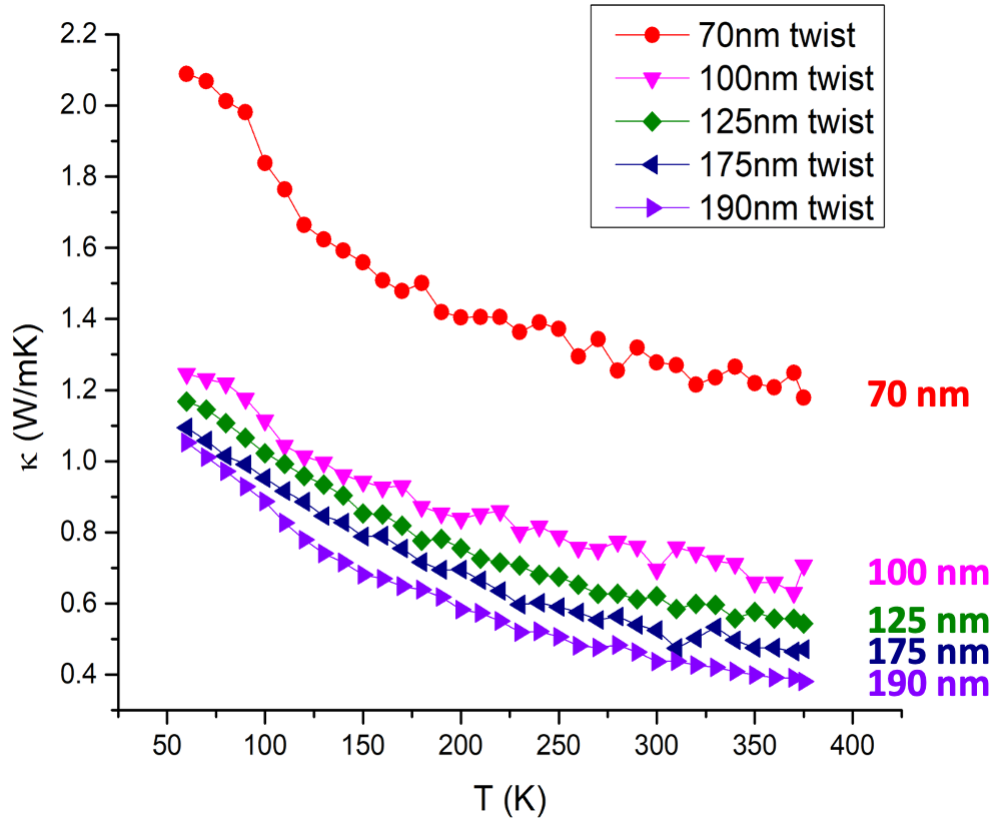


Figure 4.4. The thermal conductivity of twisted GeS nanowires with screw dislocation core. Thinner nanowires have higher thermal conductivities which is against the trend of common nanowires that governed by boundary scattering. The diameters of nanowires vary from 70 to 190 nm.

The measured thermal conductivities of twisted GeS nanowires are shown in figure 4.4. The overall decreasing trend of $\kappa(T)$ curves can be explained by Umklapp scatterings. The trend of thermal conductivity with respect to diameter, however, is against the prediction of boundary scatterings where thinner nanowires should have lower thermal conductivities due to more phonon scatters with the surfaces of nanowire (88). As shown in figure 4.4,

the thinnest nanowire ($D=70$ nm) has the highest thermal conductivities while the thickest one (with its $D=190$ nm) has the lowest thermal conductivities. This abnormal thermal transport behavior must origin from the screw dislocation core and its associated twisting topology, as non-twisted layered GeS nanowires show normal $\kappa(D)$ trend that can be explained by boundary scattering (shown in section 4.2.2). The efforts to explain such abnormal behavior are shown in section 4.3.

4.2.2 The non-twisted GeS nanowires

To understand the thermal conductivities of twisted GeS nanowires, thermal conductivities of non-twisted GeS nanowires are also measured. The TEM images in figure 4.5 shows non-twist nanowires with pristine single-crystalline qualities. No dislocation core (shown as black line in TEM image) is observed. The wrinkle-like patterns that observed in twisted nanowire disappear in non-twisted nanowires. This implies that non-twisted nanowires are strain free. The van der Waals layers are arranged as perfect parallel planes to each other. The phonon transport is fully in cross-plane direction. The additional spiral heat flow channel does not exist in non-twisted nanowires.

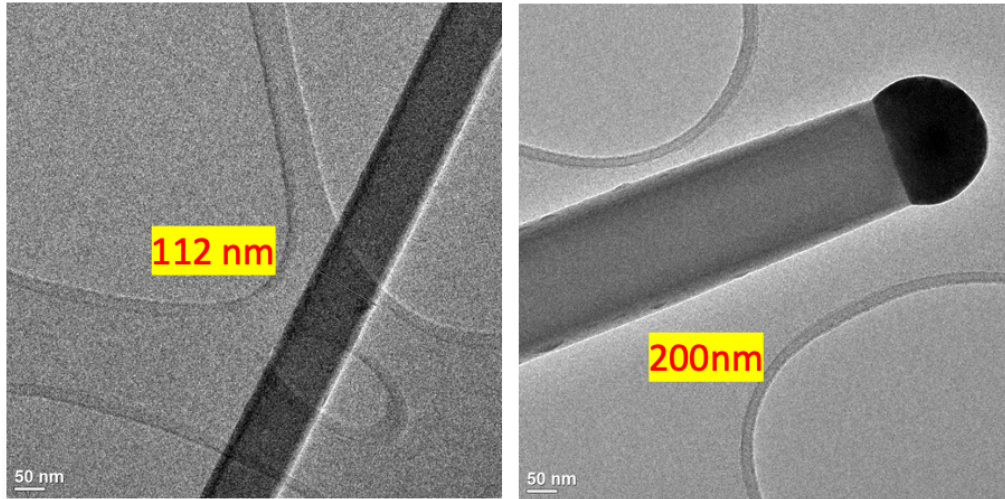


Figure 4.5. The TEM images of two non-twisted GeS nanowires with diameters of 112 and 200 nm respectively. The clean and clear look of nanowire implying pristine qualities without dislocation core or strain.

The measured thermal conductivities of non-twisted GeS nanowires are shown in figure 4.6. The overall decreasing in thermal conductivity with increasing temperature in thick nanowires (112 and 200 nm) can be explained by Umklapp scatterings. The curve $\kappa(T)$ becomes flat of $D=80$ nm and with slightly positive slope of $D=55$ nm. This is a typical

trend of $\kappa(T)$ curves of nanowire affected boundary scattering, such as Si nanowires. The observation of boundary scattering effect in dislocation-core-free non-twisted GeS nanowires further implies that the abnormal thermal conductivity-diameters dependence of twisted nanowires origins from either the screw dislocation core or the twisting topology.

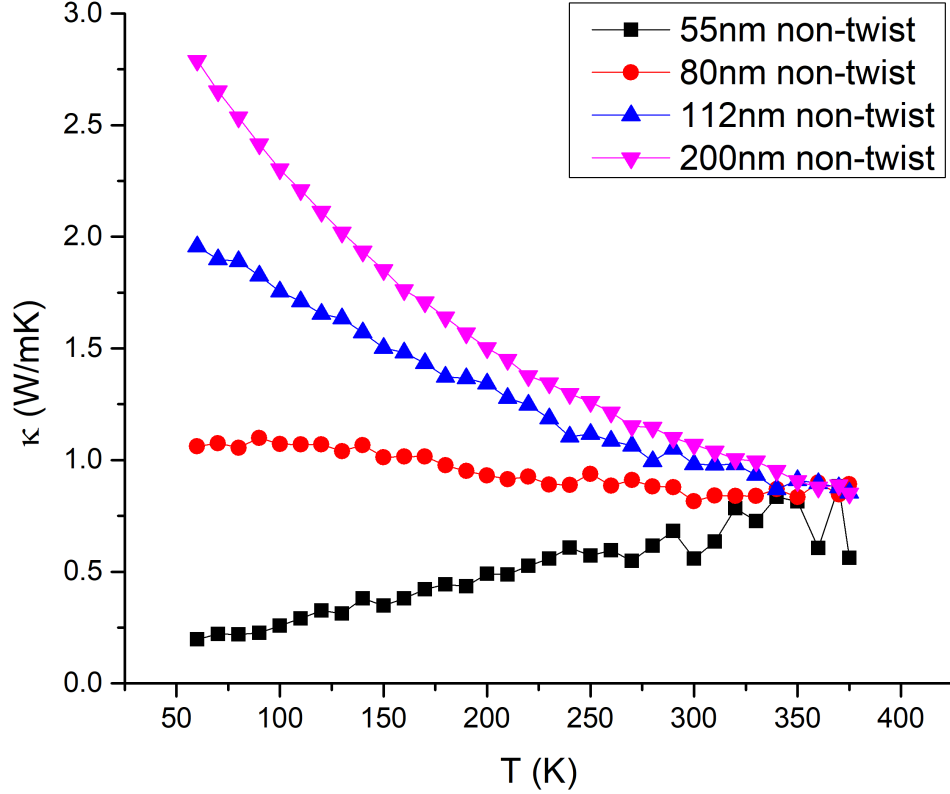


Figure 4.6. The thermal conductivity of non-twisted GeS nanowires without screw dislocation core. Thinner nanowires have lower thermal conductivities which can be explained by boundary scattering. The diameters of nanowires vary from 55 to 200 nm.

4.2.3 The overall thermal conductivities

The comparisons between non-twisted and twisted nanowires can unveil the effects of the core on layered GeS nanowires. As shown in figure 4.7, for nanowires of diameters larger than 100 nm, twisted nanowires have lower thermal conductivities compared to that of non-twisted ones. This is because the phonon-phonon scattering is enhanced by more harmonicity in atomic interaction potentials induced by the screw dislocation core (as discussed in section 4.2.1). The strain-free and dislocation-core-free non-twisted nanowires

therefore have higher thermal conductivities. On the contrary, as shown in figure 4.8, twisted nanowires have higher thermal conductivities than non-twisted nanowires, for diameters smaller than 100 nm. This is caused by the abnormal enhancement of thermal conductivity in thin twisted nanowires.

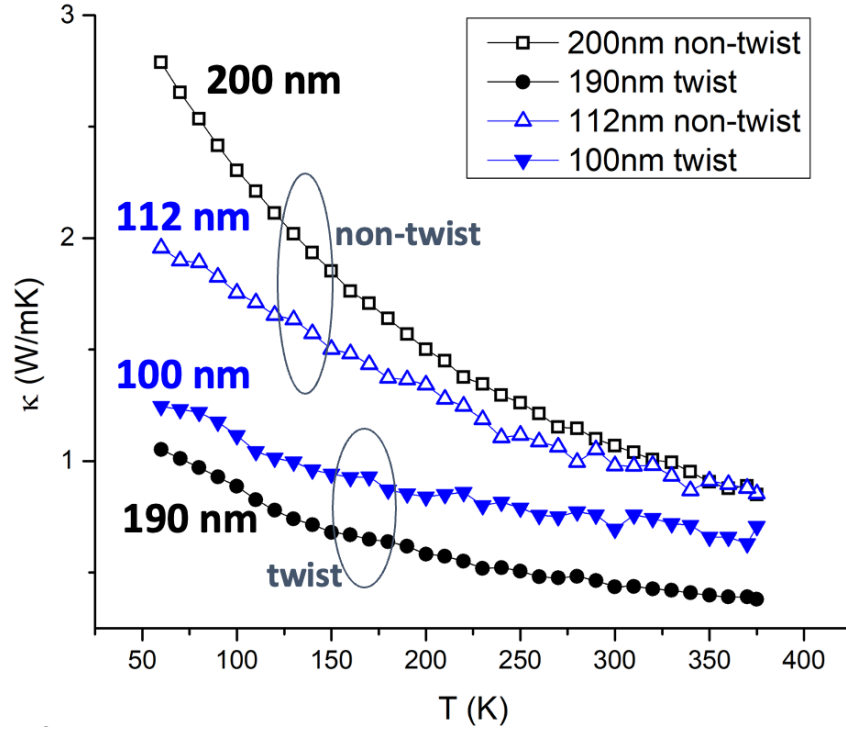


Figure 4.7. The thermal conductivities of non-twisted nanowires are higher than that of twisted ones if the D of nanowire is higher than 100 nm.

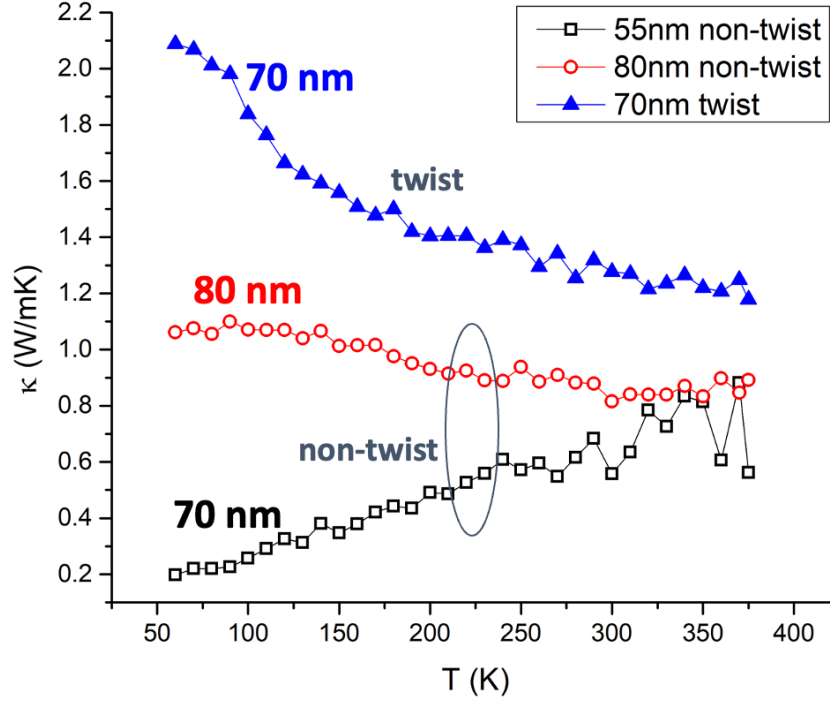


Figure 4.8. The thermal conductivities of non-twisted nanowires are lower than that of twisted ones if the D of nanowire is small than 100 nm.

As mentioned in section 4.2.1, the core is expected to have higher thermal conductivities than cross-plane thermal conductivities in van der Waals layers. As the diameter of the core region is not scalable with that of nanowires (usually a few nanometers), thinner nanowires can have higher core/body ratio in terms of cross-section area. Thus, the overall averaged total thermal conductivities in thinner nanowires can be higher. In section 4.3.1, we construct a conductive core model to further discuss this effect. In addition, the spiral heat flow that origins from the twisting topology between layers can also enhance the total thermal conductivity of twisted nanowires, which will be discussed in section 4.3.2.

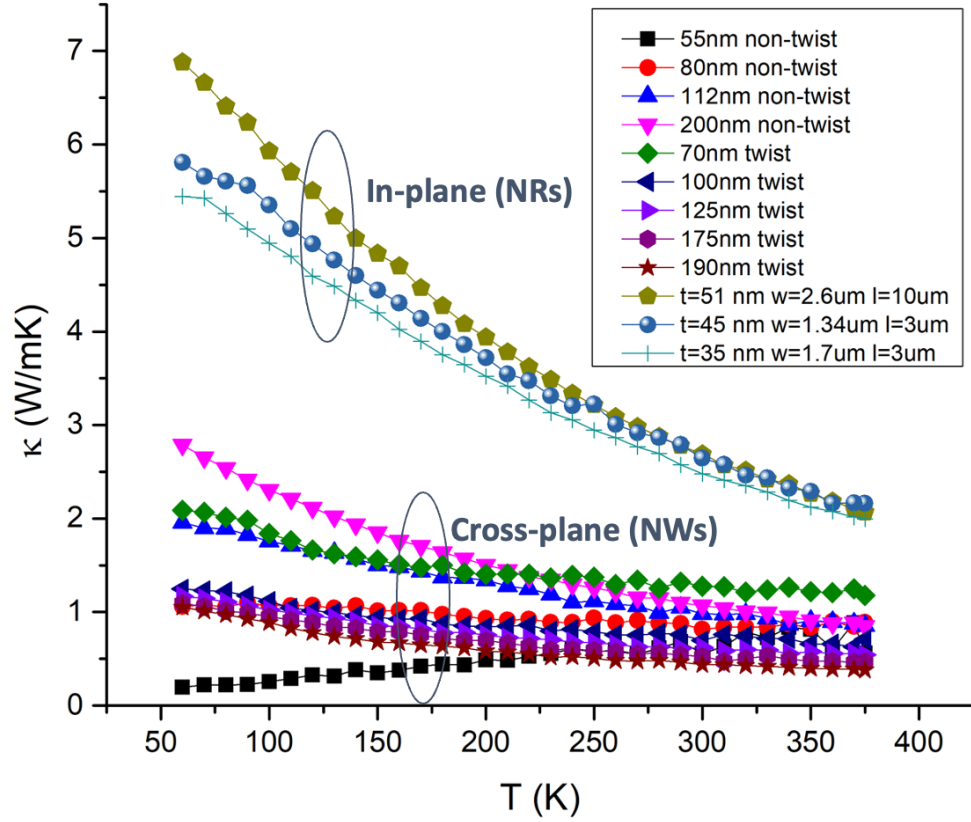


Figure 4.9. the overall thermal conductivities of GeS nanowire with cross-plane (non-twisted and twisted nanowires) and in-plane (nanoribbon) directions.

Besides nanowires, we also measured thermal conductivities of GeS. The measurement is along the in-plane directions of van der Waals layers. In figure 4.9, the thermal conductivity of GeS along in-plane direction is higher than that along cross-plane direction. The overall thermal conductivities measured also agrees with the literature's data (89, 90).

4.3 Theoretical efforts to explain the abnormal thermal transport in twisted GeS nanowire

As mentioned in section 4.2.3, two factors that may contribute the abnormal thermal transport in GeS nanowires, the core and the twisting topology. Section 4.3.1 shows conductive core model to explain the core effects and section 4.3.2 shows spiral heat model to explain the twisting topology effect.

4.3.1 Conductive core model

In common non-layered nanowires, the core region usually has smaller thermal conductivity compared to noncore region due to its increased distortedness. However, in van der Waals layered materials, the core has different type of atomic bonding, and it is reasonable to assume a more thermally conductive core in twisted layered GeS nanowires.

Figure 4.1 shows the schematics of conductive core model, which consists of a covalently bonded core region and a van der Waals bonded noncore region, with conductivity as κ_{core} and κ_{VdW} , and with diameter as d_{core} and d_{VdW} , respectively. The total thermal conductivity of nanowire, κ_{NW} , consists of the core contribution and the noncore contribution, which can be expressed as,

$$\kappa_{NW} = d_{core}^2 \cdot (\kappa_{core} - \kappa_{VdW}) \left(\frac{1}{d_{NW}} \right)^2 + \kappa_{VdW}, \quad (4-1)$$

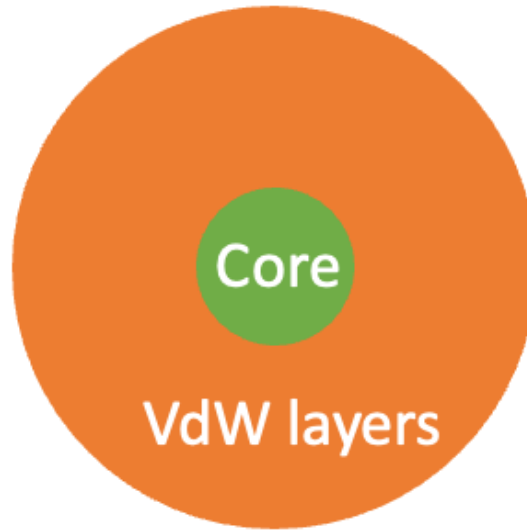


Figure 4.10. Schematics of conductive core model consisting of core region and van der Waals layer (noncore) region.

In equation (4-1), the experimental measurables are κ_{NW} and d_{NW} , therefore, at given temperatures, linear fittings of κ_{NW} and $(1/d_{NW})^2$ can be performed. The fitting parameters are κ_{VdW} and $d_{core}^2 \cdot (\kappa_{core} - \kappa_{VdW})$, which can be further break down into κ_{VdW} , κ_{core} and d_{core} with one degree of freedom of unknown. The overall fitting results for all twisted nanowires shown in figure 4.11 matches well to experimental data.

We can further check the validity of conductive core model with κ_{vdW} , which represents the thermal conductivity of strained van der Waals layers of twisted nanowires. In figure 4.12, we compared κ_{vdW} with the thermal conductivities of non-twisted nanowires with unstrained van der Waals layers. The $\kappa_{vdW}(T)$ shows a typical decreasing curve which is caused by phonon-phonon scattering. The magnitude is almost in the same level of that of 55 nm-thick non-twisted nanowires. This implies the phonon scattering from the dislocation core is equivalent to that from boundary surfaces with nanowires' diameters of 50 nm.

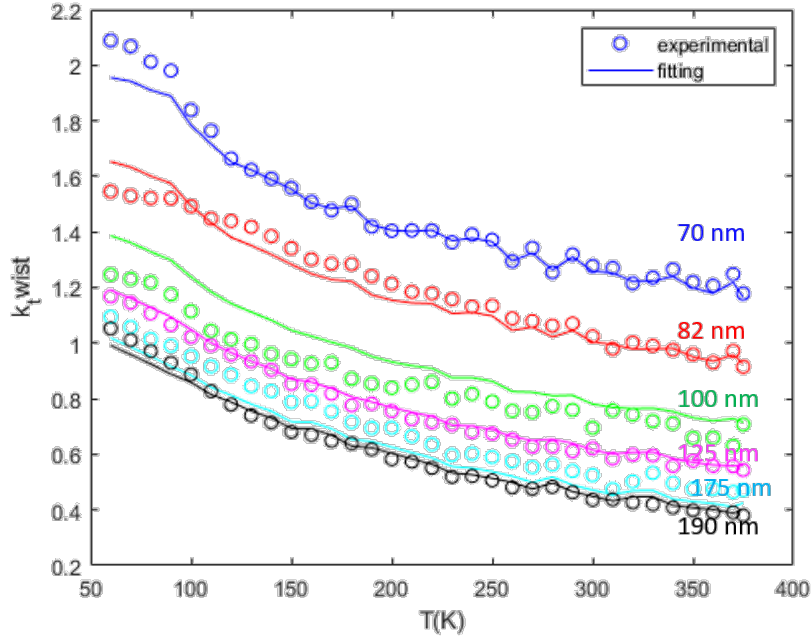


Figure 4.11. The fitting results of conductive core model on twisted GeS nanowires with their diameters range from 70 to 190 nm.

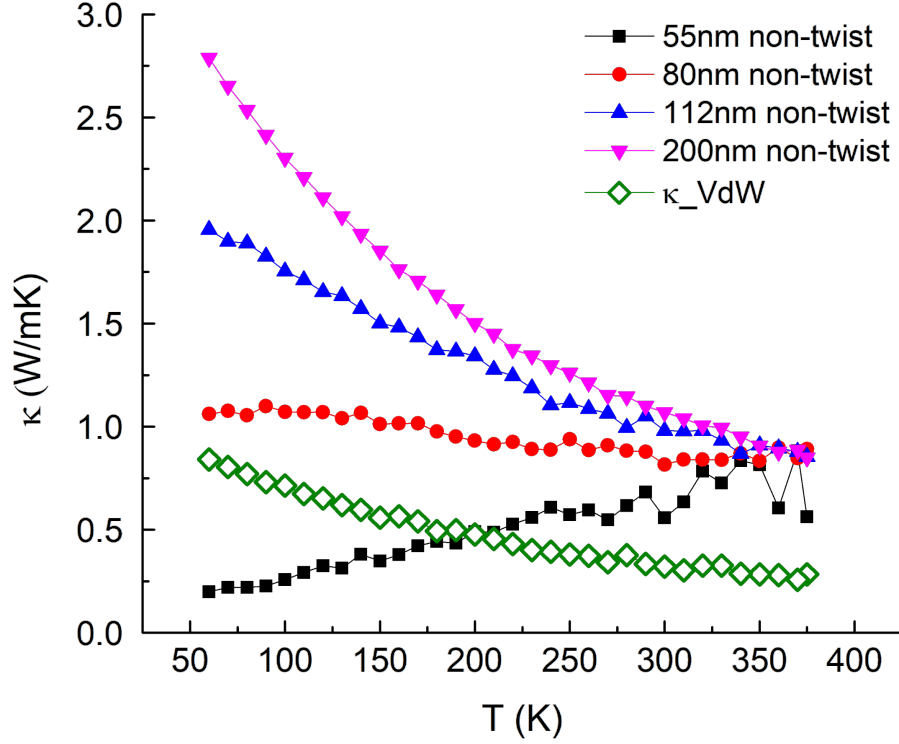


Figure 4.12. Comparison of the fitted parameter κ_{VdW} with respect to the thermal conductivity of unstrained van der Waals layers in non-twisted GeS nanowires, with their diameters range from 55 to 200 nm.

Experimental measurements on the exact size of cores in nanowires is very challenging. Figure 4.13 shows the curves of κ_{core} with respected to assumed d_{core} at temperatures of 60 and 375 K, respectively. If $d_{core} = 3$ nm, which is a very reasonable assumption for most of dislocation cores, κ_{core} has a value of the thermal conductivity of Cu (~ 300 W/mK). This is too conductive for a dislocation core. On the other hand, if κ_{core} take the value of the thermal conductivities of GeS along in-plane direction, which is also a reasonable assumption for covalently bonded GeS material, the d_{core} is around 25 nm. The diameter is also too large for a common core in nanowires.

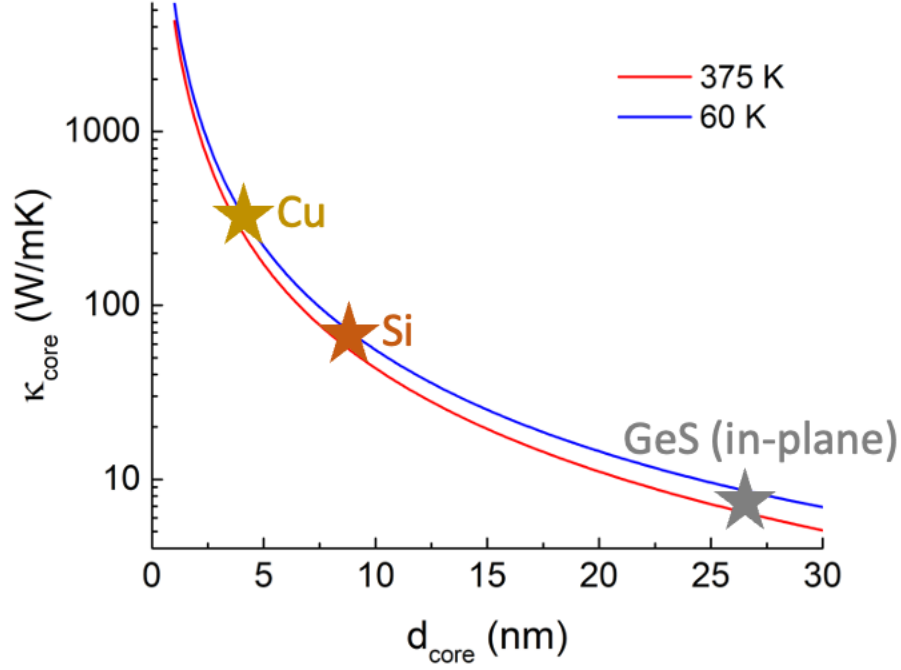


Figure 4.13. The κ_{core} with respected to d_{core} at temperatures of 60 and 375 K respectively. Values of thermal conductivity of Cu, Si and GeS (along in-plane direction) are also given for references.

Although the conductive core model can give good data fittings, the fitting results implies either a very wide core or very conductive core, which is hard to justify in GeS nanowires. Therefore, there must exist additional mechanisms which are not considered in conductive core model.

4.3.2 Spiral heat conduction model

The Eshelby twist in layered nanowires can generate a spiral heat flow that transferring along in-plane direction from layers to layers. Figure 4.14 shows a COMSOL simulation of one such heat flow. This artificial layered nanowire consists of 2 nm-thick Cu layers and 8 nm-thick SiO₂ layers arranged alternatively. The diameter of the nanowire is 20 nm. A screw dislocation core is introduced in the center and a spiral staircase-like topology of layers are created. The blue arrows represent the heat flow. It is clearly observed that the heat flow has a formation resembling spiral vortex. The intensity of heat flow is larger when it is near the dislocation core. This is because for the heat flow that passes near the core, by ascending one period (one Cu layer and one SiO₂ layer) along nanowire, the heat flow needs to cover less in-plane distance. So, it is more efficient to transfer heat near the core.

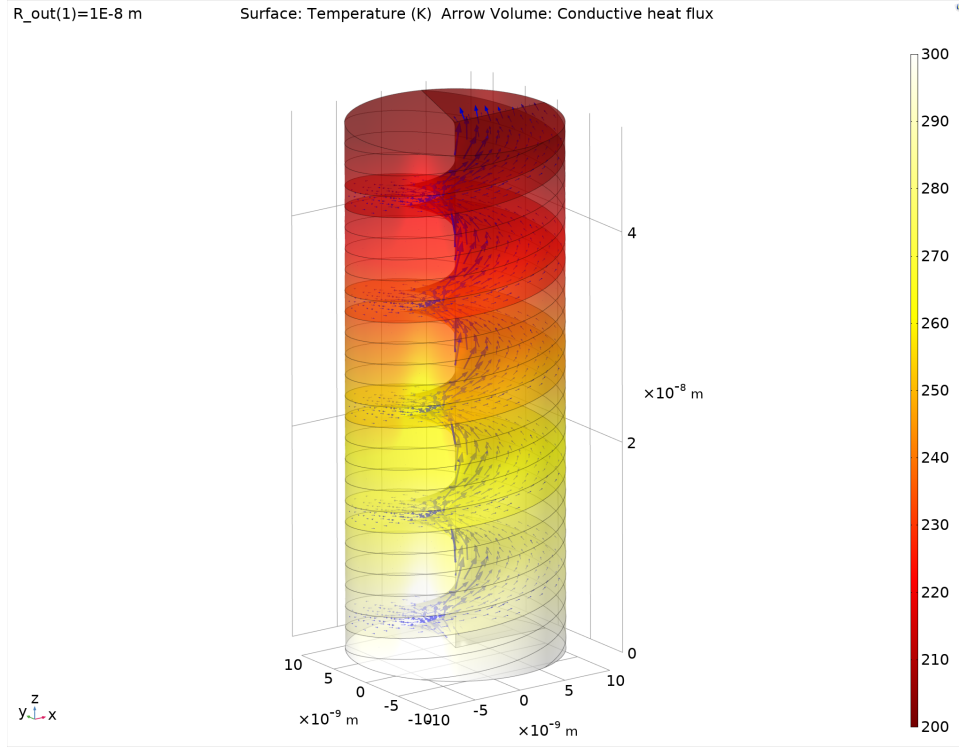


Figure 4.14. COMSOL simulation of an artificial nanowire to demonstrate spiral heat flow in twisted nanowires. The nanowire consists of two periodic layers: Cu (2 nm thick) and SiO₂ (8 nm thick) and has a diameter of 10 nm.

To study the topology effect in twisted GeS nanowires, we constructed a simplified model by assuming the nanowire consisted of two continuous layers as shown in figure 4.15. At $T = 375$ K, the in-plane thermal conductivity measured in GeS nanoribbons $\kappa_{in-plane} \approx 2$ W/mK; the cross-plane thermal conductivity measured in GeS nanoribbon $\kappa_{cross-plane} \approx 0.8$ W/mK. From the GeS crystal structure, we can estimate that $t = 2.46$ Å (the bond length in c-axis of GeS lattice) and $h = 10.4$ Å (the lattice constant in c-axis of GeS lattice). Therefore, by solving equations from parallel and serial conduction model (as indicated in figure 4.15, we can estimate that $\kappa_1 = 6.42$ W/mK and $\kappa_2 = 0.63$ W/mK.

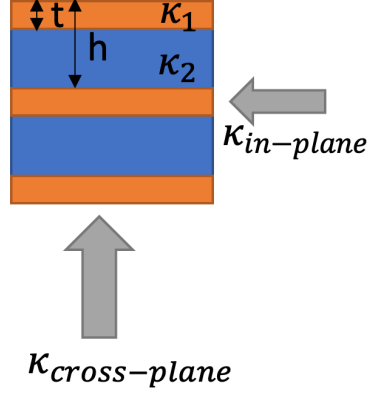


Figure 4.15. Schematics of simplified non-twisted layered GeS nanowire

To include the spiral topology, we integrate the thermal flow in each layer and get an effect thermal conductivity from the spiral heat flow,

$$\kappa_{spiral} = 2\kappa_1 \left(\frac{t}{h} \right) \frac{\sinh^{-1}(x)}{x^2} + \kappa_2 \left(\frac{h-t}{h} \right) \frac{\sinh^{-1}(x)}{x^2} = 2\kappa_{in-plane} \frac{\sinh^{-1}(x)}{x^2}, \quad (4-2)$$

where $x = \frac{\pi D}{h}$ and D is the diameter of GeS nanowire. The total thermal conductivity of nanowire is

$$\kappa_{NW} = \kappa_{cross-plane} + \kappa_{spiral}. \quad (4-3)$$

The calculated κ_{NW} with parameters from fitted data at $T=375$ K is shown in figure 4.16. The enhancement for small D is not significant. At $D=50$ nm, the enhancement is only 1%. This effect cannot fully explain the abnormal thermal conductivity of twisted nanowire. The reason is that in twisted nanowires, $h \ll D$ and $x \rightarrow \infty$, where $\frac{\sinh^{-1}(x)}{x^2} \rightarrow 0$. Only if $h = 10$ nm, that is the lattice constant of GeS in c-axis is 10 nm, the spiral heat flow effect can be as significant as to fully explain the enhancement of thermal conductivity at small D (as shown in figure 4.17).

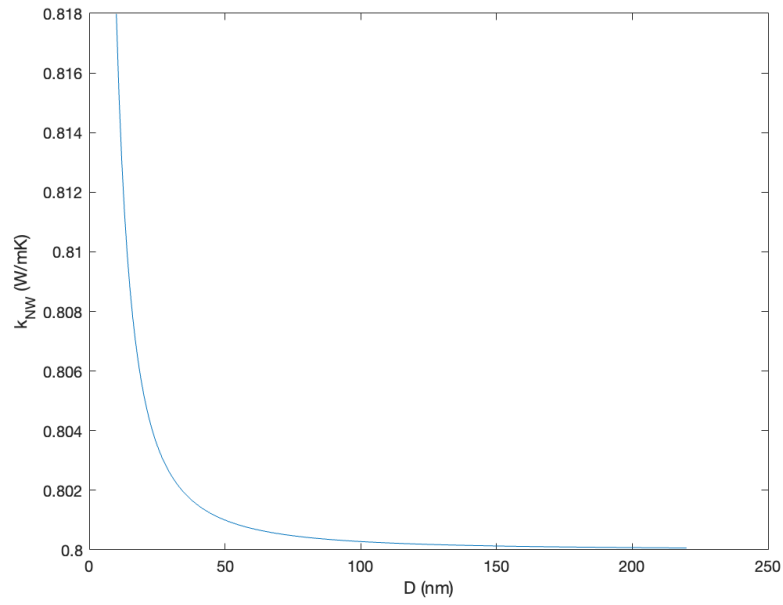


Figure 4.16. The calculation of thermal conductivity of nanowires κ_{NW} with spiral heat flow effect in GeS nanowires with diameters of D .

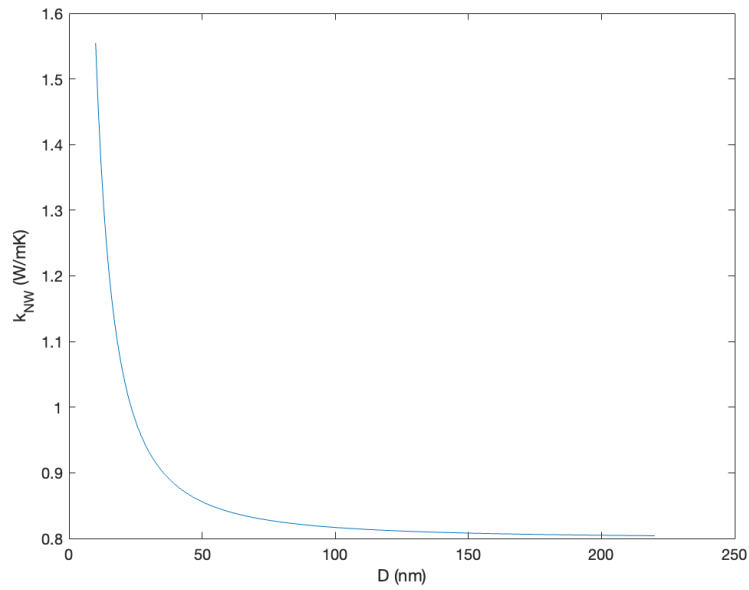


Figure 4.17. The calculation of thermal conductivity of nanowires κ_{NW} with spiral heat flow effect in artificial GeS nanowires with diameters of D and an artificial lattice constant in c-axis equaling to 10 nm.

Therefore, spiral heat flow effect is negligible in twist GeS nanowires and future theoretical investigation need to be conducted.

4.4 Conclusions

We have experimentally observed the abnormal thermal conductivity increasing of twisted GeS at small diameters measured by suspended microdevices. A classical conductive core model and spiral heat conduction model is proposed but cannot fully explain the increasement. The failure of classical models implies some hide mechanisms of heat conduction is yet to be found in this type of layered twisted nanowires. For examples, other possible explanation can be that surface phonon mode may exist or a special coupling mode between phonons and screw dislocation core may occur. Further theoretical efforts to unveil the complete mechanisms behind this abnormal thermal transport behavior is required.

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