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The Friction Between Nanowires and Highly Oriented Pyrolytic Graphite

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Abstract

The study of friction has been on-going from centuries ago till date yet the fundamental relations between macro-, micro- and nano- scale friction have not been fully grasped. Friction is present in everyday and everywhere, from engineering systems to geophysical occurrences around the world. In the world of engineering friction plays two extremely different roles. On one hand you have friction forces that are beneficial for example the traction of automobile tires and on the other you have detrimental effects of friction like wear and tear.

This study investigates the effects of friction on a nanoscale by studying the effects of friction between nanowires and substrates. This study aims to bridge the gap between nanoscale friction and macroscale friction. Currently, results showed that the frictional forces calculated tend towards a common idea that local asperities on both substrate and nanowires are the key causes of friction. There is also an argument that plastic deformation of the local asperities would contributed to the frictional forces occurring in two surfaces.

Further research is recommended to access the actual cause of friction and its origin. In order to attain these results, the experiments will have to be repeated across different types of nanowires and substrates and hopefully a conclusion can be drawn when the results are compared to each other.
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1. Introduction

Over the years since the first studies of friction began, it has been known that friction plays a huge part in physical systems and it occurs at different scales. Friction by definition is the force generated that resist motion. The magnitude of friction depends on the following properties, the environment, contact surface, material properties and geometries. They range from a micro/nanoscale like the study of tribological aspects of nanowires and different substrates, to a macroscale, like geophysical occurrences like earthquakes. [29]

This study is called tribology where researchers studied the friction caused by two surfaces moving relative to one another. Tribology plays an important role in the engineering industry, this is because a large amount of energy is lost due to friction between components. Apart from losing energy to friction, friction also causes wear which damages machinery. This study hopes to shed some light as to how we can minimize the amount of energy that is wasted.

On a macroscopic level when two objects sliding across each other, the friction is calculated using the apparent contact area. It was previously assumed that the surface of friction on a nanoscale is perfectly smooth. However, when looking at the surfaces of the objects in a microscopic level it is observed that the surfaces of the two objects are not completely flushed against each other. It is found that the true surface area of contact is magnitudes smaller than the apparent surface of contact. This is due to surface asperities of the objects in contact, these surfaces asperities are also subjectable to wear, plastic deformation which influences the amount of friction between two objects in contact. [3] The figure below shows the macroscopic and microscopic surfaces of two objects in contact.

![Figure 1: Evolution of Areas of Contact (André Schirmeisen, 2009)](image-url)
Even if the surfaces of both objects were perfect, the surfaces will never be truly smooth this is
due to the shapes of atoms. No much research has been completed in this area as it is still unclear
how individual atoms or molecules will behave on a sliding surfaces. The Figure 2 shows an
amorphous carbon tip sliding over a diamond surface on an atomic scale. [11]

![Figure 2: Amorphous Carbon Tip on Diamond Surface by Izabela Szlufarska](image)

Many studies on friction have been done since the late 1990’s, Sheehan and Lieber did an
investigation of MoO3 nanocrystals along an MoS2 substrate using atomic force microscopy
(AFM), to the early 2000’s where Dorogin et al. completed his investigation of Zinc Oxide
(ZnO) nanowires on SiO substrate. [17] Even though much effort has been put into this field of
research over the years, there are still many key aspects of friction that are not understood well
enough. Therefore, it is still a challenge to bridge the gap and understand the relations of friction
on a microscopic and macroscopic scale.

By investigating previously published articles on the tribological aspects of nanowires and
substrates more can be understood about the effects of static and kinetic friction between
nanowires and substrate. In order to conduct an effective investigation of nanowires on highly
oriented pyrolytic graphite (HOPG) surface, research into the types of nanowires (ZnO, SiC
and Al2O3), the relationship between macro-, micro- and nanoscale friction, the advantages
and disadvantages of AFM and scanning electron microscope methods must also be
investigated.

The aim of this investigation is to use the knowledge gained by prior research to aid in the study
and experimentation to shed light on the effects of friction between Zinc Oxide (ZnO)
nanowires and how it behaves on a HOPG substrate. With this data, we can then compare that
to the effects of friction between other nanowire types with different substrates and identify the
strengths, constraints and limitations of the model in use which will benefit future work in this area.

This thesis firstly will cover the limitations and assumptions made before the experiments were conducted. Next, a literature review is done to investigate past experiments done to help build a better foundation of knowledge in regards to nanotechnology. This section is important as there is much to learn from the results obtain and also the methodology used when conducting the experiments. Section 5 of the report will be the main body of the report where the methodology used to conduct experiments for Zinc Oxide (ZnO) nanowires and HOPG substrate for this thesis will be discussed. The following section will then discuss the results obtained. Finally, the conclusion will give an overview of the whole thesis.

The main bulk of images collected throughout the experiments will be attached to the appendix along with the Matlab coding which was used to interpret the results.
2. Scopes and Objectives

The main aim of this thesis is to determine the kinetic and static friction force acting between ZnO nanowires and HOPG substrate and then, try to identify if there are any trends that follow experiments done in the past. In order for the experiments to be carried out, a set of scopes and objectives were set:

- Investigate past experiments through literature review and establish a better understanding of the techniques used to investigate nanoscale friction.
- Use Matlab’s polynomial fitting function, derive a 4th order polynomial curve equation to calculate static friction.
- Use Paint and other image processing software, identify the maximum deflection of the nanowires to calculate kinetic friction.
- Use the Scanning Electron Microscope to obtain high resolution images of the nanowire to identify the cross-section type and dimensions.
- Calculating the kinetic and static frictional forces using methods identified through literature review.

3. Assumptions

Due to the limited knowledge and limitations of current technology used to investigate nanoscale friction, some assumptions had to be made before experiments were carried out. The following assumptions were made when carrying out experiments and calculations.

- The Young’s modulus of all ZnO wires were assumed to be constant at 140GPa.
- The cross-sectional area (rectangular and hexagonal) of all ZnO wires are constant regardless of length.
- The hexagonal cross-section ZnO wires have sides of equal length.
- When performing the experiments, it the ZnO wires are in full contact with the HOPG substrate.
- When performing the experiments, the ZnO wires will not roll or twist.

4. Literature Review

Throughout the duration of the thesis, prior investigation was done to understand the fundamentals of static and kinetic friction and the effects it had on nanowires on top of a substrate. Information obtained from this prior research was used to facilitate in the analysis of results obtained by the experiments carried out for this thesis.
4.1 The nature of frictional forces

The initial studies of friction began with Leonardo da Vinci (1452-1519) and was pioneered by other scientists later on, one of whom was a French physicist and inventor by the name of Guillaume Amontons (1663-1705) in 1699 and have been ever evolving since then. [2] These days it is commonly accepted that force is a combined effect which comprises of adhesive forces, surface topography and chemistry, etc. and can dominate the given system depending on the length scale force exerted. [13] This study of friction and the forces/effects in relation to it is commonly known as tribology today. The summary of their findings are found in these 3 laws:

1. The force of friction is directly proportional to the applied load (Amontons 1st Law)
2. The force of friction is independent of the apparent area of contact. (Amontons 2nd Law)
3. Kinetic Friction is independent of the sliding velocity. (Coulomb’s Law)

These laws are only applicable to dry friction as it has already been known from a long that that any form of lubrication would alter the tribological properties. [4] According to Amontons’ law [2] in macrotribology regarding the interacting between two surfaces in contact, the governing equation used to calculate the frictional force $F_{fr}$ is:

$$F_{fr} = \mu N$$

Where $\mu$ is the coefficient of friction and $N$ is the normal force acting on the contact surface. This shows that Amontons’ law states that friction is in itself independent of the contact area and the velocity of the objects in contact but directly proportional to the normal load acting on both objects. [25]

It was not till 1950 that two other pioneering physicists Bowden and Tabor introduced a physical explanation regarding the laws of friction. They proposed that friction was strongly dependant on real area of contact which is defined by local asperities formed on the surface of both objects in contact and that friction was caused by these plastic deformities interlocking. The both of them then took into consideration Hertz contact theory and finally concluded that the frictional force can be governed by the following equation:
\[ F_{fr} = S \pi \left( \frac{R N}{K} \right)^{\frac{2}{3}} \]

Where S is the shear stress, R is the radii of curvature and K is the reduced Young’s moduli of the asperities in contact. [13] The table below shows the comparison and differences between Amonton’s and Bowden and Tabor’s theory.

<table>
<thead>
<tr>
<th></th>
<th>Amontons</th>
<th>Bowden and Tabor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{fr} )</td>
<td>( \mu N )</td>
<td>( S \pi \left( \frac{R N}{K} \right)^{\frac{2}{3}} )</td>
</tr>
<tr>
<td></td>
<td>The frictional force acting between two bodies is linearly proportional to the normal load and is independent of the contact area.</td>
<td>The frictional force acting be between two bodies is dependent on the contact area and is also dependant on the shearing strength caused by the adhesive bonds.</td>
</tr>
</tbody>
</table>

**Figure 4: Comparison of Theory [7]**

Due to this a contradiction arose, this was because Bowden and Tabor’s Hertzian elastic theory had a non-linear friction-load dependence of \( F_{fr} = N^{\frac{2}{3}} \) while Amonton’s \( F_{fr} \) is proportional to N. [4] [13] It was only when Archard (1953) who realized the relation between Bowden and Tabor’s hypothesis and Amonton’s equation, changed the Bowden and Tabor’s assumption of assuming constant number of asperities to that of the load dependent asperities did the controversy be resolved. [4] [7]

Another factor which is also know to play and important role in the coefficients of friction would be the generation of and transfer of material from one surface to another due to wear and tear. This material also commonly referred to as “third body” effects (friction is usually assumed to be a two-body problem) or fretting wear and can dominate steady-state sliding over the two test surfaces as it has a directly affects the properties of the contact surface. [13][22] This refers to the wearing down of the asperities between two surface in contact under repeated relative loading; corrosion may also be the culprit of this occurrences. More research has to be done in this are to discover to prevent or mitigate this effect.

### 4.2 The evolution of Methods of Analysis

In the 20\textsuperscript{th} century there were a number of physicist that started the investigation the frictional force between a nanostructure and a substrate. The first being Sheehan and Lieber in 1996, they did an investigation by analysing the frictional forces of a by using nano manipulation methods
to move nanocrystals along a substrate. They observed that the sliding direction of the crystals coincided with the crystal lattice of the substrate and in order to change the direction away from the direction it tended to much more force had to be applied to the crystal. [23] Their researched showed the relation of friction anisotropy to the commensurability of the nanocrystal and substrate surfaces.

In the year 1997 Wong et al conducted experiments on Silicon Carbide (SiC) nanorods and multiwall carbon nanotubes (MWNTs). They used an Atomic Force Microscope to investigate the mechanical properties of these nano-materials. [12]

In the year 2000 Falvo et al. did an experiment on multiwall carbon nanotubes (CNTs) which were nano-manipulated under an AFM microscope on a Highly Oriented Pyrolytic substrate. Their research showed that the CNTs moved smoothly and rotated in plane when under an incommensurate state. The motion is disrupted however and discrete in plane orientations. This is because the CNTs “locks” itself to the surface when it enters a low-energy state. Much more force had to be applied to move the CNT. Their research showed that the sliding motion of CNTs were vastly affected by the transition from an incommensurate to commensurate state. [26]

Following that in the year 2007, Bordag et al investigated the shear stress measurements on Indium Arsenide (InAs) on a SiO$_2$ substrate. [28] Their experiments aimed to investigate the shear stresses between the nanowire and the substrate in the hopes of validating the equation that suggest the lateral frictional force is proportional to the contact area instead of the load force. The method of which they used was to the method of most bent state, where they bent the nanowire on the substrate under an AFM using nano-manipulation technique. They proposed that by measuring the radius of curvature along the wire they were able to identify the friction forces by probing the wire locally. The constraint they had during these experiments was that the wire they had bent was still in the elastic region of deformation else their data would be invalidated. From their experiments, they determined that the nanowires stored elastic energy $U$ and is given by the following formula.

$$U = \frac{EI}{2} \int \frac{1}{R(x)^2} dz$$

Where $E$ is the Young’s Modulus and $l$ is the moment of inertia. Where $\frac{1}{R}$ can be related to the radius of curvature $\kappa$. The equation can then be rearranged to calculate static friction $q_{st}$ and the formula is indicated below.
Further investigation was done an it came to realization that the equation was not accurate as it did not account for the curvature and forces across the wire. This energy conservation model is still currently being used for an approximation of isotropic bodies but is only applicable in specific regions of deformation. [8]

Next in year 2009 Strus et al. presented a new technique as to how the frictional force can be calculated. This technique made use of a program called DataThief and it involved the skeletonizing of the structure for calculation. Skeletonization is a process by which a picture is taken and reduced to a binary image this preserves the main connectivity of the nanowire but excludes other unnecessary regions. [17] Modifying the previous equation, the new equation took the average of five points on the curve. The formula he derived would be:

\[ F_n(s) = -EI \frac{d^2\kappa}{dl^2} e_n \rightarrow q_n^{st} = -EI \frac{d^2\kappa}{dl^2} \]

This equation though largely more accurate produced incredibly high shear stresses and further investigation identified the probable cause to be localized buckling.

Then in 2011, Dorogin et al. furthered his investigation on nanowires, the new model he came up with treated the kinetic frictional force acting on the nano-manipulated beam as a uniformly distributed load (UDL).

Dorogin’s investigations led him to develop the following full equilibrium equations [8]:

\[
\text{Elastic Force} = F_i = \int_{s}^{0} \sigma_{\gamma\gamma} n_{\gamma} dS \\
\text{Momentum} = M_i = \int_{s}^{0} \sigma_{\beta\gamma} n_{\gamma} e_{\alpha\beta \gamma} r_{\alpha} dS
\]

Where \( \sigma_{\beta\gamma} \) represents the stress tensor components, \( r_{\alpha} \) the radial vector, \( n_{\gamma} \) the normal vector and \( e_{\alpha\beta \gamma} \) the anti-symmetric vector.

By using Timoshenko Beam theory and the assumption that the tangential component of friction acting on the nanowire is negligible, he determined the normal and tangential component force of friction along the nanowire to be [17]:

\[ q^{st} = \left( \frac{EI}{2} \right) \kappa^3 \]
\[ F_t = -EI \int_0^l \kappa \frac{d\kappa}{dl} dl = -EI \frac{\kappa^2}{2} \]

\[ q_{st}^n = EI \left( \frac{d^2 \kappa}{dl^2} + \frac{\kappa^3}{2} \right) \]

It is important to note that when using this equation, the model will always be under the assumption that the frictional force \( q_{st} \) needs to be close to the direction of which the nanowire tends to unbend. Additionally, the tangential forces calculated does not affect the bending of the nanowires. [8]

4.3 Why the use of Nanowires?

In the recent years, a lot of effort has been put into the study nanostructures. Nanowires, basically wires that have a thickness of less than one micrometer, have garnered the interest of my researchers due to its high potential in advanced technological applications as they are the foundational building blocks of nano-devices.

Since nanowires are known to have unique properties different from bulk materials, this lead to the investigation of nanowires and its many possible applications. It consists of piezoelectric applications which uses kinetic energy to generate electricity, photodetectors, resonators and including biomedical applications. [17] [19] Subsequently this lead on to the study of friction on a nano-scale (sliding nanostructures over substrates) as friction is one of the major causes of energy losses and also the cause of the breakdown of a structure after long cyclical use due to wear and tear. This study of friction could open up a whole new frontier allowing us to use it to our advantage; this would aid in the design of wall-climbing robots to super adhesive materials. [33] In this field of research nanowires were manipulated with various methods on a substrate under and Atomic Force Microscope. The nanowires have much better flexibility in comparison to bulk material and at a nano-scale the static friction and adhesion between nanowire and is high enough to keep the nanowires in a bent state. The deflections caused by bending the nanowires and its equilibrium state between frictional forces allowed us to analyse the distributed friction between the two surfaces were then used to calculate static friction theoretically and experimentally. The formula used are known as the nanowire bending profile and elastic modulus. [30]

Another reason as to why nanowires are used is because of their integrity and qualities of its structure, it being on a nano-scale, their single-crystalline nature has a very low defect density
and suffers very minimal surface irregularities. This in itself eliminates two main contributors to friction which are ever so present in bulk sized materials. [21]

4.4 Zinc Oxide Nanowires

ZnO nanowires have been gaining popularity over the years compared to the other kinds of nanowires due to their remarkable physical properties. They are low in cost due to its abundance, they are non-toxic (ZnO is commercially used as protective coatings for metals, paint and even sunscreen) and biocompatible therefore much more favourable compared to other nanowires. [6] [24] ZnO nanowires are also tested to have very high fracture strain properties which makes them very suitable for nanoscale sensors or actuators. [1]

4.5 Investigating Properties of Nanowires

There are several methods as to how researchers investigate the properties of nanowires, this is usually a challenge as the sizes of the nanowires are miniscule. Firstly, there is nanoindentation, a method developed in the mid-1970s to measure the hardness of nanomaterials. This method uses a hard tip (usually made of diamond) to make gradually make an indentation on the surface of the material. Once the tip indents the specimen the tip is removed and the area of indentation on the sample can be used to calculate the hardness of the material and it is given by the following equation.

\[ H = \frac{P_{\text{max}}}{A_r} \]

Where \( H \) is the measure of hardness and \( P_{\text{max}} \) is the maximum load exerted by the tip on the test surface and \( A_r \) is the residual indented area. [1]

Another method of analysis would be through the transmission electron microscope (TEM), this method utilizes an oscillating electrostatic field inside the TEM and vibrates the nanowire till resonance is reached. The collected data is then used to plot the phase response of the applied field and then using the amplitude we can find the Young’s modulus of the nanowire to be measured. This method though removing the need to manually manipulate the nanowires as direct contact is not needed, it is not able to measure other important properties like toughness and the fracture strain of the nanowires. [1]

Fracture strain measurements can be done by using piezo-actuators to strain the nanowires axially till fracture occurs. Firstly, the nanowires are separated from each other using ultrasonicification (wires usually come clumped together). Next a silicon chip with a thin layer
of aluminium is attached to the piezo-actuator. A crack was then induced to the silicon chip surface and the nanowires placed across it perpendicular to the crack. The piezo actuator was then used to induce a strain on the nanowires in a focused ion beam chamber, the data was then processed. Using the images captured before and after the fracture the fracture strain of the nanowires can then be estimated. [1]

The young’s modulus of the nanowires can be measured using microelectromechanical (MEMS) system. One of these methods of nano-measurements was to use a transmission electron microscope. This method uses resonances which is induced by an electrical field to calculate the Young’s Modulus of the nanowire and is highly versatile as it works for both insulating or conductive nanowires. [37]

4.6 Past Experiments

Before starting on this thesis there has already been much research done in regards to nanotechnology. In order to further familiarise with the methods that have been developed and used, this section aims to investigate past experiments done on determining the kinetic and static friction between nanowires and substrates.

4.6.1 Characterising Nanoscale Kinetic Friction

H Xie et al. Worked on characterising the nanoscale kinetic friction using force-equilibrium method and energy conservation method via optical manipulation on Silicon Carbide (SiC) nanowires on a Silicon Nitride (SiN) substrate. They found that results from both methods were consistent with each other thus both were valid for characterising kinetic friction on a nanoscale. They also suggested that force-equilibrium method was better for short nanowires and energy conservation method was better for longer nanowires. [16]

4.6.2 Al2O3 Nanowires Experiment

H Xie et al. Worked on calculating the kinetic and static friction of Alumina (Al2O3) nanowires on Silicon (Si) substrate. In this experiment the nanowires were bent into a “hooked” shape and then an analytical model was used to obtain the kinetic friction force. This experiment was conducted based on the initial hypothesis that the elastic energy stored when the nanowire was bent into a “hooked” shape was lost to friction. Their experiments showed that this method was reliable in calculating the kinetic and static frictional forces acting between nanowire and substrate regardless of length and width of the Al2O3 nanowires. [16]
4.6.3 A Comparative Study of Nanowires Bent on a Flat Substrate

In 2014 M. Antsov et al. conducted experiments of ZnO nanowires using four different analytical expressions to determine the static friction generated between nanowires and substrate. They found out that the methods employed by Bordag, Strus and Stan neglected the free ends of the nanowires thus resulting in a nonzero magnitude when calculating total force. This issue was fixed using Dorogin’s method which made used of special polynomials in his calculations.

4.6.4 Nanowires on Different Substrates

In 2015 H.-J. Kim et al. tested oxidized Silicon (Si) nanowires on SiO2 and graphene substrates. Their purpose for these experiments was to primarily to obtain further understanding of nano-scale friction which were the root cause of problems encountered in nano-scale devices. Graphene was selected particularly as it had amazing mechanical properties to act as a protective layer for nano-technological devices. They employed the following equations to calculate the static and kinetic frictions between nanowires and substrates.

\[
\begin{align*}
    f_{\text{kinetic}} &= \frac{8EdL}{L^2} \\
    f_{\text{static}} &= \frac{EI}{2R^3}
\end{align*}
\]

Where E is the Young’s modulus, I is the moment of inertia, D is the diameter and R is the radius of curvature of the nanowire. Their experiments found that graphene had significantly lower friction compared to that of the SiO2 substrate which confirms is suitability to act as a lubricant or protective layer for nano-technological devices. [19]

4.7 Synthesizing ZnO Nanowire

There are two main approaches as to how ZnO nanowires are synthesised. The first method which is a method commonly used is the vapour-liquid-solid method (VLS). This process takes place over a horizontal quartz tube which is placed in a rapid thermal furnace. [31] VLS is a method in which that promotes the growth of one dimensional structures such as nanowires. A catalytic liquid is used and it absorbs the surrounding vapour to supersaturated levels which promotes crystal growth which starts off from nucleated seeds.
Another form of synthesis is by the means of Vapour Trapping Chemical Vapour Deposition method. This method introduces n-type carriers into ZnO wires. [31] The wires made from this method are high quality and single crystalline wires but has a limitation and that these processes have to be undergone with elevated temperatures of approximately 450-900 degrees C.

4.8 Highly Oriented Pyrolytic Graphite (HOPG)

HOPG unlike graphite in its natural state that has plenty of defects on its surfaces, has a very smooth surface. This is due to its molecular structure where the carbon atoms are stacked in parallel layers giving it a very smooth surface on an atomic level. The grade of the HOPG can measure by the mosaic spread angle of HOPG. The higher the mosaic spread angle the higher the quality of HOPG. [27]

Most of the experiments have been done on other substrates which displayed a high level of asperity which has a direct relation to kinetic and static friction. The start of experimenting on HOPG which has a very low asperity level would hopefully shed more light as to how surface asperity affects friction.

![Figure 5: Graphite Structure (Ted Pella)](image-url)
5 Methodology

When doing experiments on such a small scale, it is of utmost importance to follow a strict set of procedures so as to not compromise on the integrity of the results obtained. This section aims to cover the equipment, processes and data processing methods used when carrying out the experiments throughout the duration of the course.

5.1 Equipment

In order for the experiments to be carried out, advanced nano-technological equipment had to be used. Listed below are the equipment used to carry out the experiments.

1. Polytec MSA 500 Micro System Analyser:
   This equipment is used for image processing and used to view the manipulation of nanowires. Attached to it were three objective lens which provided a 10x, 50x and 100x magnification.

2. Tungsten tip nano-manipulator attached to adjustable stand:
   The thick nano-manipulators are used to transfer nanowires from one substrate to another whereas the thin nano-manipulators are used for sliding the nanowires across to substrate. These manipulators are attached to an adjustable stand via blue tack. This adjustable stand is rigid and stable therefore allowing the user to move the nano-manipulator extremely precisely (nm range of adjustment) in the X-Y-Z plane.
3. **SEM Sample Holder:**
   
   This is where the HOPG substrate is placed on when conducting experiments.

4. **Carbon tape:**
   
   Carbon tape a double side adhesive is used to attach the HOPG substrate to SEM sample holder so as to prevent it from siding during experiments. This tape enhances the conductivity and allows better SEM quality images.

5. **Thermoline – Ultrasonic cleaner set (Model: WUC-A02H):**
   
   This ultrasonic cleaner set is used to clean the nano-manipulators and substrates before experiments are conducted. It uses ultrasound and water to remove any objects (usually too small for the naked eye) from the surface of the substrate and the tip of the tungsten nano-manipulator.

6. **Scanning Electron Microscope**
   
   This equipment uses a strong focus beam of high-energy electrons, hence the name, to produce a variety of signals from the surface of the specimen involved. These signals are able to show the texture or crystalline structure and orientation of the specimen. The range of magnification of an SEM is approximately 20x to 30,000x and has a spatial resolution of 50 to 100 nano-meters. [34]

7. **Highly Oriented Pyrolytic Graphite Substrate**
   
   HOPG is the material where by the nanowires will be placed on and where the experiments will be conducted. This substrate is obtained TED PELLA (Product 626-1) measures 10mm x 10mm x 2mm.

### 5.2 Preparation for experiment

Before the experiments were carried out the following task were accomplished to ensure the integrity of the results obtained through the experiments. The methods employed will aid in the study of friction between ZnO nanowires and HOPG substrate. Listed below are the steps used for preparation.

1. The first step would be to attach the HOPG substrate to the SEM holder. This is done so using carbon tape. This tape ensures that the substrate does not move when the experiment is being conducted. The tape, being conductive also helps generate a better image when the substrate and nanowires are places below an SEM.
2. The surface of the substrate needs to be clean. Any impurities attached to the surface of the substrate will hinder the experiments. Two different methods were employed in order to obtain a clean substrate surface. The first method was to flush the surface with Ethanol (C2H5OH) or de-ionised water. The next method would be to use a brand-new piece of tape to remove the initial layer of substrate surface. This exposes an entirely new surface with minimal impurities. This can be observed in Figure 8, (a) shows the scotch tape being attached to the HOPG substrate surface and (c) shows the initial surface of the substrate being removed exposing a brand-new surface for experimentation.

![Figure 8](image)

**Figure 8:** (A) Attaching of scotch tape to substrate, (B) Process of removing initial layer, (C) Initial layer of substrate removed
3. The tungsten tip nano-manipulator will also have to be cleaned this is done so by flushing the tip using Ethanol and submerging it into water contained in the Ultrasonic cleaner set. The vibrations caused by the cleaner set to the water will knock off any unwanted foreign objects attached to the tip of the nano-manipulator.

4. The nano-manipulator and SEM holder with substrate is then attached to separate adjustable stand.

5. The following step would be the transferring of nanowires to the HOPG substrate. First, the nano-wires are transferred from their original location to a silicon substrate. This is done so by flipping the original plate surface and placing it on top of the silicon substrate surface. This causes a large amount of ZnO nanowires to drop from the original surface to the Silicon substrate surface. From SEM image with a x1,000 magnification Figure 9, we can see that the contents transferred consist of nanowires and nanobelts. Nanobelts were not used for the experiments.

![Figure 9: Nanowires and Nanobelts](image)

6. After the transfer, Dr Wang, using the Micro System analyser nanowire are carefully selected and then picked up via the nano-manipulator and transferred to the HOPG substrate. This process can be seen in Figure 10. This process is repeated till a few nanowires are transferred to the HOPG substrate surface.
7. When the transfer is completed, the process of manipulation of nanowires can then begin. The current nano-manipulator was not swapped out for a thinner one as it was sufficient enough for the manipulation of nanowires. The two main methods of manipulation will be discussed in section 5.3 of the report.

8. After the manipulation, the substrate and nanowires will then be placed under a Scanning Electron Microscope to determine the shape of the cross section (Rectangular or Hexagonal). Dimensions are also obtained from the images and used to calculate the moment of inertia of the nanowires which are required when calculating kinetic and static frictional forces. We can see the two different cross-sections of nanowires in Figure 11, Figure 12 and 13.
This section aims to cover the methods used to obtain the data required to calculate the kinetic and static frictional forces on the nanowires. The first method employed is the force equilibrium model, this method will be used to calculate the kinetic friction of the nanowire as it is pushed across the HOPG substrate. The second method would be to use the energy conservation model,
this method will be used to calculate the static friction of the nanowire in when it is in its most bended state on the HOPG substrate. These methods were employed in past experiments by Wang et al. and H Xie et al. [16] [33]

5.3.1 Force Equilibrium Model

With this model a force is applied at midpoint to the ZnO nanowire on the HOPG substrate, this force causes the nanowire to slide across the substrate as shown in Figure 14. When sliding across the substrate it is assumed that the kinetic frictional force is uniformly distributed over the entire length of the nanowire. The driving force of the nano-manipulator tip acting on the nanowire is equivalent to the kinetic frictional force. Hence the equation $F = 2f \times L$ where $f$ represents the kinetic friction, $L$ the half-length of the nanowire and $F$ the force exerted by the nano-manipulator in the nanowire. This model can be simulated as a fixed cantilever beam in bending with a uniform load applied to it, this can be seen in Figure 14. From this we can consider the following equation. [30]

$$EI \frac{d^2 \theta}{dl^2} = -fl\cos\theta$$

With $E$ as the Young’s modulus of the nanowire, $I$ as the second moment of area, $l$ is the arc length of the nanowire and $\theta$ is the angle between of a tangent line and the nanowire at any given point. The formula for second moments of area of a rectangular and hexagonal cross-section are as follows.

$$I_{\text{rectangle}} = \frac{b^3h}{12}$$

$$I_{\text{hexagon}} = \frac{5\sqrt{3}}{16}a^4$$
Since the nanowire can be modelled as a fixed cantilever beam with a uniformly distributed load short nanowires with small deflections can be modelled using the following formula. \[ 33 \]

\[
y(x) = \frac{fx^2}{24EI} (x^2 + 4Lx + 6L^2)
\]

Hence the kinetic friction can be found using the formula

\[
f = \frac{8EI D}{L^4}
\]

### 5.3.2 Energy Conservation Model

This model is used to calculate the static friction between the nanowire and the substrate. After removal of the force acting on the nanowire, the elastic restoration forces of the nanowire will be inclined to return the nanowire to its original shape. This restoration force however is met by the static friction between the nanowire and the substrate. This forces will the equalize and the nanowire, still bent, will be in its most bended state. The static friction can be then be calculated using the maximum radius of curvature with the following formula which were derived by Bordag et al, Strus et al and Dorogin et al. \[ 19 \] \[ 30 \]

<table>
<thead>
<tr>
<th>Authors</th>
<th>Analytical Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bordag et al.</td>
<td>( f_n^{st} = \left( \frac{E I}{2} \kappa^3 \right) )</td>
</tr>
<tr>
<td>Strus et al.</td>
<td>( f_n^{st} = -EI \left( \frac{d^2 \kappa}{d l^2} \right) )</td>
</tr>
<tr>
<td>Dorogin et al.</td>
<td>( f_n^{st} = EI \left( \frac{d^2 \kappa}{d l^2} + \frac{\kappa^3}{2} \right) )</td>
</tr>
</tbody>
</table>
Where $\kappa$ is $1/R$ and $R$ is the radius of curvature which can be derived using the following formula.

$$R(x) = \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^\frac{3}{2} \left| \frac{d^2y}{dx^2} \right|$$

The higher orders of $\kappa$ will be calculated with the aid of Matlab and will be further discussed in the next section 5.4 Data Processing.

### 5.4 Data Processing and Results

The aim of this section is to cover the methods used to extract data from the images collected and how the data was used to calculate the kinetic and static friction between nanowires and substrate.

#### 5.4.1 Calculation of Kinetic Friction

Before we start calculating the kinetic friction between ZnO nanowires and HOPG substrate, the following properties have to be identified. $L$ the length of the nanowire, $b$ the width of the nanowire and $h$ the height for rectangular cross-section nanowires and $a$ for hexagonal cross section nanowires. With these properties, we can calculate the second moment of inertia of the nanowires with the formula:

$$f = \frac{8EI\theta}{L^4}$$
Sample set 1 will be used to explain the process of obtaining the data required. From the Figure 16 we can see the before and after stages of manipulation of sample set 1. We can see that the small pieces of broken nanowire all came from the same original long piece. With this information, we can view the image generated to determine the geometry and dimensions of the nanowire. The SEM image can be seen in Figure 17 and 18.
The distance $D$ is measured using image resolution. For a standard size 100x zoom image captured by the Micro System Analyser 1392(L) x 1040(W) and the blown-up image size is 87.5μm (L) x 65.4 (μm) using these indications we can determine the end point coordinates of the bent nanowire and line tangent to the curve. A perpendicular is line from the tangent point to the end point of the bent nanowire is drawn. The length of the line will be the deflection $D$ of the nanowire.

SEM was used to determine the cross-sectional dimensions of the nanowires. With the help of Dr Wang, close of SEM images of the nanowires were obtained. From the Figure 19 below we can see that the nanowires from sample set 1 have a cross-section of a hexagon (Top view). Using the formula:

$$I_{\text{hexagon}} = \frac{5\sqrt{3}}{16} \alpha^4$$

The second moment of area for a hexagon cross section can be determined. It is also important to note that the formula used above is only valid for a perfect hexagon. Though the cross-section of the nanowires were nowhere near perfect as there are bound to be deviations and faults, this equation is still used as it is the most reasonable and accurate representation for the cross-section of the nanowires.

![Figure 19: SEM Image Sample Set 1](image-url)
The data collected was then tabulated and exported to excel for ease of calculation and can be found in the table below. The nanowires have been given a four-character length alphanumerical serial code to reduce confusion. The first two characters determine the Folder number (eg. F1) the second number determines which nanowire we are working on and the final letter indicates if it was a kinetic of static friction test. So F11K would mean folder 1 nanowire no.1 with kinetic friction test. All the images (MSA and SEM) are also indicated as such and can be found in the appendix attached at the end of the report. The generalized map with all tested nanowire locations is also attached at the back of the thesis. Of all the tested wires, there was only one with a rectangular cross section F42K.

The selection process of which nanowires would be most suitable for calculations, would be that the nanowires had to have at least 3 similar frames that were captured during the nano-manipulation process. This can be seen in the images below accordingly in Figure 20. The three frames look very similar but if observed closely enough it is possible to see slight movement at the right end of the nanowire.

![Figure 20: Nano-manipulation of 3 separate frames of F11K](image)

An example of the calculation for no. 1 nanowire F11K is calculated below:

\[ f = \frac{8EID}{L^4} = \frac{8 \times 140 \times 10^9 \times 1.3 \times 10^{-29} \times 0.759531 \times 10^{-6}}{(2.5 \times 10^{-6})^4} = 0.28303 \, \text{nN} \, \text{nm} \]

The shear stress acting on the nanowire can be calculated by:

\[ P_t = \frac{f}{\text{width of contact area}} = \frac{0.28303}{70 \times 10^{-9}} = 4.04329 \, \text{MPa} \]

For the ease of calculation excel was used and the summarized results can be seen below in Table 1. The full excel spread sheet can be found in the Appendix B.
<table>
<thead>
<tr>
<th>No.</th>
<th>Nanowire</th>
<th>$L$ (m)</th>
<th>$a$ (nm)</th>
<th>$I$ (mm$^4$)</th>
<th>$D$ (um)</th>
<th>$F$ (nN/nm)</th>
<th>Shear (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F11K</td>
<td>2.50E-06</td>
<td>70</td>
<td>1.30E-29</td>
<td>0.759531</td>
<td>0.28303</td>
<td>4.04329</td>
</tr>
<tr>
<td>2</td>
<td>F12K</td>
<td>3.50E-06</td>
<td>70</td>
<td>1.30E-29</td>
<td>0.819584</td>
<td>0.07950</td>
<td>1.13572</td>
</tr>
<tr>
<td>3</td>
<td>F21K</td>
<td>3.1E-06</td>
<td>50</td>
<td>3.38E-30</td>
<td>1.57148</td>
<td>0.06442</td>
<td>1.28952</td>
</tr>
<tr>
<td>4</td>
<td>F22K</td>
<td>2.20E-06</td>
<td>50</td>
<td>3.38E-30</td>
<td>0.56223</td>
<td>0.09094</td>
<td>1.81882</td>
</tr>
<tr>
<td>5</td>
<td>F41K</td>
<td>1.80E-06</td>
<td>60</td>
<td>7.02E-30</td>
<td>0.490946</td>
<td>0.36746</td>
<td>6.12426</td>
</tr>
<tr>
<td>6</td>
<td>F42K(R)</td>
<td>3.10E-06</td>
<td>60</td>
<td>5.33E-31</td>
<td>0.893397</td>
<td>0.07601</td>
<td>1.26680</td>
</tr>
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<td>7</td>
<td>F51K</td>
<td>3.75E-06</td>
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<td>3.38E-30</td>
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<td>0.02992</td>
<td>0.59835</td>
</tr>
<tr>
<td>8</td>
<td>F61K</td>
<td>7.00E-06</td>
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<td>1.39E-30</td>
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<td>0.00149</td>
<td>0.03735</td>
</tr>
<tr>
<td>9</td>
<td>F62K</td>
<td>3.39E-06</td>
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<td>1.39E-30</td>
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<td>0.01258</td>
<td>0.31449</td>
</tr>
<tr>
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<td>1.39E-30</td>
<td>0.800067</td>
<td>0.05112</td>
<td>1.27806</td>
</tr>
</tbody>
</table>

**Table 1: Kinetic Friction Calculations**

The results tabulated in Table 1 show a slight variation in data. Nanowires 2, 3, 4, 6, 10 showed that the kinetic friction and frictional shear forces are in close approximation to one another and nanowires 1, 5, 7, 8, 9 were either magnitudes higher or lower. Investigation was done on these wires which had different variation of values.

It was found that just a frame after the initial three frames (the 4th frame) for nanowire 1 and 8, it was observed that the nanowires snapped. This can be observed in Figure 35 and 47 in Appendix A. The immediate snapping of nanowires in the next frame would mean that there could already have been a fracture or crack propagating through the center of the nanowire as it was being manipulated. This fault in the nanowire is highly likely to be the cause in the large variation of kinetic friction and frictional shear stress values.

As for the other nanowires, it was observed that though the curve shape was maintained there were slight skips at both ends of the nanowire. The sudden skips in frame is due to the human reaction lag time when capturing the images of the nanowire during manipulation, this slight variation of data is the most probable cause of the inaccuracies in the results obtained.

The average values of nanowires 2, 3, 4, 6 and 10 are 0.0725 nN/nm and 1.378 MPa. Thought the frictional shear stress is lower, the kinetic friction values are within range of that of Boris Polyakov et al. who did a similar experiment of ZnO on HOPG obtaining an average range of 0.04-0.5 nN/nm and 2.75 MPa. [8] The shear stress values are also comparatively lower than that of the experiments done by Wang et al. on Al2O3 nanowires on Si and SiN substrates.
Wang et al. obtained a frictional shear stress of 2MPa. The difference in data is highly likely due to the difference in nanowire and substrate material, and on top of that their nanowires had a much larger width of approximately 133nm whereas the ones used for this thesis were approximately 80nm. [33]

5.4.2 Calculation of Static Friction

The following program called WebPlotDigitizer was used to extract the coordinates of the nanowire. Images of the nanowire were imported into the program and the reference axis was set and aligned.

![Align X-Y Axes](image)

**FIGURE 21: ALIGN AXES WITH WEBPLOTDIGITIZER**

The x-axis was set from 0 to 0.0000875m and the y-axis 0 to 0.0000654m which is the exact length in meters of the image taken under the Micro System Analyser.

![X and Y Axes Calibration](image)

**FIGURE 22: X-Y AXES CALIBRATION**
The points that were marked will then be appointed coordinates which will be used to plot the curve in order to obtain the curve equation of the nanowire.

\[ y(x) = ax^6 + bx^5 + cx^4 + xd^3 + ex^2 + fx + g \]

Initially a 4\textsuperscript{th} order polynomial curve equation was used but for better accuracy a 6\textsuperscript{th} order was used instead.

Next, the first and second derivatives of \( y \) were found.

\[ y'(x) = 6ax^5 + 5bx^4 + 4cx^3 + 3xd^2 + 2ex + f \]

\[ y''(x) = 30ax^4 + 20x^3 + 12cx^2 + 6xd + 2e \]

Both \( y'' \) and \( y' \) were plugged into the equation below to determine the radius of curvature.

\[
R(x) = \frac{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{\frac{3}{2}}}{\left|\frac{d^2y}{dx^2}\right|} = \frac{\left[1 + (y'(x))^2\right]^{\frac{3}{2}}}{|y''(x)|}
\]
The radius of curvature was then used to calculate the static friction of Bordag et al.’s analytical expression.

\[ f_{n, Bordag}^{st} = \left( \frac{EI}{2} \kappa^3 \right) = f_n^{st} = \left( \frac{EI}{2} \left( \frac{1}{R(x)} \right)^3 \right) \]

After determining the radius of curvature for the nanowires and with the knowledge that \( \kappa = \frac{1}{R(x)} \), Matlab was then used to help derive \( \frac{d^2 \kappa}{dl^2} \) which will be used for Dorogin et al.’s and Strus et al.’s analytical expression.

\[ f_{n, Strus}^{st} = -EI \left( \frac{d^2 \kappa}{dl^2} \right) \]

\[ f_{n, Dorogin}^{st} = -EI \left( \frac{d^2 \kappa}{dl^2} + \frac{\kappa^3}{2} \right) \]

Using Trigonometry (Figure 21) \( dl = ds = \sqrt{dx^2 + dy^2} \)

\[ l'(x) = \frac{dl}{dx} = \sqrt{1 + \left( \frac{dy}{dx} \right)^2} \]

Where \( \frac{dy}{dx} \) is the first derivative of the 6th order polynomial obtained before, using Matlab’s polyfit function.

\[ \text{Therefore, } \frac{d\kappa}{dl} = \frac{d\kappa}{dx} \times \frac{dx}{dl} \]
In order to obtain a higher order derivative of \( \frac{d\kappa}{dl} \) chain rule, must be applied to get \( \frac{d^2\kappa}{dl^2} \)

\[
\frac{d^2\kappa}{dl^2} = \frac{d}{dl} \left( \frac{d\kappa}{dl} \right)
\]

\[
\frac{d^2\kappa}{dl^2} = \frac{d}{dl} \left( \frac{d\kappa}{dx} \cdot \frac{dx}{dl} \right)
\]

Hence after Chain Rule, \( \frac{d^2\kappa}{dl^2} = \frac{d^2\kappa}{dx^2} + \left( \frac{dx}{dl} \right)^2 \cdot \frac{d^2\kappa}{dx^2} \)

The results were calculated and tabulated using MatLab and the code used is attached at the end of the report in Appendix C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nanowire</th>
<th>( B ) (nm)</th>
<th>( H ) (nm)</th>
<th>( A ) (nm)</th>
<th>( I ) (mm(^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 F11S</td>
<td>NA</td>
<td>NA</td>
<td>70</td>
<td>4.0017e-29</td>
</tr>
<tr>
<td>2</td>
<td>2 F12S</td>
<td>NA</td>
<td>NA</td>
<td>70</td>
<td>4.0017e-29</td>
</tr>
<tr>
<td>3</td>
<td>4 F31S</td>
<td>NA</td>
<td>NA</td>
<td>50</td>
<td>1.0417e-29</td>
</tr>
<tr>
<td>4</td>
<td>5 F41S</td>
<td>NA</td>
<td>NA</td>
<td>60</td>
<td>2.1600e-29</td>
</tr>
<tr>
<td>5</td>
<td>6 F42S</td>
<td>100</td>
<td>40</td>
<td>NA</td>
<td>3.3333e-30</td>
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<td>6</td>
<td>7 F51S</td>
<td>NA</td>
<td>NA</td>
<td>70</td>
<td>4.0017e-29</td>
</tr>
<tr>
<td>7</td>
<td>8 F61S</td>
<td>NA</td>
<td>NA</td>
<td>70</td>
<td>4.0017e-29</td>
</tr>
<tr>
<td>8</td>
<td>9 F62S</td>
<td>NA</td>
<td>NA</td>
<td>70</td>
<td>4.0017e-29</td>
</tr>
</tbody>
</table>

**Table 2: Second Moment of Area Calculations**

Following the calculations of the second moment of area, using Matlab the skeletonized version of the nanowire is plotted. The \( x \) coordinate of the minimum value of \( y \) was taken to be the point of inspection for the maximum static frictional force. This can be seen in the plot below in Figure 24.
The value of the input variable $x$ was then used to calculate the static friction using Bordag, Strus and Dorogin et al.’s three different analytical expressions. The static frictional force acting throughout the entire length of the nanowire was also calculated and plotted below as seen in Figure 25. It is also observable how much Bordag’s analytical expression underestimates the static friction.

The calculated values of static friction were tabulated below as seen in Table 3 for easy comparison. The actual captured images of the nanowires in their most bended state can be found in the Appendix A and are labelled accordingly.
<table>
<thead>
<tr>
<th>No.</th>
<th>Nanowire</th>
<th>$F_{Bordag}$ (nN/nm)</th>
<th>$T_w_{Bordag}$ (MPa)</th>
<th>$F_{Strus}$ (nN/nm)</th>
<th>$T_w_{Strus}$ (MPa)</th>
<th>$F_{Dorogin}$ (nN/nm)</th>
<th>$T_w_{Dorogin}$ (MPa)</th>
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<tbody>
<tr>
<td>1</td>
<td>F11S</td>
<td>0.0245</td>
<td>0.35</td>
<td>1.0271</td>
<td>14.67</td>
<td>1.0026</td>
<td>14.32</td>
</tr>
<tr>
<td>2</td>
<td>F12S</td>
<td>0.0350</td>
<td>0.5</td>
<td>0.3075</td>
<td>4.39</td>
<td>0.2725</td>
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</tr>
<tr>
<td>3</td>
<td>F31S</td>
<td>0.0023</td>
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<td>0.2003</td>
<td>4.01</td>
<td>0.1981</td>
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<tr>
<td>4</td>
<td>F41S</td>
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<td>1.7743</td>
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<td>0.4074</td>
<td>5.82</td>
<td>0.3876</td>
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</tr>
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<td>F61S</td>
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<td>0.1324</td>
<td>1.89</td>
<td>0.1299</td>
<td>1.86</td>
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<tr>
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<td>F62S</td>
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<td>0.22</td>
<td>0.3738</td>
<td>5.34</td>
<td>0.3586</td>
<td>5.12</td>
</tr>
</tbody>
</table>

**TABLE 3: STATIC FRICTION CALCULATIONS**

From the results below for all analytical expressions the values are in close approximation to each other than nanowires 1 and 4 for Strus and Dorogin models. The average values for nanowires 2, 3, 5, 6, 7 and 8 for each expression are:

$$F_{Bordag} = 0.016443 \text{ nN/nm}$$

$$F_{Strus} = 0.288217 \text{ nN/nm}$$

$$F_{Dorogin} = 0.271783 \text{ nN/nm}$$

The values are in close relation to that of the values obtained by Mikk Antsov when he investigated the static friction between ZnO nanowires on a Silicon substrate. The slight deviation of data is most likely due to the different dimensions of nanowires he used, they ranged from 10 to 20µm and 60 to 200nm in diameter. [30]

It is also observed that the calculations followed the same trend with Bordag severely underestimating the friction forces and the values obtained using Strus and Dorogin’s analytical model are in close approximation.

The reasons as to which analytical model is most accurate is still not fully understood and more research is still currently on going but it would be out of scope for this thesis to further investigate.
6 Discussion

In this section, we aim to discuss the possible causes of the variation in data in comparison to that of the data obtained by other experiments.

6.1 Van der Waals Forces

One of the possible explanations for the variance in data could be the effect of van der Waals forces acting between the nanowire and substrate. Though widely known to have the weakest forces when it comes to intermolecular reactions, these forces play a significant role on a nano-scale. A post grad student Vincent Lenji, from the University of Arizona, said that as manufacture components become smaller and smaller, van der Waals forces will start to become more and more dominant. [5]

Nanowires being so small in size would never-the-less be one of the forces acting between nanowires and substrates. This forces however is not taken into account when using the analytical expressions when calculating the kinetic and static friction of the ZnO nanowires on the HOPG substrate.

Thus, much more research has to be done to study the intermolecular forces and how much influence do they actually have on the kinetic and static friction of nanowires.

6.2 Third Body Effect

The third body effect is a result of mechanical transfer of material which acts like lubrication and is caused by dry friction. This was a concept that Maurice Godet introduced in the mid 70’s. [10] The fundamentals of wear can be classified into three different stages depending on the behaviour of debris between surfaces according to Jean Denape.

1. The first stage initiates when particles detach from the surface of the bodies in contact due to abrasion, adhesion or delamination.
2. The second stage is when the said particles, not being able to escape, are trapped between the two surfaces within the contact zone.
3. The final stage is when the debris finally escapes the contact zone and the surfaces comes in contact once again and the cycle repeats.

The three stages are illustrated in the pictures as seen in Figure 26.
These third body effects might also be a cause in the variance in the static and kinetic friction forces calculated. Should there be wear and tear between nanowire and substrate surface these third body particles could have resulted in a higher or lower static or kinetic frictional value. The nanowires being so small would result in even smaller debris, this third body effect was not taken into account for using the analytical expressions as it was impossible at the time during the experiments to account for such effects.

6.3 Unusual Occurrence Observed

During one of the experiments with Dr. Wang, an unusual occurrence was observed. This section will explain in detail what actually happened and will also provide a possible explanation of this occurrence.

Throughout the experiments, nano-manipulation was conducted to test the kinetic and static friction of the nanowires. In order to test the kinetic friction of the ZnO wires on a HOPG substrate the nanowires were pushed across the substrate with a nano-manipulator until the elastic restoration forces overcame the kinetic frictional forces by snapping back into shape or snapping into two. However, for the static friction experiment, Dr Wang would attempt to leave the nanowire in its most bended state where the static friction forces and elastic restoration forces were in equilibrium.

This can be observed in the diagram below where the nano-manipulator (initial force acting on nanowire) is removed. In this most bended state the Energy-conservation model was used to calculate the static friction between nanowire and substrate.
After the test, the nanowires were then sent to be place under a SEM for further inspection to determine the type of cross-section and the dimensions of the cross-section. There was some time before the SEM scanning took place after the actual experiment. It was observed that the nanowires in their most bended state were slowly but surely returning to their original shape. This can be observed from the images below, that particular piece of nanowire was much closer to its original shape compared to before.

More research was done to investigate the cause of this occurrence. It was found that in 2015 a handful of researchers from North Carolina State University and Brown University also encountered this occurrence whereby their nanowires which were bent also began to slowly return to their original shape. They identified the cause as one of the properties called anelasticity. [35] One of their researchers quoted that anelasticity is present in all materials to a certain degree but it is negligible and unobservable at a macroscopic level. Nanowires being so small are greatly affected by this property. [35]
They carried out an experiment on a bent nanowire and took images at different intervals ranging from half a second up to 20 minutes. The image below shows one of the experiments conducted with the top left image showing just before release and bottom right image showing the state of the nanowire 20 minutes after release.

![Image of nanowire experiments](image_url)

**Figure 30: Experiment conducted by NC State University [35]**

Their explanation was that when the nanowires were bent, the atomic bonds between atoms were stretched to accommodate to the bending caused by the applied force. However, on a nanoscale the bending causes so much stretching that the atoms actually move/diffuse from the area that undergoes compression to the area that experiences tension. On a macroscale, the atoms of a bent object would almost snap back instantaneously however on a microscale the atoms that were out of place actually had to take some time before returning to its original position. This time lag is the major characteristic of anelasticity. They mention that nanowires (material of nanowires was not mentioned) with a diameter of approximately 50 nano-meters can take as long as 30 mins to return to about 20 percent of their original shape and that Zinc Oxide nanowires exhibited the largest anelastic behaviour. [35]

A study conducted by Huaping et al. also concluded that the magnitude of anelasticity is highly dependent on the diameter metal nanowires as thicker surface amorphous layer would result in a higher driving force compared to that of a thinner one. [18]
7 Error Analysis

The largest room for error would be the measuring of the deflection of and dimensions of the nanowire. For the deflections, pixel distances would be the contribution. The image generated by the micro system analyser is 1392 pixels wide which is approximately $87.5\mu m$ in actual length. This would mean one pixel is roughly 62.8 nano-meters wide being off by one pixel on a nanoscale would cause a significant variation from the original value. However, this cannot be avoided due to the technological limitations and the image captured is already at the highest resolution available. Another contribution would be the measurement of the height of the nanowires, the images captured were not able to show the exact cross-sectional area of the nanowire hence when calculating the second moment of area some error would be present, though it would not be very significant as the nanowires are bending sideways.

Another reason could be due to the imperfect surfaces of the substrates. Defects such as cracked, scratched or uneven layers of HOPG substrate surface would affect the kinetic and static friction between nanowires and substrate. A sever image of layering damage can be seen in the image below from Figure 31. This is caused during the initial preparation phase when the top few layers of HOPG is remove with tape to reveal a clear new surface for experimentation.

![Figure 31: Defective Area on HOPG Substrate](image)

Other forms of contribution of error could be defects in the nanowires like cracks and inconsistent cross-sectional area could also affect results. Cracks are sometimes observable under the Micro System Analyser as the reflect light differently, an unusual light or dark spot seen under the MSA could mean that there are defects present on the nanowire. Observations of these defects are much more prominent on the SEM as show in the Figure 32 and Figure 33.
Microscopic dirt attached to the nano-manipulator tip, nanowire or substrate surface could also have significant impact on results.
8 Future Work

The experiments carried out to date has managed to shed some light on the effects kinetic and static friction have on nanowires. Much more research, experimentation and investigation has to be done to further understand the tribology of nanowires.

During the experimentation two kinds of methods were used to determine the type of cross-section and the cross-sectional dimensions of the nanowires. Firstly, was the use of Atomic Force, this method is employed when measuring wires on a substrate that cannot be detected by a Scanning Electron Microscopy. This method makes use of a scanning probe which slides across the substrate surfaces and moves up when the probe comes in contact with an object or irregularity on the surface of the substrate. Though accurate this method has its limitations due the shape of the probe tip. There will always be areas unreachable due to the geometry of the AFM tip. A crude illustration of why it is not entirely accurate can be seen in the image below.

The next method of accessing the geometry of the cross-section and its dimensions would be via a Scanning Electron Microscope. This provides an extremely close up look at the nanowire. Though having a close up look, the images are usually at an angle as it is extremely difficult to position the microscope to obtain a perfect picture of the nanowire’s cross-section. Therefore, there are some difficulties when obtain the height of the nanowire.

Though reasonably accurate there is room for improvement as to how these dimensions can be obtained. A small miss measurement could result in a large variance in data considering the test objects are extremely small.

As for the calculation of static and kinetic friction, different substrates and types of nanowires could also be investigated to determine how material properties affect them in general.
9 Conclusion

The investigation of the friction of Zinc Oxide nanowires on a Highly Oriented Pyrolytic Graphite surfaces is presented. The main goals of obtaining the kinetic, static friction between nanowire and substrate were completed by implementing analytical expressions from past literature. Force equilibrium method was used to calculate the kinetic friction and three different energy conservation models were used to calculate the static friction. Throughout the experiments it was assumed that all ZnO nanowires had a Young’s modulus of 140GPa.

The average kinetic friction calculated for ZnO nanowires is approximately 0.07 nN/nm which is in close relation to that of the experiments done by Boris Polyakov et al. of ZnO nanowires on HOPG substrate.

The average static friction calculated for ZnO nanowires is approximately 0.016 nN/nm for Bordag, 0.288 nN/nm for Strus and 0.272 for Dorogin’s analytical expressions. The values are pretty close to the values obtained by Mikk Antsov when he did a comparative study of ZnO wires on Silicon substrate. The variations in data is most likely due to the different dimensions of nanowires used.

Overall this was a successful investigation and it laid out the ground work for future investigations. This investigation proved to be a very good learning experience and as always there is room for improvement.

10 Recommendations

In regards to the data obtained throughout the thesis projects, some recommendations as to how to further obtain more accurate results include.

- When calculating the static friction of the nanowires, instead of using the immediate image of its most bended state, allow some time for the effects anelasticity to take place before measuring its most bended state.
- Instead of capturing images manually frame by frame, use a video recording software to record the entire process of the nano-manipulation. The speed of a human capturing images is roughly 1-3 frames per second where as one done by video recording could go up to as high as 30-60 frames per second.
References


Appendix A – Set 1

Figure 35: F11K Frames 1 to 4

Figure 36: F12K Frames 1 to 3
Figure 37: F11S

Figure 38: F12S

Figure 39: F1 Overall View and SEM
Appendix A – Set 2

Figure 40: F21K Frames 1 to 3

Figure 41: F22K Frames 1 to 3
Figure 42: F31S

Figure 43: F2 and F3 overall view with SEM
Appendix A – Set 3

Figure 44: F41K Frames 1 to 3

Figure 45: F42K Frames 1 to 3
Figure 46: F51K Frames 1 to 3

Figure 47: F61K Frames 1 to 4
Figure 48: F62K Frames 1 to 3

Figure 49: F63K Frames 1 to 3
Figure 53: F61S

Figure 54: F62S

Figure 55: F4, F5, F6 Overall View with SEM
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**Figure 56: Excel Spreadsheet for Kinetic Friction Calculation**
Appendix C

clc
clear all
close all
imtool close all

%% Importing from excel spreadsheet
P = xlsread('F12S.xlsx'); % Change accordingly
a1 = P(:,1); % Reads first column of excel
b1 = P(:,2); % Reads second column of excel

coefficient = polyfit(a1,b1,6); % Obtains 6th order polynomial coefficients
a2 = linspace(min(a1),max(a1),500);
b2 = polyval(coefficient,a2);

plot(a2,b2,'Linewidth',3);
xlabel('x (m)');
ylabel('y (m)');

%% Calculations
syms x
coe = coefficient; % Reassign coefficients

% Generation of the 6th order polynomial
y(x) = (coe(1))*x^6 + (coe(2))*x^5 + (coe(3))*x^4 + ...
     (coe(4))*x^3 + (coe(5))*x^2 + (coe(6))*x + coe(7);

dy(x) = diff(y,x); % First Derivative of y
ddy(x) = diff(dy,x); % Second Derivative of y

R(x) = ((1+((dy)^2))^(3/2))/(abs(ddy)); % Calculate of Radius of Curvature

k = 1/R;

dk = diff(k,x); % dk/dx
ddk = diff(dk,x); % d2k/dx^2
dl = sqrt(1+(dy)^2); % dl/dx
ddl = diff(dl,x); % d2l/dx^2

% Chain rule is used to obtain higher order derivative of dk/dl
ddkdll = (ddk*((1/dl)^2)) + (dk*(1/ddl)); % d2k/dl^2

x = 0.0000423; % Point of inspection x coordinate
  % Switching the number to a2 will cause the code to calculate using the analytical expressions across the entire nanowire.

d2kdll2 = eval(ddkdll); % Evaluating using x coordinate d2k/dl2
ROC = eval(R); % Evaluating using x coordinate radius of curvature
k1 = eval(k); % Evaluating using x coordinate kappa

%% Variables
E = 140e9; % Young's modulus of ZnO nanowire

% Comment and Uncomment to calculate second moment of area depending on % cross sectional area of tested nanowire
Rectangular Cross-Section

% b = 100e-9;        % Width
% h = 40e-9;         % Height
% I = (b*b*b*h)/12   % Second Moment of Area

Hexagonal Cross-Section

a = 70e-9;
I = ((5*sqrt(16))/12)*a^4; % Second Moment of Area

Analytical Expressions used to calculate Static Friction
Fst_bordag = ((E*I)/2)*k1.^3 % by Bordag et al.
Fst_strus = -E*I*d2kdl2 % by Strus et al.
Fst_dorogin = -E*I*(d2kdl2 + ((k1.^3)/2)) % by Dorogin et al.

Plotting Static Friction Across Entire Nanowire length
plot(a2,Fst_bordag,'Linewidth',2)
hold on
plot(a2,Fst_strus,'Linewidth',2)
hold on
plot(a2,Fst_dorogin,'Linewidth',2)
hold off
xlabel('length (m)');
ylabel('static friction (nn/nm)')
legend('Bordag','Strus','Dorogin')