SIZE EFFECT ON THE MECHANICAL PROPERTIES IN ZINC OXIDE NANOWIRES

A Dissertation in Mechanical Engineering

by

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ABSTRACT

As the size of material decreases to nanoscale, the fundamental material properties such as Young’s modulus become different from that at the bulk scale. New phenomena begin to emerge when the size of the material is reduced that are unique to the small scale. Nanowires are quasi one-dimensional solids, and their diameters are typically in the range of 10 nanometers to 500 nanometers. The range of nanowire diameters coincides with the critical length scales in materials, where the properties and phenomena are different from bulk. Hence, nanowires serve as excellent systems for studying material properties and behavior at the small scale. Along with their scientific significance, nanowires are also technologically important, and are expected to play an important role in the trend towards miniaturization. However, the small size of the nanowires and lack of sophisticated instrumentation pose several challenges in performing experiments on nanowires.

The size effect on the mechanical properties of nanowires was investigated, specifically Young’s modulus and fracture strain. The representative material was chosen to be zinc oxide because of its technologically significant properties, such as being both, a semiconductor and piezoelectric material. The zinc oxide nanowires were synthesized using vapor-liquid-solid process. Uniaxial tensile and cantilever bending experiments were performed in-situ inside electron microscopes on single zinc oxide nanowires. Novel application of post-buckling mechanics was exploited to develop microdevices for high resolution force and displacement in sensing and actuation. For performing the mechanical characterization experiments, different techniques for nanowires specimen
preparation were developed that were generic, reliable and robust. Fracture strain and Young’s modulus of zinc oxide nanowires were measured for different diameters and lengths.

The fracture strains of zinc oxide nanowires were experimentally measured for the first time, and the strains were between 4 % and 14 %, which is unusually high considering zinc oxide is a brittle material (ceramic) at the bulk scale. It was also observed that the fracture strains increased with decreasing diameter of the wires. The high fracture strains and diameter dependent strains were attributed to reduced number of defects and increasing contribution of surfaces. The Young’s modulus of the zinc oxide nanowires was measured to be 26 ± 9 GPa by uniaxial tensile experiments and 18 – 44 GPa by cantilever bending experiments. The tensile experiments were used to obtain stress-strain plots for the first time for single crystal zinc oxide. The Young’s modulus values were comparable to modulus values estimated by other researchers on zinc oxide nanostructures, but significantly lower than the modulus of bulk zinc oxide (140 GPa). The significant decrease in Young’s modulus cannot be explained by existing theories such as surface effects and non-ideal boundary conditions. New mechanisms, such as strain induced charge redistribution and influence of electromechanical coupling, were explored. These mechanisms could qualitatively and to some extent, quantitatively explain the reasons for the significant decrease in modulus of zinc oxide nanowires, compared to bulk zinc oxide.
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<td>Atomic Force Microscope</td>
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<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
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<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
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<tr>
<td>MEMS</td>
<td>Microelectromechanical Systems</td>
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<td>MWCNT</td>
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<td>SWCNT</td>
<td>Single Wall Carbon Nanotube</td>
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<td>TEM</td>
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1.1 Size Effect in Materials

As the size of material decreases to nanoscale, the fundamental material properties such as Young’s modulus become different from that at the bulk scale. In some cases, the properties are a function of size, and are not constant like at the macro scale. For example, researchers have observed that, for electroactive polymers, the elastic modulus (Young’s modulus) increases with decreasing size, if the diameter of the fibers is less than 100 nanometers (figure 1-1 A) [1]. This is contrary to our understanding of material behavior at the bulk scale, where Young’s modulus is independent of size. New phenomena begin to emerge, when the size of the material is reduced to micro and nanoscale that are unique to the small scale. For instance, the conductance of a metal wire decreases continuously as the wire is stretched. However, when the diameter of gold wires is a few nanometers, then the conductance of wires decreases in discrete steps as the wires are strained (figure 1-1 B) [2]. This phenomenon is known as quantized conductance and is observed only at the nanoscale.

One of the probable reasons for size effect is that when the size of the material is reduced to micro and nanoscale, it coincides with the critical length scales in materials [3]. In figure 1-2, some of the critical length scales in material are shown for different physical phenomena.
Figure 1-1: (A) Elastic Modulus dependence on Diameter of Polymer Nanofibers [1]. (B) Conductance vs Strain for Nanoscale Gold Wires [2].

Figure 1-2: Critical Length Scales in Materials.
For instance, when the size of the material is between 10 and 100 nm (magnetic length scale), then the material is approximately the size of the critical magnetic domain. As a result, the magnetic properties of nanoscale materials are expected to be very different from the bulk scale. At the critical length scales, the configuration and energy of the atoms and molecules are different had the atoms and molecules been a part of bulk material. Since the material is affected at the atomic level, the various physical properties such as mechanical and electrical properties are expected to be different.

Nanowires are quasi one-dimensional solids with their lengths generally from 1 micron to 100 microns and diameters typically in the range of 10 nanometers to 500 nanometers, which coincides with the critical length scales in materials. Hence, nanowires serve as excellent systems for studying material properties and behavior at the small scale. Along with their scientific significance, nanowires are also technologically important. In recent years, there is a trend towards miniaturization, and nanowires are expected to play an important role in achieving that goal. With miniaturization there are the advantages of higher integration density and enhanced performance. For instance, researchers in Hewlett-Packard Laboratories have developed an integrated chip (IC) architecture using nanowires as interconnects [4], and the new architecture would result in smaller chips that consume lesser power and are more efficient (figure 1-3 A). As another example, studies have shown that the piezoresistance effect in silicon nanowires (coupling between strain and resistance) is much higher than bulk silicon [5] (figure 1-3 B). This is an example where the properties of the material are enhanced at the nanoscale.
In the next section, the challenges with performing experiments on nanowires will be discussed. It is to be noted that in literature, the terms nanowires and nanorods are interchangeably used, but in this thesis, the term nanowire will be consistently used.

1.2 Challenges with Experimental Studies on Nanowires

The properties of nanowires are relatively less explored since they have been only recently synthesized. From an experimental point of view, there exist several issues with nanoscale characterization. It is important to perform experiments on individual
nanowires, but the nanowires after the synthesis process tend to occur in clusters. Figure 1-4 A shows a Scanning Electron Microscope (SEM) image of as-synthesized zinc oxide nanowires. Hence, it is desirable to develop synthesis processes that would yield single nanowires as the end-product for experimental specimens. Until sufficient control can be achieved over the synthesis processes, the alternative to prepare individual nanowire specimens is to manipulate single nanowires out of the clusters to the site of experiment. In figure 1-4 B, a single zinc oxide nanowire is manipulated to a micro-device (experiment site) for mechanical characterization experiments. However, the sizes of the nanowires are very small and hence, there exist not many reliable and robust nano-sized specimen manipulation techniques.

Figure 1-4: (A) Zinc Oxide Nanowires as Synthesized. (B) Single Zinc Oxide Nanowire on a Micro-device for Experiments.

Another important concern for experiments at the nanoscale, where the specimen cannot be directly visualized for boundary conditions, is the issue of *in-situ* testing, for which high resolution microscopes are used for visualization. *In-situ* experiments provide...
direct visualization and description of the events as they happen, and reveal qualitative information about the experiment along with quantitative data. However, the small size of the electron microscope chambers (required to merely ‘see’ the nanowires) leads to severe constraints on the experimental setup. \textit{In-situ} experiments also ensure integrity and accuracy of the experimental procedure and data, which is crucial for nano-scale characterization.

In this thesis, the focus is on mechanical properties of nanowires, and uniaxial tensile loading is the preferred technique for mechanical characterization of materials. The main advantage of uniaxial tensile loading is that it is able to provide a direct understanding of several mechanical properties and phenomena such as Young’s modulus, plastic deformation, yielding, fracture mechanics and fatigue behavior. The loading and stress state in uniaxial loading is analytically simple, and hence, it is able to provide better understanding of the mechanics governing material deformation. Additionally, for studying coupled fields interactions such as piezoelectric, piezoresistive or thermomechanical properties of materials, uniaxial tensile loading is the preferred experimental technique, since it precludes effects of non-planar stress and strain fields, strain gradients, and effect of surfaces. However, due to the small size of the nanowires, it is experimentally challenging to adapt uniaxial tensile loading to the nanoscale. Simple issues such as appropriate specimen alignment and gripping for mechanical characterization are difficult to address for nanowires. Also, since the sizes of the nanowires are small, high resolution force and displacement (nano-Newton and nanometer respectively) sensing and actuation are needed for meaningful quantitative
data. In the next section, the research described in the thesis is summarized along with the scientific and technological contributions of the research.

1.3 Research Summary

In this research, uniaxial tensile and cantilever bending experiments were performed \textit{in-situ} inside a SEM on single zinc oxide nanowires. Fracture strain and Young’s modulus of zinc oxide nanowires were measured for different diameters and lengths. The measured mechanical properties were different from bulk, and several theories were analyzed and possible reasons were suggested to explain the observed size effect.

The scientific contributions of the thesis are as follows:

– Several existing theories were explored for their applicability in explaining the size effect in mechanical properties along with quantitative analysis.
– The effects of piezoelectricity and electromechanical coupling on the measured mechanical properties of piezoelectric nanostructures were considered as possible reasons for the observed size effect.
– Directions for further research in nanoscale mechanical characterization and size effects are presented.

The technological contributions of the research are as follows:

– A novel application of post-buckling mechanics for design of microdevices for force and displacement sensing was implemented.
Different types of micro-devices for performing uniaxial tensile experiments were developed. The salient features of the microdevices are as follows:

- High resolution force and displacement sensing and actuation.
- Ability to perform in-situ experiments inside electron microscope chambers.
- Adaptability of the microdevices for different applications such as life-sciences studies or coupled-field investigations.

Different specimen preparation techniques were explored that are generic, robust, reliable and/or less cost and time intensive.

Synthesis process for growth of zinc oxide nanowires was developed.

An outline of the thesis is presented in the next section.

1.4 Outline of the Thesis

In the next chapter, the existing experimental techniques for mechanical characterization of nanowires are discussed. Various theories for size effects in mechanical properties of materials are presented along with experimental observations for the size effects in Young’s modulus of nanostructures. Also, the mechanical properties of zinc oxide nanowires are reviewed. In the third chapter, the design philosophy, fabrication, calibration and operation of different microdevices for mechanical characterization of nanowires are discussed. The fourth chapter explores several specimen preparation techniques for nanoscale characterization experiments, along with the synthesis process for zinc oxide nanowires. In the fifth chapter, the
experimental techniques for uniaxial tensile testing and cantilever bending experiments on nanowires are explained. The sixth chapter presents the results of experiments on zinc oxide nanowires. Several theories for the observed size effect are discussed in detail. Finally, the seventh chapter consists of a summary of the thesis and directions for further research.

1.5 References


Chapter 2

Literature Review

Experimental studies on the mechanical properties of nanowires (nanostructures in general) are challenging due to the requirements of high resolution force and displacement sensing, ability to perform in-situ experiments and lack of reliable and robust techniques for specimen preparation at the nanoscale. In recent years, there have been significant developments in the instrumentation for nanoscale material characterization, but there still exists some issues in adapting the existing techniques for mechanical characterization of nanowires. In the next section, the various techniques for mechanical characterization of individual nanowire specimens are discussed along with specimen preparation techniques at the nanoscale.

2.1 Mechanical Characterization Techniques for Nanowires

2.1.1 Piezoelectric Transducer based Techniques

Piezoelectric transducer based techniques are popular techniques for mechanical characterization because of their high displacement resolution in actuation and sensing. Piezoelectric transducers are materials that can convert electrical energy (in the form of electric field) to mechanical energy (in the form of strain) and viceversa. These techniques have been mainly used to study electrical phenomena such as conductance
quantization and tunneling effect in metallic nanowires and nanocontacts. In this literature review, the piezoelectric transducer based studies in literature are discussed that focused on the mechanical properties of nanowires. One variation of the above technique involves driving a Scanning Tunneling Microscope (STM) tip (a sharp tip with nanometer radius) into a metal sample, and then pulling it out. During the retraction process, monoatomic or very thin nanowires are formed between the tip and metal sample (figure 2-1).

Figure 2-1: Schematic of a STM Setup Modified for Characterizing Nanowires.

Agrait et al. [1] used this technique to quantitatively study the plastic deformation in nanometer size structures (lead and gold). This technique has also been used by researchers to study iridium [2, 3], gold [3-7], lead [4], tin [5], copper [5], mercury [5] and platinum [3] nanocontacts and nanowires. Ohnishi et al. [8] adapted the STM
technique to perform *in-situ* experiments inside a Transmission Electron Microscope (TEM), and observed self-ordering of gold atoms during retraction of the STM tip.

The other commonly used piezoelectric transducer based technique employs a mechanically controllable break-junction (MCBJ). In this technique, a macroscopic notched wire or a nanofabricated metal bridge is mounted on a flexible substrate. The wire or bridge is broken at low temperatures in vacuum, and contact is re-established between the fractured surfaces by piezoelectric control of the substrate to form nanowires between the fractured surfaces. Researchers have used this technique to study spontaneous spin polarized transport in magnetic nanowires [9], influence of strain on electrical conduction in bismuth nanowires [10], piezoresistivity in silicon nanowires [11] and interatomic potentials in gold nanowires [7]. The piezoelectric transducer based techniques provide for rapid characterization of materials at the nanoscale. However, these techniques are limited to a few materials, mostly metals that are able to form nanowires between fractured surfaces. Also, these techniques are primarily restricted to study of strain related properties of nanowires, and are difficult to adapt to measure force related mechanical properties, such as Young’s modulus and tensile strength. Additionally, the technique employing MCBJ involves experiments on nanostructures lying on a substrate, and hence, the mechanical response of the nanowires is prone to ‘substrate effects’, i.e. the response of the material is influenced by its interaction with the substrate.
2.1.2 Atomic Force Microscope based Techniques

Atomic force microscope (AFM) has been the workhorse for nano-mechanical characterization, due to its high force and displacement resolution. The AFM consist of a sharp tip (probe) in the form of a cantilever with very low stiffness (figure 2-2) [12].

Displacement of the tip is measured by focusing a laser beam on the tip and processing the reflected beam using photodiodes. The low stiffness of the tip coupled with high resolution of displacement measurement using photodiodes (nanometer resolution) enables measurement of forces with very high resolution (nano-Newton and pico-Newton).

There are two typical configurations for AFM based measurement of mechanical properties. In the first configuration (shown in figure 2-3 A), the nanowire is suspended.
across a trench, and the AFM tip is used to vertically deflect the nanowire (downwards); this type of experiment is called a three-point bending test.

Salvetat et al. [13] used this technique to measure mechanical properties of carbon nanotubes. Minor modifications of this technique have been used for mechanical characterization of carbon nanotubes [14], silver nanowires [15-18], chromium nanocantilevers [19], copper oxide nanowires [20], gallium nitride nanowires [21, 22], boron nanowires [23], zinc sulphide nanowires [24], gold nanowires [25], silica nanowires [26, 27], silicon nanowires [28, 29] and silicon nanocantilevers [30, 31]. In another configuration of AFM based techniques, the nanowire is oriented vertically (or grown vertically) on a substrate (figure 2-3 B), and the AFM tip is moved sideways to bend the nanowire (towards the right in the figure). This technique is called cantilever
bending, because the nanowires are in the cantilever configuration. Song et al. [32] and Hoffman et al. [33] have used this technique to measure the Young’s modulus of zinc oxide nanowires and silicon nanowires, respectively.

The superior resolution of AFM based techniques allows for characterization of individual nanowires, but the technique in its basic form lacks in-situ capabilities. In-situ experiments provide for direct visualization and description of the events as they happen, and give qualitative information about the mechanics of deformation along with quantitative data. For example, Yu et al. [34] performed tensile loading experiments on individual multi-walled carbon nanotubes (MWCNT) attached between two AFM tips inside a Scanning Electron Microscope chamber (SEM). During in-situ experiments, they observed that the nanotube broke in the outermost layer; this failure mode is known as "sword-in-sheath" failure. Erts et al. [35] studied force interaction between gold nanostructures using an AFM in-situ inside a Transmission Electron Microscope (TEM), and observed van der Waals force enhanced diffusion of gold atoms. In-situ experiments also ensure integrity and accuracy of the experimental procedure and data, which is crucial for nano-scale characterization.

2.1.3 Nanoindentation

Indentation is a standard technique for estimating mechanical properties of materials, and has traditionally been used for measuring hardness of materials like Brinell hardness and Vickers hardness. In a typical indentation test, a hard tip, generally made out of diamond, is pressed into the sample with a known load, and then the load is
removed. The material hardness is estimated from the residual indented area and the maximum applied load. Recently, this technique has been adapted for mechanical characterization of nanostructures, and is known as ‘nanoindentation’. The schematic of a nanoindenter is shown in figure 2-4 [36].

In a typical nanoindenter, the force is applied using a magnet and coil. The displacement of the tip is measured using capacitive sensors, and the force on the tip is estimated from the stiffness of the springs and displacement of the tip. In a nanoindentation test, the force during loading and unloading and the indentation depth are measured with high resolution (nano-Newton and nanometer, respectively).

In a nanoindentation test, a hard tip is pressed into a nanowire lying on a substrate, and the mechanical properties of the nanowire are estimated from the loading and unloading curves. Nanoindentation has been used to determine the hardness and
modulus of gallium nitride and zinc oxide nanowires [37], tantalum oxide nanowires [38], single crystal and polycrystalline copper wires [39], gold nanowires [40], zinc oxide nanobelts [41] and carbon nanotubes [42]. In order to provide in-situ experiment capabilities, Stach et al. [43] developed a novel nanoindentation technique for real-time observation of material deformation inside a TEM. There are certain issues in adapting nanoindentation for material characterization, and one of the main concerns is that the deformation is essentially gradient-dominated, which makes data interpretation and modeling difficult [44]. Also, the technique is sensitive to ‘substrate effect’, which is a concern for testing of nanowires on substrates.

2.1.4 Resonance based Techniques

Another technique used for measuring the Young’s modulus of nanowires is the analysis of the response of vibrating nanowires. In this technique, the nanowire is subjected to an alternating electric field inside a TEM or SEM that vibrates the wire, due to the electric charges on the wire. The frequency of the applied field is varied to vibrate the nanowire to resonance, and the resonance is detected from direct visual observation. From the values of fundamental resonant frequency and nanowire dimensions, the Young’s modulus of the nanowire can be estimated. Figure 2-5 shows TEM images of a vibrating silicon nanowire [45]. The left image shows a stationary silicon nanowire, the center image shows the nanowire subjected to an alternating electric field, and the right image shows the nanowire vibrating in its first resonant mode (174.5 kHz is the resonant frequency). This technique has been used by researchers to determine the Young’s
modulus of carbon nanotubes [46], zinc oxide nanobelts [46], silica nanowires [47, 48], silica-silicon carbide composite nanowires [47], silicon nanowires [45], gallium nitride nanowires [49], tungsten oxide nanowires [50] and diamond like carbon nanopillars [51]. As a modification of this technique, Osakabe et al. [52] measured the Young’s modulus of platinum nanowires driven by thermal noise oscillations, inside a TEM by detecting the vibrations using a electron counting technique.

The resonance based technique avoids the need for specimen manipulation and allows for in-situ experiments. However, it cannot be used to measure other important mechanical properties of nanowires, such as fracture strain and toughness, and is applicable only in the elastic deformation region of the specimen. Also, dynamic techniques tend to overestimate the modulus values. During dynamic experiments, an oscillating electric field is applied to the nanowire, which induces charges on the nanowire surface, and the nanowire is deflected by electrostatic forces. Zheng and Zhu [53] have analytically shown that, due to the presence of induced charges on the surface, the measured modulus in presence of electric fields is higher than the actual modulus of the material. The extent of overestimation of modulus increases with increasing aspect ratio of the nanowire. For copper nanowires with aspect ratios as 100, the measured modulus is 1.5 times the actual modulus. As a result, the modulus values measured during dynamic experiments, where the nanowire deflection is induced by electrostatic fields, tend to be the overestimated modulus values.
2.1.5 Micro-devices based Tensile Loading

Micro-devices or MEMS (micro-electro-mechanical systems) based experimental techniques are suited for mechanical characterization of nanowires, because they are able to apply pure uniaxial loading on the specimen (challenging to achieve with the techniques discussed in the previous sections), which is the preferred loading technique for mechanical characterization experiments. The micro-devices are miniature versions of the Instron Universal Testing Machine, which is the standard instrument for measurement.
of mechanical properties at the macro scale. The small size of the micro-devices enables for *in-situ* experiments inside a SEM or TEM. Demczyk *et al.* [54] used a micro-scale tensile testing device inside a TEM to determine the tensile strength and Young’s modulus of carbon nanotubes. Lu *et al.* [55] and Zhu *et al.* [56] have also developed MEMS experimental test-beds for mechanical characterization of nanowires and nanotubes. Figure 2-6 shows a MEMS based experimental test-bed used for mechanical characterization of nanowires and nanotubes [56]. The device is actuated thermally, and the force and displacements are measured using capacitive sensors (labeled as ‘load sensor’ in figure).

Specimen preparation is an important issue in nano-scale material characterization, due to the small size of the specimen. In the next section, some of the techniques in literature for specimen preparation and manipulation are discussed.

Figure 2-6: MEMS based Experimental Test-bed [56].
2.2 Specimen Preparation Techniques

Some of the experimental techniques for mechanical characterization of nanowires require specimen manipulation from the cluster of as-synthesized nanowires. In addition to manipulation, it is essential that the specimen be free-standing for mechanical characterization, in order to minimize the influence of substrate on mechanical properties. The techniques for nanoscale specimen preparation broadly fall in three categories: 1) on-site growth 2) specimen co-fabrication 3) direct specimen manipulation.

2.2.1 On-site Growth

One of the popular techniques for preparation of free-standing nanoscale specimens is fabrication of templates (generally of alumina) on the required substrate, followed by deposition of the specimen material into the holes on the templates. The size and spacing of the holes on the template is controlled, according to the application. The template is then dissolved to obtain free-standing specimens (nanowires or nanotubes) on the substrate. Free-standing specimens of carbon nanotubes [57], silver nanowires [58], gold nanowires [59] and bismuth nanowires [60] have been fabricated using this technique. In this technique, it is challenging to integrate the specimen with the experimental test-bed, and the adhesion of the nanowire is not necessarily good enough for mechanical characterization. Another technique for on-site growth of nanostructures is to synthesize the nanowires from catalyst, patterned at the desired sites. In this technique, the catalyst required for growth of the nanowire (such as gold thin films for
zinc oxide nanowires) is patterned using lithography or other micro-fabrication techniques on the site of experiments. This technique has been used by researchers to prepare free-standing specimens of carbon nanotubes [61, 62], zinc oxide nanowires [63] (figure 2-7), silicon nanowires [64] and carbon nano-fibers [65]. Although on-site growth is an elegant technique for specimen preparation, its application is determined by the ability to integrate the template or catalyst patterning with the experimental test-bed. Also, the current understanding of synthesis process of nanowires is not advanced enough to control the growth of nanowires, selectively.

2.2.2 Specimen Co-fabrication

Another technique for nanoscale specimen preparation is to disperse the nanotubes and nanowires, and then pattern the micro-devices, required for the experiment, around them. For example, researchers have used this technique to prepare specimens in order to study the electrical characteristics of gallium nitride nanowires.

Figure 2-7: Zinc Oxide Nanowires Grown on Silicon [63].
platinum nanowires [67] and carbon nanotubes [68]. This specimen preparation technique is useful for experiments on nanowires lying on substrates, but has not yet been used to fabricate free-standing nanowires or nanotubes. In order to prepare free-standing nanoscale specimens, researchers [69] have sandwiched nanostructures between two layers of photoresist (a photosensitive material), and then used lithography to obtain free standing nanowires or nanotubes gripped between photoresist layers (figure 2-8).

2.2.3 Direct Specimen Manipulation

A popular technique for preparing free-standing nanowire specimens is the pick-and-place technique. In this technique, an individual nanowire is picked using a sharp tip or tweezers, and placed at the site of experiment. For instance, this technique has been used to prepare specimens in order to study mechanical properties of carbon nanotubes [56, 70-73] and palladium nanowires [56]. Researchers have developed nanopositioning stages [34, 48, 74], nanorobotic manipulators [75] and electrostatic tweezers [76, 77] to
facilitate the picking and the specimen manipulation process. Figure 2-9 shows SEM images of an electrostatic tweezer. The left image in the figure shows the tweezer attached to a manipulation stage, and the right image in the figure shows a magnified view of the tweezer. The tweezer can be opened and closed by applying voltage. Although the pick-and-place technique is tedious and time intensive, it is a generic specimen preparation technique, and is independent of the specimen chemistry, structure and physical properties. Hence, it is not affected by the process compatibility issues (mainly from chemistry point of view) that affect ‘on-site growth’ and ‘co-fabrication’ techniques for specimen preparation.

Figure 2-9: Electrostatic Tweezers [76].
2.2.4 Other Techniques for Specimen Preparation

Dielectrophoresis is another specimen manipulation and alignment technique. Nanostructures have significant surface charges due to their small size, and hence, can easily be manipulated using an electric field. For example, researchers have manipulated and aligned carbon nanotubes [78-80] and zinc oxide nanowires [81, 82] with dielectrophoresis. Dielectrophoresis involves manipulation of nanostructures suspended in liquids, and hence, this might present problems when integrated with micro-devices, since the liquid could cause stiction in the free-standing structures of the micro-device [83]. Salalha and Zussman [84] manipulated and aligned gold nanowires via manipulation of a droplet composed of dilute nanowire suspension by creating thermocapillary motion inside a micro-channel. Huang et al. [85] have developed a novel direct mechanical transfer technique, which involves manipulation of a nanostructure lying across a slit to the site of experiments under an optical microscope, and demonstrated the technique for individual carbon nanotubes. In the next section, a brief review of the existing theories for size effect is discussed.

2.3 Theories for Size Effect on Mechanical Properties

The increasing contribution of surface properties is believed to be the main reason for the size effect in materials. In fact, size effect on mechanical properties in material is analyzed primarily within the framework of surface effects. In the next sub-section, the various theories in literature for surface effects on mechanical behavior of materials are reviewed.
2.3.1 Surface Effects

The surface atoms have a lower co-ordination number than bulk atoms, i.e. they have fewer neighbors [86]. As a result, the charge density in the vicinity of the surface is redistributed. Correspondingly, the nature of the chemical bond and the equilibrium interatomic distances at the surface are different from that inside the bulk [87]. From the point of view of mechanical properties, the difference in nature and length of interatomic bonds at the surface compared to bulk leads to surface stresses and surface energy (figure 2-10) [87, 88]. Hence, the mechanical properties of surfaces are different from that of bulk material.

Figure 2-10: Surface Effect on Mechanical Properties of Materials.
As the size of material is reduced to nanoscale, the percentage of surface atoms increases. Figure 2-10 shows the plot for percentage of surface atoms in zinc oxide as a function of the diameter of the wire. It can be seen that for diameters as low as 10 nm, 40 percent of the total atoms are at the surface. Since the number of surface atoms is higher at the nanoscale, the properties of surfaces significantly contribute to overall behavior of the material; this is called surface effect.

Researchers have incorporated the surface effect on mechanical properties of nanoscale materials in several ways. One of the most popular methods for quantifying surface effects is to incorporate surface stresses into the mechanical response of the material. Gurtin and Murdoch [89] developed a surface elasticity formulation, in which a surface stress tensor is introduced to augment the bulk stress tensor that is typically utilized in continuum mechanics. This approach has been modified by researchers to study the surface effect on nanoscale materials such as nanoplates, nanowires and nanorods [88, 90-94]. Along with surface stresses, researchers have also considered the thermodynamics and energy of surfaces to study the surface effect on mechanical behavior of materials [95-98]. Surface tension is another important surface property. Shuttleworth related surface tension to surface free energy via a strain dependent component [87, 99], which was later used by Cuenot et al. [100, 101] to explain the observed size effect on Young’s modulus in their experiments on silver and lead nanowires and polymer nanotubes. Sun et al. [86] related the bond relaxation at the surface to the difference in interatomic bond energies between surface and bulk atoms. The difference in energies can be used to estimate the effect of surfaces on mechanical properties. Shankar et al. [102] proposed that the surface stresses influence the
mechanical properties of nanowires, because nonlinear stress effects become significant at the small scale leading to cross terms between the applied stress and surface stresses. Wang et al. [103] showed that most of most of the physical quantities obey a simple scaling law as long as the size of the material is larger than the intrinsic length scale, \( l_{in} \). They also derived various expressions for \( l_{in} \) in case of mechanical properties. Jiang et al. [104, 105] modeled the surface stresses in a semiconductor and showed that the surface energy is size dependent. Most of theories for surface effects predict that the surface effects will dominate for nanowires with diameters in the range of a few angstroms to a few nanometers. However, the experimental data in literature is reported for nanowires with diameters that are one to three orders larger, and hence, there is a need to explore non surface dependent phenomena for understanding the size effect.

\[2.3.2 \textbf{Other Non-surface Based Theories for Size Effect}\]

Researchers have observed that in some cases, the mechanical properties of the nanowires are different from bulk properties, but do not show any diameter dependence. For instance, the modulus values of zinc sulphide nanowires [24] and PZT (Lead Zirconate Titanate) nanofibers [106] are smaller than the modulus values of their bulk counterparts, and not dependent on the diameter of the wire or fiber. The fact that the properties are not diameter dependent, but different from bulk implies that there exist some phenomena unique to the nanoscale and not influenced by surface effects. Researchers have studied the interdependency of quantum fluctuations and mechanical vibrations for suspended nanostructures [107, 108]. These studies are analytical and valid
for nanotubes with diameters as small as a few nanometers. Another phenomenon that is influenced by quantum effects is quantized conductance, where the conductance decreases in discrete steps with strains. The quantized conductance is caused by rearrangements of the bond configurations, due to quantum effects [4, 109]. Bond rearrangement phenomenon can be used to study other types of mechanical behavior such as plastic deformation [1]. In another research, the piezoresistivity of vibrating semiconductor nanocantilevers was greatly enhanced in the presence of magnetic fields, due to quantum effects [110].

Pugno et al. [111, 112] have proposed a new energy based theory, quantum fracture mechanics (QFM) that adapts the continuum based fracture mechanics for nanostructures. They used QFM to explain fracture properties of carbon nanotubes, silicon carbide and nitride nanorods, and polysilicon thin films. On the subject of fracture mechanics, materials at the nanoscale are known to fracture at high strains [113, 114], because the number of defects are lower and there are fewer sites for crack nucleation. At large strains, materials have been computationally shown to undergo phase transformations at the nanoscale [115, 116], and this might result in novel mechanical behavior. Another reason for the observed differences in material behavior at the nano and bulk scales is the differences in the experimental conditions. At the bulk scale, mechanical characterization of materials is performed in compliance with well-established standards (such as ASTM standards, American Society for Testing and Materials) to ensure maximum accuracy, reliability and robustness of the experimental data. However, at the nanoscale, there are several challenges in performing the experiments according to the standards, such as small size of the specimen and the
inability to perform in-situ experiments. As a result, the boundary conditions are not well understood, and this could influence the measured mechanical properties. Chen et al. [17] and Ding et al. [23] have demonstrated the effect of boundary conditions on the measured mechanical properties for nanowires. In this thesis, the main focus is on the Young’s modulus of nanowires. In the next section, the size effect on the Young’s modulus of materials is discussed.

2.4 Size Effect on the Young’s Modulus of Materials

Young’s modulus is a fundamental mechanical property, and hence, is the most studied property in nanowires. It is a function of the interatomic bond strength, bond length and structure of the material and is conventionally a material property, independent of size. However, at the nanoscale researchers have observed that Young’s modulus value is not only different from bulk value, but also is size-dependent in some cases. Table 2-1 shows the experimentally observed size effect for Young’s modulus in nanostructures. For the first six rows in table 2-1 (upto polypyrrole nanotubes), the first modulus value is the reported value for modulus at the bulk scale. In case of polymer fibers (polypyrrole [15] and electroactive polymer [117]), the size effect for modulus is due to the increasing contribution of surface tension to the measured modulus, as the size of fibers is decreased. Researchers also attribute the size effect for modulus in nanowires of other materials to surface effects, due to intrinsic surface stresses. However, the length scales at which the surface effects manifest are much larger than predicted by theory (this
fact will be quantified in section 6.3). Also, in the cases of silicon and gallium nitride, there are contradicting evidences of size effect, as is shown in table 2-2.

### Table 2-1: Size effect in Young’s Modulus of Nanostructures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameters (nm)</th>
<th>Increased or Decreased from bulk value</th>
<th>Modulus Values (GPa), 1\textsuperscript{st} value is bulk if reported</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver Nanowires 10 – 150</td>
<td>Increased</td>
<td>75 to 140</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>Silver Nanowires 25 – 150</td>
<td>Increased</td>
<td>76 to 160</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>Lead Nanowires 10- 150</td>
<td>Increased</td>
<td>15 to 30</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>Chromium Cantilevers 50 – 100</td>
<td>Decreased</td>
<td>248 to 40</td>
<td>[19]</td>
<td></td>
</tr>
<tr>
<td>Silicon Cantilevers 12- 300</td>
<td>Decreased</td>
<td>170 to 53</td>
<td>[31]</td>
<td></td>
</tr>
<tr>
<td>Polypyrrole Nanotubes 10- 150</td>
<td>Increased</td>
<td>10 to 120</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>Electroactive Polymer Fibers 55 – 110</td>
<td>Increased</td>
<td>0.2 to 2</td>
<td>[117]</td>
<td></td>
</tr>
<tr>
<td>Gallium Nitride Nanowires 35 – 85</td>
<td>Decreased</td>
<td>300 to 220</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>Tungsten Oxide Nanowires 15 – 40</td>
<td>Increased</td>
<td>100 to 300</td>
<td>[50]</td>
<td></td>
</tr>
<tr>
<td>Silicon Carbide Silica Nanowires 60 – 300</td>
<td>Decreased</td>
<td>80 to 46</td>
<td>[118]</td>
<td></td>
</tr>
<tr>
<td>Silicon Carbide Silica Nanowires 58 – 92</td>
<td>Decreased</td>
<td>64 to 54</td>
<td>[118]</td>
<td></td>
</tr>
<tr>
<td>Copper Oxide Nanowires 60 – 160</td>
<td>Increased</td>
<td>40 to 220 (rough) 170 to 300 (smooth)</td>
<td>[20]</td>
<td></td>
</tr>
</tbody>
</table>
In some cases, experimental studies have shown that the Young’s modulus of nanostructures is different from bulk value, but not dependent on diameter of the wire (or critical dimension in case of cantilevers).

Table 2-2: Observations of No Diameter Dependence in Nanostructures

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameters (nm)</th>
<th>Modulus Values (GPa)</th>
<th>Bulk Value (GPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium Nitride Nanowires</td>
<td>57 – 135</td>
<td>195 – 300</td>
<td>356</td>
<td>[21]</td>
</tr>
<tr>
<td>Gallium Nitride Nanowires</td>
<td>60 – 110</td>
<td>33 – 62</td>
<td>356</td>
<td>[22]</td>
</tr>
<tr>
<td>Zinc Sulphide Nanobelts</td>
<td>50</td>
<td>43 – 64</td>
<td>108</td>
<td>[24]</td>
</tr>
<tr>
<td>Gold Nanowires</td>
<td>40 – 250</td>
<td>40 – 110</td>
<td>80</td>
<td>[25]</td>
</tr>
<tr>
<td>PZT Nanofibers</td>
<td>40 – 140</td>
<td>43</td>
<td>63-94</td>
<td>[106]</td>
</tr>
<tr>
<td>Silicon Cantilevers</td>
<td>300 – 500</td>
<td>80 – 100</td>
<td>130</td>
<td>[119]</td>
</tr>
<tr>
<td>Silver Nanowires</td>
<td>22 – 35</td>
<td>80 - 125</td>
<td>76</td>
<td>[18]</td>
</tr>
<tr>
<td>Silicon Carbide Nanorods</td>
<td>20- 30</td>
<td>610 – 660</td>
<td>492</td>
<td>[14]</td>
</tr>
<tr>
<td>Silver Nanowires</td>
<td>65 – 140</td>
<td>80 – 100</td>
<td>76</td>
<td>[17]</td>
</tr>
<tr>
<td>Silicon Nanowires</td>
<td>45 – 100</td>
<td>90 – 250</td>
<td>170</td>
<td>[120]</td>
</tr>
<tr>
<td>Silicon Nanowires</td>
<td>120</td>
<td>186 – 207</td>
<td>186</td>
<td>[28]</td>
</tr>
<tr>
<td>Silicon Nanowires</td>
<td>140 – 200</td>
<td>93 – 250</td>
<td>186</td>
<td>[29]</td>
</tr>
<tr>
<td>Silicon Cantilevers</td>
<td>150 – 300</td>
<td>172</td>
<td>170</td>
<td>[121]</td>
</tr>
<tr>
<td>Silicon Cantilevers</td>
<td>200 – 1 mm</td>
<td>169</td>
<td>170</td>
<td>[30]</td>
</tr>
<tr>
<td>Silica Nanowires</td>
<td>50 – 100</td>
<td>57 – 93</td>
<td>73</td>
<td>[27]</td>
</tr>
<tr>
<td>Silica Nanowires</td>
<td>250 – 2000</td>
<td>68 – 76</td>
<td>73</td>
<td>[26]</td>
</tr>
<tr>
<td>Germanium Nanowires</td>
<td>20 – 80</td>
<td>80 - 125</td>
<td></td>
<td>[122]</td>
</tr>
<tr>
<td>Boron Nanowires</td>
<td>40 – 95</td>
<td>230 – 410</td>
<td></td>
<td>[23]</td>
</tr>
</tbody>
</table>
Table 2-2 lists all the experimental studies, where researchers have not observed any diameter (or critical dimension) dependence of Young’s modulus in nanostructures. The first nine rows in table 2-2 (upto silver nanowires) correspond to the cases where researchers have observed no diameter dependence, but the modulus of the nanostructure is different from its bulk counterpart (generally lower). In the remaining studies (except the last two rows), the researchers observed that the average modulus at the nanoscale is almost the same as modulus at the bulk scale. In case of the last two rows, the modulus at the bulk scale is unknown for the particular crystal structure of the nanowire. From tables 2-1 and 2-2, it can be inferred that there are no definite trends for modulus dependence on diameter and differences in modulus values between bulk and nanoscale. Also, in some cases such as silicon, gallium nitride and zinc oxide (as will be seen in the next section), there are contrasting evidences for size effect in modulus for the same material. One of the main reasons for the discrepancies is that the differences in experimental techniques used to estimate modulus values results in different boundary conditions and loading conditions, which ultimately affect the measured modulus values. The effects of different techniques on measured mechanical properties are discussed in detail in Chapter 6. In the next section, the literature on modulus values and fracture strains for bulk zinc oxide and zinc oxide nanowires is reviewed.

2.5 Mechanical Properties of Zinc Oxide

Zinc oxide is a key technological material, and can be used in nanoelectronics, piezoelectric devices, opto-electronics, chemical sensors and AFM tips. It has three key
properties from a technological viewpoint. It is a semiconductor, with a direct wide band
gap of 3.37 eV and a large excitation binding energy (60 meV). Secondly, because of its
noncentral crystal symmetry (wurtzite structure), zinc oxide is highly piezoelectric, which
is a key property in building electromechanically coupled sensors and transducers.
Finally, zinc oxide is a bio-safe and biocompatible material and can be used for
biomedical applications [123]. There are many studies available on the mechanical,
electrical, electromechanical coupling, optical and chemical properties of zinc oxide bulk
crystals and thin films [124, 125]. Based on the remarkable physical properties of zinc
oxide, motivation for device miniaturization and exploitation of nano-scale phenomena,
in recent years, there has been significant emphasis on the synthesis, characterization and
device applications of zinc oxide nanostructures; these aspects are exhaustively reviewed
in numerous technical articles [123, 126-129]. However, there have been few studies on
the mechanical properties of zinc oxide nanowires, and this was one of the main
motivations for choosing zinc oxide as the sample material.

One of the earliest measurements on the mechanical properties of bulk single
crystal zinc oxide was performed by Kobiakov [130], and the values reported in his paper
are considered to be the standard for mechanical properties of zinc oxide. Since zinc
oxide is an anisotropic piezoelectric material, the method of resonance-antiresonance was
used to measure the six independent elastic constants [131-133]. Later, researchers used
different experimental and computational techniques to estimate the elastic constants of
single crystal and polycrystalline zinc oxide, and they have been exhaustively reviewed
by Ozgur et al. [124]. In recent years, nanostructures of zinc oxide such as nanowires are
attracting interest, and there are several experimental studies on the mechanical properties
of zinc oxide nanowires and nanobelts. Table 2-3 lists the experimental results on the modulus of zinc oxide nanowires and nanobelts.

### Table 2-3: Young’s Modulus of Zinc Oxide Nanowires and Nanobelts.

<table>
<thead>
<tr>
<th>Young’s Modulus (GPa)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>TEM Resonance</td>
<td>[128]</td>
</tr>
<tr>
<td>38.2</td>
<td>AFM Bending</td>
<td>[134]</td>
</tr>
<tr>
<td>31.3</td>
<td>Nanoindentation</td>
<td>[134]</td>
</tr>
<tr>
<td>55, 108</td>
<td>Nanoindentation</td>
<td>[135]</td>
</tr>
<tr>
<td>29 ± 8</td>
<td>AFM Bending</td>
<td>[32]</td>
</tr>
<tr>
<td>140 – 210 *</td>
<td>SEM Resonance</td>
<td>[136]</td>
</tr>
<tr>
<td>58</td>
<td>TEM Resonance</td>
<td>[137]</td>
</tr>
<tr>
<td>90 – 100</td>
<td>Nanoindentation</td>
<td>[37]</td>
</tr>
<tr>
<td>106±25</td>
<td>Optical Microscope Resonance</td>
<td>[138]</td>
</tr>
<tr>
<td>97 ± 18</td>
<td>Tensile Loading</td>
<td>[113]</td>
</tr>
<tr>
<td>117, 229, 454</td>
<td>Measured Critical Buckling Load</td>
<td>[139]</td>
</tr>
</tbody>
</table>

In all the experimental studies on mechanical properties of zinc oxide nanostructures, the growth of the nanostructure was along the same direction ([0001]), and the modulus of the wire or belt along the length ([0001] direction) was reported, except for nanoindentation studies. The first four rows correspond to experimental results on zinc oxide nanobelts, and the rest are modulus values for nanowires. In the sixth row in table 2-3 (marked with *), researchers observed a size effect in modulus, where the modulus increased from 140 GPa (bulk value according to Kobiakov [130]) to 210 GPa, as the diameters of the nanowires decreased from 550 nm to 20 nm. Most of the other
researchers observed that the modulus of nanoscale zinc oxide is less than bulk zinc oxide. The reasons for the decrease in modulus and the scatter in modulus values among different experimental results on nanowires and nanobelts are discussed in Chapter 6.

Researchers have measured the average fracture strain of zinc oxide nanowires to be between 3 and 8% [113, 140]. The fracture strains are relatively high, considering that zinc oxide is a ceramic material (brittle) at the bulk scale. However, as the size of material decreases, the number of defects decreases, and hence, the probability of failure is lower. As a result, the fracture strains are higher at the small scale. In the next chapter, the design and fabrication of the microdevices required for the experiments are explained.

2.6 References


Chapter 3
Microdevices for Nanoscale Mechanical Characterization

The main component of the experimental technique employed in this research is the microdevice. In this chapter, the design, fabrication and calibration of different microdevices are discussed.

3.1 Motivation for Development of Microdevices

Uniaxial tensile loading is the preferred technique for mechanical characterization of materials. Typical uniaxial loading involves spring loading of the specimen, i.e. the specimen is connected in series between two springs (or in some cases to one spring), as shown in figure 3-1 [1-3].

![Figure 3-1: Schematic of Uniaxial Tensile Loading.](image)
The specimen is loaded by pulling to the left. The spring constants of the two springs are $k_1$ and $k_2$, and their deflections are $x_1$ and $x_2$, respectively. The change in length of the specimen is given by $x_1 - x_2$, and the force on the specimen is given by $k_2 x_2$. Most of the force and displacement measurement sensors at the macro, micro and nano scales transduce the displacement of a structural element, such as a beam or a membrane, into electrostatic (capacitive), magnetic, piezoelectric or optical signals, which are then sensed to determine the force [4]. Hence, the force resolution in such systems is primarily limited by the spring constant of the structural member. In order to increase the force resolution, the spring constant of the structural element has to be decreased (e.g. by the use of thinner beams and membranes). Additionally, by decreasing the size of the measuring equipment, the experiments can be performed in-situ inside electron microscope chambers, which place severe constraints on the size of the experimental set-up.

Displacement resolution is more critical than force resolution in experiments for nanoscale mechanical characterization, because nanowires are generally a few microns long and the total elongation is typically on the order of nanometers. The displacements of nanowires are comparable with white noise in the typical data acquisition systems for macro scale mechanical characterization techniques, and nanometer-level resolution is required for displacement measurement. High displacement resolution is achieved by electrical, magnetic or optical sensing, but this makes the sensing schemes susceptible to interference from external environments (air, liquid, electro-magnetic etc.), and also imposes restrictions on the medium surrounding the experimental set-up. Additionally, since the transduction principals are indirect, accurate calibration of the displacement
sensing scheme is required before experiments. One of the motivations for the design of the microdevice was to develop a system with capability for studying coupled field properties such as piezoelectricity. In the proposed device design, post-buckling deformation of slender columns (made of silicon) is applied to address the issues mentioned in the previous paragraphs.

3.2 Application of Post-Buckling Mechanics to Microdevice Design

The microdevice design exploits stiffness attenuation and displacement amplification in the post-buckling deformation of slender columns. When axial load on a column reaches a critical value (critical buckling load), the column buckles and displaces in the lateral direction as shown in figure 3-2 A. After the column buckles, the lateral displacement, \( D \), is related to the axial displacement \( \delta \) as [5]

\[
\delta = \frac{\pi^2 D^2}{4L},
\]

where \( L \) is the length of the column. The plot of \( \delta \) vs \( D \) is shown in figure 3-2 B. It can be seen from the plot that an axial displacement, which will be the displacement of the specimen, as low as 200 nm is magnified to 8 \( \mu \)m of lateral displacement in a 1000 \( \mu \)m long column. A displacement of 8 \( \mu \)m can be easily resolved in standard electron microscopes such as SEM. Thus, the displacement resolution is mechanically enhanced without any transduction of signal.
Figure 3-2: Force and Displacement Plots for Post-Buckling Deformation.
Force in a column after buckling is given by [5]

\[ P = \frac{P_{cr}}{1 + \frac{\pi^2 D^2}{8L^2}}, \]  

(3.2)

where \( P_{cr} = 4\pi^2 \kappa / L^2 \) is the critical buckling load in the device (\( \kappa \) is the smallest flexural rigidity of the column). The force is plotted versus lateral displacement in figure 3-2 C. The graph is almost horizontal in the beginning, and hence, the spring constant (slope of the curve) of the column is small (0.77 mN/m) in the initial deformation region (where \( D < 40 \) μm). In typical tensile loading experiments on nanowires, the maximum elongation of the nanowires is 1000 nm, which corresponds to 20 μm of lateral displacement, using equation 3.1. Since the graph is almost horizontal for 20 μm lateral displacement of the column, the stiffness of the beam is very small for the entire range of nanowire displacement. Hence, high force resolution can be achieved by using beams with relatively large dimensions. To illustrate the concept of stiffness attenuation in buckled columns, consider a silicon beam with same dimensions as in figure 3-2, but in a cantilever configuration. The stiffness of the cantilever beam is 3.4 mN/m, which is about 50 times larger than the stiffness of the buckling column. The use of a buckling column as a motion amplifier has been demonstrated by researchers at the macro [6] and micro scales [7, 8]. For the first time, in this thesis the displacement amplification is used in conjunction with stiffness attenuation to obtain high force and displacement resolution. In the next section, integration of post-buckling mechanics in the design of a microdevice is presented.
3.3 Microdevice Design and Operation

In uniaxial tensile testing, the specimen is attached between two springs as illustrated in figure 3-1. In the microdevice design, two sets of slender silicon columns in a cascading configuration are used such that each set functions as a spring. The schematic of the device design is shown in figure 3-3. The two sets of beams are cd – c’d’ and ab – a’b’. The lower set of columns, cd and c’d’, are slightly longer than the upper set of columns, ab and a’b’. A piezoelectric actuator (piezomotor) is used to apply displacement loading to the lower set of columns. After the critical buckling load of the lower set is reached, the lower set of columns buckle, but the upper set of columns do not buckle as they have a higher critical buckling load because of their shorter lengths. Further application of displacement will continue to buckle the lower set of columns, and at some particular instance (when the critical buckling load of the upper set of columns is reached) ab and a’b’ will also buckle. At this point, the central section (represented by the rectangle bb’cc’ in figure 3-3 A) will move upwards. The specimen is connected between the fixed jaw and the moving jaw (a part of the central section). When both the sets of columns buckle, the central section moves upwards, thus applying tensile load on the specimen. Figure 3-3 B shows the configuration of the device when both sets of columns have buckled. By placing the fixed support on the upper side of the central section, the device can also be used to apply compressive load on the specimen.
Figure 3-3: Schematic of the Microdevice.
3.4 Expressions for Force and Displacement on the Specimen

From figure 3-3, the force on the specimen is given by

\[ P_{\text{specimen}} = (P_{cd} + P_{c'd'}) - (P_{ab} + P_{a'b'}) \]  \hspace{1cm} (3.3)

where \( P_{cd} \) is the force on column \( cd \), and so on. The displacement of the specimen is the displacement of the central section and is given by

\[ \delta_{\text{specimen}} = \delta_{ab}. \]  \hspace{1cm} (3.4)

The expressions for displacement of the column and force on the columns are given by equations 3.1 and 3.2, respectively, and can be substituted in equations 3.3 and 3.4 to estimate force and displacement of the specimen, respectively. The lateral displacement \( (D) \) of the columns can be read using the verniers, and this in turn is used to calculate the force and displacement on the specimen using equations 3.1, 3.2, 3.3 and 3.4. The verniers can also be part of a capacitive or an optical sensing scheme for real-time automated data acquisition. Since the load on the specimen is the difference of the forces on the columns (springs) with low stiffness, the device is able to apply small force on the specimen. The low stiffness of the structure also allows for nanometer-level displacement loading of the specimen. Both, the force and displacement on the specimen can be calculated from the highly amplified lateral displacement values. Thus, the device is able to achieve sensing and loading with high force and displacement resolution (nano-Newton and nanometer, respectively), due to differential measurement of force and displacement on beams with high compliance. The differential sensing and loading
scheme, by using two pairs of cascading beams, enables measurement of small forces, otherwise not possible with a single beam.

A buckling column with rectangular cross-section is a bi-stable system, and can assume one of the two configurations after buckling, as illustrated in figure 3-4 A (to the left or right). This is not desirable as the columns are required to buckle in a preferential direction in the microdevice to assume the configuration shown in figure 3-3 B. To achieve this, an initial imperfection ($\zeta$) is introduced (by designing a bent beam) as shown in figure 3-4 B; this leads to the initial configuration of the column being a highly obtuse triangle. Due to the initial imperfection, the column always buckles in the direction of the imperfection, i.e. always to the right in figure 3-4 B. Hence, by introduction of an initial imperfection, the device structure buckles symmetrically and assumes the desired configuration, as in figure 3-3 B. The expressions for axial displacement and force on the column, given by equations 3.1 and 3.2, respectively, are for a column with no initial imperfection. The derivation of expressions for force and displacement on a column with initial imperfection in the form of an obtuse triangle is explained in appendix A. The force and displacement for a single bent column are given by the following equations:

\[
P = P_{cr} \left[ (1 - \frac{\psi}{D}) + \omega^2 D^2 (1 - 1.6624 \left( \frac{\psi}{D} \right)^3) \right] \tag{3.5}
\]

and

\[
\delta = \frac{\omega^2 D^2 L}{16} \left( 1 - 0.7697 \left( \frac{\zeta}{D} \right) \right), \tag{3.6}
\]
where \( P_{cr} = \frac{4\pi^2EI}{L^2} \) is the critical load for buckling in fixed-fixed columns, and

\[
\omega = \frac{2\pi}{L}, \quad \psi = \xi \left( \frac{8}{\pi^2} \right).
\]

Hence, the force on the specimen and axial displacement of the specimen can be estimated from lateral displacements using expressions 3.3, 3.4, 3.5, and 3.6. In the next section, the operation of the devices is simulated in ANSYS, a commercial available finite element analysis (FEA) software, and the accuracy of the expressions for force and displacement (equations 3.5 and 3.6, respectively) is analyzed.
3.5 Finite Element Analysis of the Microdevice

The operation of the microdevice discussed in the previous section was simulated using ANSYS. Initially, the expressions for force and displacement were validated for a single column. The column (1000 μm long, 10 μm deep and 2 μm thick) was axially loaded, and the values of lateral deflection ($D$) and axial force ($P$) were extracted from the FEA simulation. To validate the expressions, the analytical values for axial force and displacement were estimated from the lateral displacement values from ANSYS and equations 3.5 and 3.6. Figure 3-5 shows the plots for force and displacement on a column with initial imperfection, and compares the values obtained analytically (dotted line) and by FEA (solid line). The deviation between the analytical and FEA simulation values for force and displacement were 1.2 % and 5 %, respectively. The reasons for the deviation between the analytical and simulation values are computational inaccuracies in non-linear modeling in ANSYS and modeling of the imperfection in the analytical expressions.

After verifying the analytical expressions for a single column, the device was simulated using FEA, adopting a similar approach as above. The tensile loading experiment was performed on a specimen (with known Young’s modulus) inside the framework of FEA simulation, and the lateral displacement values of the shorter and longer buckling columns were extracted from the simulation. The force and displacement values of the specimen were computed from the lateral displacements using equations 3.5 and 3.6, and were compared with the values obtained from FEA simulation. Table 3-1 shows the parameter values for the device and table 3-2 shows the parameter values for the specimen.
Figure 3-5: Force and Displacement Graphs for a Single Column.
From the force and displacement values, obtained analytically and by FEA simulation, the Young’s modulus of the specimen was estimated, and the results are shown in table 3-3. The deviation between the analytical and FEA simulation values for force and displacement on the specimen are 11.8 % and 4.8 %, respectively and the force-displacement plot for the tensile experiment is shown in figure 3-6.

### Table 3-1: Device Parameters for the Simulation.

<table>
<thead>
<tr>
<th>Device Parameter</th>
<th>Value (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the Longer Column (cd and c’d)</td>
<td>500</td>
</tr>
<tr>
<td>Length of the Shorter Column (ab and a’b’)</td>
<td>490</td>
</tr>
<tr>
<td>Width of the Columns</td>
<td>2</td>
</tr>
<tr>
<td>Depth of the Columns</td>
<td>10</td>
</tr>
<tr>
<td>Initial Imperfection (ε)</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 3-2: Specimen Parameters for the Simulation.

<table>
<thead>
<tr>
<th>Specimen Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus</td>
<td>20 GPa</td>
</tr>
<tr>
<td>Length</td>
<td>3 µm</td>
</tr>
<tr>
<td>Diameter</td>
<td>200 nm</td>
</tr>
</tbody>
</table>
Table 3-3: Comparison of the Young’s Modulus Values.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Young’s Modulus Value (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Value</td>
<td>20</td>
</tr>
<tr>
<td>FEA Simulation Value</td>
<td>20</td>
</tr>
<tr>
<td>Analytical Value</td>
<td>23.36</td>
</tr>
</tbody>
</table>

Figure 3-6: Force vs. Displacement Plot for the Simulated Tensile Experiment.

The reasons for the deviation between the analytical and simulation values are computational inaccuracies in non-linear modeling in ANSYS, modeling of the
imperfection in the analytical expressions and the deviation in force and displacement values for single beam between analytical expressions and FEA simulation.

During FEA simulation, it was observed that, for larger applied displacements or stiffer specimens the device structure shifts into the next mode of buckling, as illustrated in figure 3-7 A. This shift of buckling mode causes translation of one end of the specimen (perpendicular to the specimen axis), in addition to tensile loading. This undesired shift of buckling mode can be avoided either by fabricating moment supports (shown in figure 3-7 B) for the device or by increasing the effective moment of inertia (increasing the gap between the columns ab and a′b′/ and columns cd and c′d′).

The analytical expressions were used to estimate the resolution of the device for different kinds of specimens and the results are tabulated in table 3-4. The resolution of the device is defined as the change in force and displacement on the specimen that corresponds to 1 µm change in lateral displacement, which can be resolved in optical and electron microscopes. It is to be noted that since the applied load distributes between the sensor beams and specimen, the force resolution is higher for specimens with lower stiffness (Young’s modulus) or softer materials such as polymers and biological specimens. Thermomechanical noise of these structures is on the order of 1.5 nanometers (calculated using equipartition energy methods at room temperature for individual columns), which can be neglected while measuring displacements on the order of a few microns or a few hundred nanometers [9]. The device structure consists of beams that are 2 µm wide, which result in stable device structures compared to sub-micron thick cantilevers required for the same force resolution [10].
At ambient temperature, displacement measurements are on the order of microns and the structural stability makes the device less susceptible to thermal drift, expansion and
softening, which are critical issues in devices with very low signal to noise ratio. In the next section, the calibration procedure for the microdevice is discussed.

Table 3-4: Estimated Resolution of the Sensing Philosophy for Different Materials.

<table>
<thead>
<tr>
<th>Specimen Material</th>
<th>Representative Young’s Modulus (Range of modulii)</th>
<th>Typical force and displacement resolution values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon, silicon oxides, nitrides and metallic thin films</td>
<td>170 GPa (100 GPa to 400 GPa)</td>
<td>115 nN and 25 nm</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.1 GPa (1 MPa to 1 GPa)</td>
<td>750 pN and 28 nm</td>
</tr>
<tr>
<td>Biological specimen</td>
<td>0.1 MPa (100 Pa – 100 MPa)</td>
<td>0.74 pN and 35 nm</td>
</tr>
</tbody>
</table>

3.6 Calibration Procedure for the Microdevice

Uncertainties in the fabrication processes may result in the actual device dimensions being different from design (expected) values. Therefore, it is very important to have a calibration scheme for the devices. In this study, the devices are fabricated without any specimen. Hence, the device was loaded and the force on the specimen (assuming the specimen was present) was estimated from the measurement of lateral displacements of the columns. In the absence of any specimen this force is zero, but due to uncertainties in fabrication processes and approximations in analytical expressions
there might be a finite force. The force on the specimen is related to the lateral
displacements of the columns via the cross-sectional moments of inertia of the columns
(‘I’). The moments of inertia of the columns were varied to re-estimate the force,
maintaining the same values of lateral displacements. The moment of inertia values were
varied such that the force estimated was nearly zero. The effective moments of inertia
(‘effective I’) for which the force is nearly zero are taken as the calibrated values for the
device. Further details on the calibration procedure are given in appendix B.

3.7 Motivation for an Alternative Design for the Microdevice

In the device design discussed in previous sections, an initial imperfection is
introduced in the column to induce buckling in a preferred direction and obtain a
symmetric buckled configuration. However, the initial imperfection leads to high degree
of non-linearity in the initial deformation of the column. This non-linearity makes the
estimation of force (P) on the column very susceptible to errors in measurements of
lateral displacement (D) of the column. Consider the P – D curves (figure 3-8 A) for a
column (1000 µm long, 10 µm deep and 2 µm thick) with and without any initial
imperfection (initial imperfection is 3 µm). It can be seen from the plot that the curve is
highly non-linear until 20 µm of D, which corresponds to 1 µm of axial displacement
(specimen displacement). Due to the high non-linearity, the error in P with respect to D is
proportional to 1/D in a beam with initial imperfection. This results in a large error in
estimation of force when there is an error in measurement of lateral displacement, in the
early stages of loading. The percentage errors in estimation of force on a column
corresponding to a 30 nm error in measurement of lateral displacement (this is the displacement measurement resolution in SEM) for a column with and without any initial imperfection are shown in figure 3-8 B.

Figure 3-8: Errors due to Initial Imperfection.
In a beam with no initial imperfection, the error in $P$ with respect to $D$ is linear with $D$ and, as a result, the error in force estimation is small. Hence, the initial imperfection in a column causes instabilities in the initial deformation region. This leads to errors in estimation of force in the initial deformation of the specimen using the microdevice described in the previous section.

To further elaborate this point, a tensile loading experiment was simulated in ANSYS (using procedures discussed in section 3.4) and the force on the specimen is plotted against displacement of the specimen (figure 3-9). The values for the parameters of the device and the specimen are listed in table 3-1 and table 3-2, respectively and the error in measurement of lateral displacement, $D$, is assumed to be 30 nm. From the plot, for 1 $\mu$m deformation of specimen (figure 3-9 A), it can be seen that the error band (bound by dashed lines) for force on the specimen is very close to the nominal curve for force versus displacement (solid line). However, a magnified plot for 100 nm deformation region of the specimen (figure 3-9 B) indicates that the error band is large compared to the nominal value of force. As a result, the device design is susceptible to errors in measurement of lateral displacements in the initial deformation region, where the errors in force estimation are comparable to magnitudes of the forces. Hence, the microdevice is useful for studying specimens in the later deformation stages (greater than 2 % strain), where the magnitudes of force are large compared to the errors. The microdevice can be used to compute properties like Young’s modulus and tensile strength if the fracture strain of the specimen is high (greater than 2 %). Figure 3-10 plots the percentage error in force on specimen vs. specimen displacement to highlight the fact that operation of the device is suited for force measurements at higher strains.
For 100 nm (3.3 % strain) and 500 nm (16 % strain) specimen displacements the errors in estimation of force are 8.5 % and 0.4 %, respectively. In the next section, an alternative
design based on the philosophy of buckling beams is presented to minimize the errors due
to the instabilities in the initial deformation region resulting from an initial imperfection.

![Figure 3-10: Error in Force Estimation for the Microdevice.](image)

### 3.8 Alternative Design for the Microdevice based on Buckling Columns

As explained in the previous section, the initial imperfection in the columns makes the structure highly susceptible to errors during the initial deformation of post-buckled columns. To address this issue, a column with no initial imperfection is incorporated in the design of the microdevice. A column with no initial imperfection is not influenced by error in measurement of lateral displacements during the initial deformation, as illustrated in figure 3-8. Tensile experiments for mechanical characterization of material require the specimen to be connected in series between two springs, as shown in figure 3-1. The microdevice discussed in the previous section is
adequate for mechanical testing of softer specimens like biological cells, where the forces on the specimen are very low (nano to pico-Newton) and for studying large strain deformation (greater than 2%). From this perspective, nanowires are interesting specimens for mechanical characterization, because very high displacement resolution is required, due to their small lengths. However, the force resolution need not be high since the small length scale endows the nanostructures with high strength and hence the forces are on the order of hundreds of nano-Newton to tens of micro-Newton. Application of linear springs produces satisfactory results for thin films, where force and displacement resolutions are on the order of micro-Newton and a few hundreds of nanometers, respectively [3], but not for nanowires, where ultra-high resolution displacement sensing is a critical feature. Hence, a device design that exploits the displacement amplification phenomenon in post-buckled columns in linear springs is suited for mechanical characterization of nanowires.

The schematic of the proposed alternative design for the microdevice is shown in figure 3-11. The darker regions in the schematic are fixed parts of the device, while the gray structures are movable elements. The device is loaded by applying displacement to the ‘head’ (left side of the schematic) towards the right. As the load is increased on the device by pushing, the critical load of the first set of buckling columns (beams) is reached. At this point, the first set of columns buckle and the U-spring gets compressed towards the right. However, the specimen does not displace until the second buckling column is deformed. Continued application of displacement to the head of the device buckles the second column, with the force being transmitted by the U-spring. At this point the movable jaw of the device moves towards the right, thus applying tensile load
on the specimen. The other end of the specimen remains fixed to the substrate via the fixed jaw. Verniers are used to measure the lateral displacements of the buckling columns. The auto-alignment beams are used to correct any off-axis loading in the device. If the applied displacement is not in the line with the axis of loading of the specimen, the auto-alignment beams compensate the resulting moment from the off-axis displacement and ensure that the device is loaded along the specimen axis.

In order to calculate the force and displacement of the specimen, consider the spring equivalent of the device mechanism in figure 3-12.
From the spring equivalent diagram, the force on the specimen is the difference in the force on the U-spring and sum of the forces in the second buckling column and auto-alignment beams. The displacement of the specimen is the axial displacement of the second buckling column. The columns here have no initial imperfection and hence, the expressions for straight columns are valid. The force and displacement of the specimen ($P_{\text{specimen}}$ and $\delta_{\text{specimen}}$) are given by (from equations 3.1 and 3.2)

$$P_{\text{specimen}} = k_1 (\delta_1 - \delta_2) - P_{cr2} \left( 1 + \frac{\pi^2 D_2^2}{8L_2^2} \right) + k_{aa} \delta_2$$  \hspace{1cm} (3.7)

and

$$\delta_{\text{specimen}} = \delta_2,$$  \hspace{1cm} (3.8)

where,
The smallest flexural rigidities of the U-spring and auto-alignment beams are denoted by $\kappa_{uspring}$ and $\kappa_{aa}$, respectively, $l_{aa}$ and $n_{aa}$ are the length and number of auto-alignment beams respectively, $D_1$ and $D_2$ are the lateral displacements of the first set and second buckling beams, respectively, and $l_{uspring}$ is the length of one of the arms of the U in U-spring. By measuring the lateral deflections of the buckling columns and using equations 3.7, 3.8 and 3.9, the force and displacement of the specimen can be estimated. Since the lateral displacements are magnified versions of the axial displacements, the displacement resolution of the device is greatly enhanced. For example, if the lateral displacement measurement resolution is 100 nm (easily achievable in a SEM) then the specimen displacement resolution is roughly 1 nm (figure 3-2 B). Also, the spring constant of the second buckling column is very small after the column buckles, 0.77 mN/m (figure 3-2 C). Hence, the force resolution is primarily governed by the stiffness of the U-spring and the displacement measurement resolution. For a 120 μm length leg of the U-beam and cross-section dimensions of 10 μm by 2 μm, the spring constant is approximately 10 N/m. This translates to a force resolution of 10 nN (force resolution = spring constant * displacement resolution), which is adequate for mechanical testing of nanowires. The stiffness of the U-spring ($k_1$) governs the displacement ratio between the applied displacement and the displacement of the specimen and hence, it can be used to control the actuation resolution for loading the device. The calibration procedure for the
alternative design is same as the calibration procedure discussed for the previous design (section 3.6) because these microdevices are also fabricated without any specimens.

Although the alternative device design minimizes the instabilities in the initial deformation region, device could be used to perform experiments on nanowires for strains greater than a minimum value. From equation 3.7, the force on the specimen is the difference in the forces between the U-spring and sum of the forces on the second buckling column and auto-alignment beams. Since the buckling column has no initial imperfection, until the applied load is greater than the critical buckling load ($P_{cr2}$), there is no displacement of the specimen. As a result, the minimum load on the nanowire specimen is greater than $P_{cr2}$, although the force resolution thereafter is adequate for experiments on nanowires. Hence, the microdevice cannot capture deformation behavior in the initial loading region of the nanowire. More precisely, if the stiffness of the nanowires is $k_{nw}$, then experimental data can only be acquired for nanowire displacements greater than $P_{cr2}/k_{nw}$. For the dimensions of the buckling beam from the previous paragraphs (figure 3-2) and the specimen parameters from table 3-2, the experimental data is valid only after 7 % strain. This value for minimum limit on measurement strain can be reduced for a lower critical buckling load, but this will result in the buckling beam being extremely compliant and unstable. The minimum strain limit can also be lower for stiffer and longer specimens. Hence, the alternative design for microdevice is suited for stiffer and longer specimens or can be used for mechanical characterization for large deformations. In the next section, a linear spring design for the microdevice is discussed, which avoids the need for buckling beams.
3.9 Linear Spring Design for the Microdevice

In the designs discussed in the previous sections, the non-linear stiffness of the post-buckled columns makes the measurement of forces on the column very susceptible to errors in the initial deformation region. The main advantage of the previous designs was the displacement resolution that could be achieved, due to the displacement amplification in post-buckling of columns. However, the initial experiments on zinc oxide nanowires showed that the fracture strains were relatively high (upto 10% in some cases), considering that zinc oxide is a ceramic material at the bulk scale. Also, the synthesis process for the zinc oxide nanowires was optimized to yield longer nanowires (as long as 100 μm). As a result, the displacement resolution required for mechanical characterization of the nanowires was on the order of 100 nm, which can be directly resolved in the SEM. Since the displacement amplification phenomenon during post-buckling deformation was not necessary for characterization, in the proposed design for the microdevice, the springs have linear stiffness.

Figure 3-13 shows the schematic of the proposed device design with linear springs. The device is loaded by applying displacement using a piezoelectric actuator to the head towards the left. The device applies tensile load on the specimen by pulling the specimen towards the left. The force on the specimen is sensed by the force sensor beams. The auto-alignment beams ensure uniaxial loading along the length of the specimen. The displacement of the specimen can be estimated by measuring the displacements of the two ends of the specimen, and the force on the specimen can be estimated using the spring constant of the force sensing beam.
The spring equivalent of the microdevice design is same as the schematic of the uniaxial tensile loading (figure 3-1), except that in the microdevice design the first spring \( k_1 \) is absent. The expressions for force and displacement on the specimen are given by

\[
\delta_{\text{specimen}} = \delta_1 - \delta_2 \tag{3.10}
\]

and

\[
F_{\text{specimen}} = k_f \delta_2 = \left( \frac{24 \kappa}{L_{fs}^3} \right) \delta_2, \tag{3.11}
\]

where \( \kappa \) is the smallest flexural rigidity of the force sensing beam. The displacement resolution of the microdevice is essentially the resolution of SEM imaging, which is less than 100 nm. The spring constant of the force sensor for 500 \( \mu \)m long beam \( L_{fs} \) and cross-section dimensions of 2 \( \mu \)m by 10 \( \mu \)m is 0.2 N/m, and hence, the force
measurement resolution is less than 20 nN. Thus, the force and displacement resolution of the microdevice design with linear springs is adequate for mechanical characterization of long nanowires. In the current design for microdevice, the only parameter that requires calibration is the spring constant of the force sensing beams. The dimensions of the force sensing beams are accurately measured in the SEM and the spring constant of the specimen is calculated using equation 3.11. In the previous design of the microdevice based on buckling beams, a more rigorous calibration procedure was used because the non-linear stiffness of the springs made the device design very susceptible to errors in measurement of displacements and device dimensions. However, for a linear spring design, the errors in measurement of dimensions do not translate to significant errors in estimation of spring constants. Hence, no calibration procedure was used for the linear spring design for the microdevices. In the next section, the fabrication processes for the microdevices are discussed.

3.10 Fabrication of the Microdevices

The different types of microdevices were designed with different values for the various parameters (such as length and width of the columns and beams) in a mask layout editor (L-EDIT from Tanner Research). The design was converted to a positive chromium mask using a laser-writer (Heidelberg DWL66). The mask fabrication process is essentially a lithography process. The starting material is a 5 mm thick glass (transparent material) on which is deposited a thin chromium film (about 200 – 300 nm thick) that acts as the opaque material. A photosensitive polymer called photoresist
(AZ1518) is deposited on the chromium. The photoresist is exposed to the laser writer, which writes the device design (in the software form) onto the photoresist. The mask is developed in MF CD-26 (photo-developer) to obtain photoresist patterns of the device on the mask. The chromium is etched in a chrome etchant (1020 Chrome Etch) to transfer the device pattern onto chromium, and the photoresist is removed using Positrip EKC 830. The hard chromium mask can be used multiple times to create photoresist patterns of the device on silicon.

To fabricate the device, photoresist (Shipley 3012) is spun on the silicon device layer of a silicon-on-insulator wafer (SOI), which is 10 - 20 μm thick. A SOI wafer consists of three layers, a top device layer made from single crystal silicon on which the devices are fabricated, a middle silicon-oxide layer which is the sacrificial layer used for making the devices freestanding (about 2 μm thick), and the bottom handle silicon layer for handling and processing of the wafer (about 300 to 500 μm thick). The photoresist on the SOI wafer is exposed to ultraviolet light (UV) through the chromium mask using a mask aligner (Karl Suss MA6). The wafer is developed (MF CD-26) to obtain photoresist patterns of the device on the device layer of the SOI wafer. Deep Reactive Ion Etching (AMS-100 SE I-SPEEDER ICP RIE) or the Bosch Process is used to etch the patterns onto the silicon device layer with photoresist as the mask. This is a dry etching process (SF6 based) and can achieve high aspect ratio features (upto 1:20), otherwise not possible with conventional wet etching. The silicon oxide sacrificial layer was etched using a vapor HF (hydrofluoric acid) etching system, which is a modified version of the set-up developed by other researchers [11, 12]. Vapor phase HF etching is used since it avoids stiction problems, which are normally inherent in wet etching processes. The HF etching
time is controlled such that the oxide is removed from underneath those features that are required to be free-standing. Finally, the photoresist is removed using oxygen plasma (M4L) to obtain single crystal silicon microdevices. For performing electro-mechanical experiments, the devices can be coated with metal and the two ends of the specimens will act as electrically isolated pads, due to the insulating oxide layer below. The fabrication sequence for the devices is shown in figure 3-14.

Figure 3-14: Schematic of the Fabrication Process for the Microdevices.
The SEM image of the fabricated microdevice based on two sets of buckling beams (first design with initial imperfection) is shown in figure 3-15.

![Figure 3-15: SEM Image of the First Design for the Microdevice.](image)

The bottom right of figure 3-15 shows a magnified view of the jaws; the specimen is placed between the jaws. On applying displacement to the device, the movable jaw moves towards the right, thus applying tensile load on the specimen. The bottom left of figure 3-15 shows a magnified view of the verniers, which are used to measure the lateral displacements of the columns. Figure 3-16 shows the SEM image of the microdevice based on the second design with straight columns as buckling beams.
The verniers are used to measure the lateral displacement of the first set of buckling columns and the second buckling column. The bottom right of figure 3-16 shows a magnified view of the jaws; the specimen is placed between the jaws. On applying displacement to the device, the movable jaw moves towards the right, thus applying tensile load on the specimen. The bottom left of figure 3-16 shows a magnified view of the U-spring, which is used to transfer the applied load to the specimen. Figure 3-17 shows the SEM image of the microdevice with linear springs.
The inset on the left top corner is the image of a zinc oxide nanowire, placed between the two jaws of the device. The tungsten probe is used to transfer the displacement loading from the piezoelectric actuator to the devices. The verniers are used to measure the displacements of the nanowire and to estimate the force on the nanowire, using the force sensing beam.

In the next chapter, the nanowires synthesis process and the specimen preparation techniques are discussed.
3.11 References


Chapter 4

Nanowire Synthesis and Specimen Preparation

In the next section, the synthesis process for zinc oxide nanowires is discussed.

4.1 Zinc Oxide Nanowire Synthesis

Zinc oxide (ZnO) nanowires were synthesized by the vapor-liquid-solid (VLS) mechanism using gold as a catalyst [1]. The Lindberg Anneal single tube furnace (Blue M) was used for the nanowire growth process. Pictures of the furnace and quartz tube are shown in figure 4-1.

Figure 4-1: Furnace used for the Nanowire Growth Process.
Zinc oxide powder (Alfa Aesar Zinc Oxide 99.99%) and graphite powder (Alfa Aesar Graphite Powder 99.99%) are weighed in 1:1 ratio (by weight) in an alumina crucible. The crucible with the reactants is placed inside the quartz tube, which is inside the furnace. Argon gas flows in the tube (from right to left in figure 4-1) at 10 sccm (standard cubic centimeters per minute) and is used to carry the reactant vapors to the site of nanowire growth. The silicon samples with 20 nm gold film deposited on them ([100] face of silicon) are placed downstream from the crucible. The gold films are deposited on silicon using a DC sputtering machine. As the temperature of the crucible increases to approximately 1000 °C, the zinc oxide powder is reduced by graphite to form zinc (Zn), carbon monoxide (CO) and carbon dioxide (CO₂) vapors. The corresponding chemical reaction can be expressed as [2]

\[
\begin{align*}
\text{ZnO(s)} + \text{C(s)} & \rightarrow \text{Zn(g)} + \text{CO(g)} \\
\text{CO(g)} + \text{ZnO(s)} & \rightarrow \text{CO₂(g)} + \text{Zn(g)},
\end{align*}
\tag{4.1}
\]

where the subscripts ‘s’ and ‘g’ indicate solid and gaseous phase. The argon gas carries the zinc, CO and CO₂ vapors to the silicon samples. Meanwhile, the formation of eutectic alloy of gold (Au) and silicon (Si) droplet occurs at each catalyst site at approximately 500 °C. The gaseous products produced by the above reactions adsorb and condense on the alloy droplets. Subsequently, the following reaction is catalyzed by the Au-Si alloy at solid-liquid interface to form zinc oxide nanowires [2]:

\[
\begin{align*}
\text{Zn(g)} + \text{CO(g)} & \rightarrow \text{ZnO(nanowire) + C (s)} \\
\text{C(g)} + \text{CO₂(g)} & \rightarrow 2\text{CO(g)}
\end{align*}
\tag{4.2}
\]
The VLS growth of zinc oxide nanowires can be understood by considering the binary phase diagram of gold and zinc [3] (pg 331) in figure 4-2.

![Binary Phase Diagram of Gold and Zinc](image)

**Figure 4-2: Binary Phase Diagram of Gold and Zinc.**

The selection of the appropriate catalyst for VLS growth depends on a number of factors such as formation of a liquid alloy at the growth temperature, vapor-liquid-solid interfacial energies and inertness to reactants [4]. The catalyst should be ideally able to form a eutectic alloy with the nanowire material, and at that point the percentage of nanowire material in the binary phase should be relatively high [5, 6]. From the phase diagram, the eutectic temperature of Au-Zn phase is 683 °C, and the atomic percentage of
zinc is about 50%. Ideally, the growth temperature for zinc oxide nanowires should be between the eutectic point (683 °C) and the melting point of nanowire material, i.e. zinc (419.58 °C). However, from the phase diagram it can be seen that after the eutectic point, the temperature increases to 751 °C along the solidus-liquidus line, and then decreases. Hence, the ideal growth temperatures of zinc oxide nanowires are expected to be approximately between 420 °C and 750 °C. The zinc vapors, carried by the argon gas, condense on the gold droplet. When the gold droplet get supersaturated with zinc, incremental growth of the nanowire takes place at the droplet interface, constantly pushing the catalyst upwards. The nanowire growth terminates, when the reactant vapor flow stops, or the gold is completely used up during the reaction, or the temperature of substrate decreases to below the melting point of zinc [7]. The diameter of the nanowires is determined by the size of the gold droplets, which in turn is influenced by the thickness of the gold film deposited.

In most of the synthesis processes, the nanowire growth temperatures were between 500 and 800 °C, which is consistent with the binary phase diagram of gold and zinc (ideally between 420 °C and 750 °C). However, whenever the furnace tubes were new, nanowire growths were observed at higher temperatures also (upto 900 °C). A possible explanation for high growth temperatures is that the equilibrium phase diagrams at the nanoscale might be different from bulk, and could result in different preferential growth temperatures for the nanowires. Also, at 900 °C the atomic percentage of zinc is 10 %, which might be sufficient to supersaturate the gold droplet. Whenever growth was observed at higher temperatures, the lengths of the nanowires were shorter than the ones grown at lower temperatures. As the tube was reused, the nanowire growth was observed
at expected temperatures. However, after several growth runs the furnace tube degrades and no growth of nanowires was observed. Tube degradation occurs, because there is residual zinc on the sides of the tube after a growth process. During subsequent growth processes, these zinc deposits at elevated temperatures increase the vapor pressure, and lead to secondary nucleation events, which hinder the growth process. Hence, after each run the tube was cleaned by flowing argon gas at 10 sccm at 1000 °C for four hours. This process vaporized the zinc deposits, which were carried out by the argon gas. It was also observed that at higher flow rates of argon gas, there was no nanowire growth. At high flow rates, the reactant vapors were carried away by argon out of the tube, thus not allowing sufficient time for the nanowire nucleation reactions to occur. In some cases, growth of different nanostructures of zinc oxide such as nanobelts and nanoneedles was observed (figure 4-3 a, b), similar to observations by other researchers [8, 9]. The diameters of the nanowire ranged from 30 nm to 500 nm and lengths were from 1 µm to 100 µm. Some of the nanowires had a gold tip on the end (figure 4-3 C), indicating VLS (vapor-liquid-solid) mechanism for the growth process.

![Figure 4-3: Zinc Oxide Nanostructures.](image)
Zinc oxide has a wurtzite crystal structure (space group $C6mm$). The wurtzite structure can be thought of as two interpenetrating hexagonal close packed (hcp) lattices. Every zinc atom is tetrahedrally connected to four oxygen atoms and vice versa (figure 4-4 A).

![Figure 4-4: Crystal Structure of Zinc Oxide.](image)

Figure 4-4 A shows a unit cell of a wurtzite structure. The yellow and grey spheres are zinc and oxygen atoms, respectively. The unit cell has two lattice parameters, $a$ and $c$.

Figure 4-4 B shows the expected growth direction of zinc oxide nanowires ([0001]) and the direction of the six faces of the hexagon [10]. The nanowires were imaged inside a Transmission Electron Microscope (TEM) to determine the crystal structure and lattice parameters for the nanowires.
Figure 4-5 A shows the TEM image of a zinc oxide nanowire.

Combination of diffraction pattern (DP) and high resolution TEM (HRTEM) was used to determine the crystal structure, lattice parameters and growth direction. Figure 4-5 B shows the diffraction pattern for the nanowire, and was indexed assuming it is a hexagonal close packed crystal structure (hcp) or wurtzite structure, the expected crystal structure of zinc oxide. The lattice constants are $a = 0.32$ nm and $c = 0.52$ nm, which is close to the lattice parameters of bulk zinc oxide. The HRTEM image (figure 4-5 C) shows the lattice spacing for the zinc oxide atoms and the distance between the $c$-planes of zinc oxide. The DP and HRTEM images confirmed that the nanowires have wurtzite
crystal structure with lattice parameters close to bulk zinc oxide, and the growth direction is along the [0001] direction (i.e. the lowest order c-plane). TEM analysis confirmed the high quality (defect-free and uniformity) of the single crystals of zinc oxide nanowires. TEM DP and HRTEM cannot provide information on the purity of zinc oxide nanowires, but the purity can be estimated using X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDS or EDX) or Photoluminescence (PL) spectra. Although the zinc oxide nanowires were not examined for purity in this research, the purity of the zinc oxide nanowires has been confirmed to be very high by other researchers, who used the same VLS process for growing the nanowires [11-13]. Also, researchers have shown the lattice parameters are significantly influenced by presence of dopants (impurities) in zinc oxide nanowires [14, 15]. Since the lattice parameter values for the zinc oxide nanowires are close to that of pure zinc oxide, it can be indirectly confirmed that the purity of zinc oxide nanowires is very high.

Specimen preparation is a crucial aspect of experiments on nanostructures. The small size of the nanostructures makes it very challenging to manipulate individual specimens. Researchers have explored several techniques for specimen co-fabrication with the experimental test-bed as a technique for specimen preparation. However, the high reactivity and chemical susceptibility of the nanowires and nanotubes to fabrication processes poses several problems in adapting the co-fabrication technique. In the next section, a technique for co-fabrication of the specimen with microdevices is presented.
4.2 Technique for Specimen Co-fabrication

Although the technique for specimen co-fabrication has been demonstrated for carbon nanotubes in this research, it can be applied to any one-dimensional nanostructure. The proposed co-fabrication technique is based on the ‘photolithography’ process. Photolithography (also known as ‘optical lithography’) is widely used in micro-fabrication and nano-fabrication to create micro and nanometer size patterns. The process comprises of exposing a photo-sensitive polymer to ultraviolet light through a mask (the pattern to be transferred), and then developing the exposed polymer to obtain the patterns. Briefly, the proposed technique consists of the following steps.

1. The nanotubes or nanowires are dispersed in a solvent.

2. The solvent-nanostructure solution is mixed with a photoresist (photosensitive polymer). Alternatively, the dispersed solution is ‘sandwiched’ between two layers of photoresist, i.e. photoresist is spun on the substrate, then the nanowire or nanotube solution is spun on the photoresist, and finally another layer of photoresist is spun.

3. The photoresist mixture is spun on a substrate, typically silicon-on-insulator wafer (SOI).

4. The photoresist is then exposed to UV (ultraviolet) light through a mask, consisting of the patterns to be transferred.

5. After exposure, the photoresist is developed to obtain free-standing specimens of the nanostructure embedded in the photoresist.

The key point in this process is the removal of photoresist in the region, where the free-standing nanostructures are desired. The photoresist area that is exposed to light is
removed by the developer. Hence, a nanotube or nanowire in that region gets exposed, and is gripped by the photoresist, which was not removed by the developer [16]. The nanotubes and nanowires are smaller than the wavelength of the exposed light, and hence, are transparent to the light. The schematic of the photoresist removal process is shown in figure 4-6. Figure 4-6 A shows photoresist, with nanotubes or nanowires embedded in it, spun on a substrate. For illustration purposes, only a single nanostructure embedded in the photoresist is shown in the schematic. Figure 4-6 B shows the photoresist being exposed to UV light through a mask. The mask, along with the device patterns (sensors and actuators patterns required for the experiment), consists of open slots which are used to create the free-standing specimen. The placement of the slot determines the location of the free-standing specimen, and the length of the slot governs the gauge length of the specimen. It is to be noted that the slot length should be less than the length of the nanowire or nanotube. Figure 4-6 C shows the photoresist, after it is developed. The exposed regions are removed by the developer to result in a free-standing specimen. The free-standing length of the nanowire or nanotube is on the order of 1 µm, while the gaps in the device patterns are on the order of 10 µm. Hence, the free-standing nanostructures are obtained only in the areas where the slots are patterned.

A similar process can be used for fabricating free standing specimens in metal. In this case, the nanostructures are sandwiched between two layers of metal. The patterns (generally of photoresist) are transferred on to the metal surface. Using the patterns as the masking material, the metal is etched. As previously, the metal is etched only in the regions where the photoresist was exposed.
In the schematic of figure 4-6, the photoresist layer can be thought of as the metal layer, and the developing process (in figure 4-6) is the process of etching the metal. The photoresist is only used to transfer the pattern.

Multi-walled carbon nanotubes (MWCNT) were obtained from Zyvex. These nanotubes were functionalized so that they can easily be dispersed in xylene, one of the
common solvents used in photoresists. The photoresist used was UV5 and the solvent for UV5 was ethyl lactate. Initially, the dispersion of nanotubes was tested in ethyl lactate. MWCNT (15g) were dispersed in 30 ml of ethyl lactate by ultrasonication for 45 min. The solution was spun coat on a silicon wafer at 2000 rpm. The ethyl lactate was evaporated by heating and the silicon surface was observed in SEM to characterize the dispersion. After characterizing the dispersion, the nanotubes were directly dispersed in UV5. MWCNT (90 mg) were mixed in 15 ml of UV5 and ultrasonicated for 45 minutes. Excess MWCNT were used to ensure that the density of nanotubes was high. The photoresist mixture was then spun coat on a silicon wafer and exposed to ultraviolet (UV) light. After exposing the wafer to UV light, the wafer was developed and observed in SEM. The SEM observations validated the proposed technique to fabricate free-standing nanotubes in the regions, where UV5 was exposed. However, the dispersion of nanotubes was not good and instead of obtaining a single MWCNT, bundles of free-standing nanotubes were obtained. In some areas a single strand of nanotube was observed, but the occurrences of such specimens were few. The proposed technique was conceptually validated by this experiment, but the issue of dispersion needed to be addressed.

Instead of dispersing the carbon nanotubes directly in UV5, they were dispersed in a photoresist solvent. The MWCNT were functionalized to be dispersed in xylene (or any other photoresist solvent such as ethyl lactate). MWCNT (39 mg) were dispersed in 15 ml of ethyl lactate by ultrasonication for 45 min. A layer of UV5 was spun on a silicon wafer. On this layer, the ethyl lactate and nanotube solution was spun coat. After baking the wafer to remove the solvent, another layer of UV5 was spun on the wafer. Thus, the nanotubes were ‘sandwiched’ between two layers of photoresist. The wafer was exposed
to UV light and developed and the SEM image of the wafer is shown in figure 4-7. The nanotube was gripped at the ends by the patterned UV5 photoresist lines. It is important to note that the nanotube was intact during the wet development process, which indicates that the nanotube was firmly gripped at the end. The specimen preparation technique can be integrated with the fabrication of microdevices, needed to perform experiments on the nanostructures. The schematic of a free-standing nanowire or nanotube in polymer or metal matrix is shown in figure 4-8. The nanostructure in the figure is integrated with a microdevice for mechanical characterization experiments. For sake of illustration, only one wire or tube is shown. In the schematic, one end of the specimen is fixed while the other end can be moved by a piezoelectric actuator for applying tensile load (similar to the microdevice discussed in Chapter 3, section 3.9).

The salient features of the proposed co-fabrication technique are as follows:

1. The lithography technique allows for co-fabrication of nanotube and nanowire specimens with the microdevice. The technique does not require growth of the nanostructure on the device site, and the selectivity offered by lithography avoids the requirement for manipulation.

2. The high resolution of the lithography process enables co-fabrication with microdevices having high resolution force and displacement sensors and actuators, which are essential for mechanical characterization of nanowires.

3. The nanotubes and nanowires can be embedded in polymer or metal. This provides firm gripping of the specimen, which enhances the quality of the experimental data.
4. The proposed technique provides a reliable, repeatable and robust way of fabricating free-standing specimens in polymer or metals. Such specimens are required to perform interfacial testing of polymer and metal composites.

Although the above technique was demonstrated for carbon nanotubes, there were some issues in adapting the technique to zinc oxide nanowires. When the zinc oxide nanowires were dispersed in a photoresist solvent, the ultrasonication process broke the nanowires and very short nanowires were available for the tensile experiments. To successfully co-fabricate zinc oxide nanowire specimens with the microdevice, it is essential to develop a

Figure 4-7: SEM Micrograph of MWCNT on Silicon ‘Sandwiched’ between Polymer Layers.

Although the above technique was demonstrated for carbon nanotubes, there were some issues in adapting the technique to zinc oxide nanowires. When the zinc oxide nanowires were dispersed in a photoresist solvent, the ultrasonication process broke the nanowires and very short nanowires were available for the tensile experiments. To successfully co-fabricate zinc oxide nanowire specimens with the microdevice, it is essential to develop a
better dispersion technique so that the nanowire lengths are preserved during the specimen preparation process. Hence, alternative techniques were explored, and one of them was the pick-and-place technique.

4.3 Pick-and-place Technique for Specimen Manipulation

A microscale version of the pick-and-place technique in a focused ion beam machine (FIB, FEI Quanta 200 3D) is used to manipulate individual nanowires onto the jaws of the microdevice. In order to facilitate better gripping of the specimen, micro-posts were fabricated onto the jaws of the device using the ion beam in FIB. Zinc oxide
nanowires, obtained from NanoLab Inc., were dispersed in methanol by ultrasonication for 15 minutes. A drop of the nanowire solution was put on a gold coated 150 nm thick oxide grid, and the methanol was evaporated. The oxide grid was obtained by patterning silicon dioxide on silicon, followed by isotropic dry etching of the silicon to release the grids, and make them free-standing. Gold was sputtered on the oxide grid to enhance imaging in the FIB. A nanowire bridging a hole in the grid was located in FIB, as shown in figure 4-9 A. The ends of the nanowire were glued to the grid using FIB deposited platinum (Pt) for firm gripping. Then, a part of the grid was cut using the ion beam in FIB. A tungsten probe (Autoprobe 200 from Omniprobe) was manipulated to the cut-out grid, and was glued to the grid using FIB Pt. Finally, the tungsten probe was moved upward to ‘pick’ the grid with nanowire on it, as shown in figure 4-9 B. The grid was manipulated to the device jaws using the probe. The holes in the grid were aligned with the post on the jaws (figure 4-9 C). The tungsten probe was lowered to ‘place’ the grid on to the jaws of the device. The grid was secured to the jaws using FIB Pt, and the tungsten probe was detached from the grid. Finally, the grid was trimmed to obtain a free-standing zinc oxide nanowire specimen, as seen in figure 4-9 D.

The salient features of the pick-and-place technique are as follows:

1. The technique is a generic specimen manipulation technique. The technique does not depend on the chemistry and structural properties of the specimen, and hence, it avoids several issues associated with the technique of specimen co-fabrication.
2. Since the grid with the nanowire on it is manipulated and not the nanowire directly, this technique can be used for manipulating specimens with very small dimensions.
(lying on grids), and specimen that are difficult to directly pick-and-place due to their adhesive properties (or lack of it) with the substrate.

3. The technique provides for firm gripping of the specimen through FIB deposited platinum, which is crucial for mechanical characterization.

4. Specimen alignment is important for performing mechanical characterization experiments. The pick-and-place ensures almost perfect alignment, due to the ability to rotate the grid with the nanowire or the device (with high resolution), before placement of the specimen.

Figure 4-9: Pick-and-Place Technique for Nanoscale Specimen Preparation.
(The nanowire is 4 µm long)
The described pick-and-place technique was initially developed for manipulating shorter nanowires. The nanowire synthesis process was optimized to yield longer nanowires, and a simpler version of the pick-and-place technique was developed. In the new technique, since the nanowires were long they were directly manipulated. The various steps of the modified pick-and-place technique are shown in figure 4-10. A silicon chip with nanowire growth (VLS growth) is placed inside the FIB. The tungsten probe is manipulated to a nanowire that is partly not on the substrate. Since the nanowire is free (i.e. partly not lying on the substrate), it adheres to the probe due to van der Waals forces. Then, the nanowire is cut as shown in figure 4-10 A to release the nanowire from the silicon substrate. A tungsten probe (Autoprobe 200 from Omniprobe) is manipulated to the jaws of the microdevice. The tungsten probe is gently rubbed on the jaws of the device, and the nanowire is transferred from the probe on to the microdevice (figure 4-10 C). Then, the ends of the nanowire are attached to jaws of device using FIB-Pt for firm gripping (figure 4-10 D). This technique of pick-and-place can also be performed under an optical microscope. In the next chapter, the procedures for mechanical characterization of nanowires are discussed.
4.4 References


Chapter 5

Experimental Procedures

In this chapter, procedures for different experiments for mechanical characterization at the nanoscale are discussed. Focus of most of the experiments was to estimate the Young’s modulus of nanowires. However, experiments were also performed to measure the fracture strain of nanowires, and the procedure for these experiments is discussed in the next section.

5.1 Experiments for Measurement of Fracture Strain

Zinc oxide nanowires, obtained from NanoLab Inc., were dispersed in methanol by ultrasonication for 10 minutes. A silicon chip, sputtered with 100 nm thick aluminum, was glued on to a piezoelectric actuator (piezoactuator), as shown in figure 5-1. The silicon chip was tapped in the center to induce a crack (about 1 μm wide) and the piezoactuator was stretched (in the straining direction), by applying a voltage, to obtain a crack across the chip, as shown in figure 5-1. A drop of the nanowire solution was put on the crack, and the methanol was evaporated. The piezoactuator with the silicon chip was transferred to a Focused Ion Beam (FIB) chamber. Nanowires, aligned perpendicular to the crack, were located in the FIB, and the two ends of the nanowire were fixed to the silicon substrate, using FIB platinum deposition for firm gripping. Then, the piezoactuator was actuated to strain the nanowire (axially) until it fractured.
By processing the images of the nanowire before and after the fracture, the fracture strain of the nanowire can be estimated.

This experimental set-up avoids the need for specimen manipulation and is a rapid technique for determining fracture strain of nanowires, but it cannot be used to measure force on the specimen. The force values are required for estimating Young’s modulus and other mechanical properties of nanowires. In the next section, design of a customized Scanning Electron Microscope (SEM) stage is discussed, which is used to perform in-situ mechanical characterization on nanowires.
5.2 SEM Stage for In-situ Experiments

A straining stage was designed to perform experiments inside a SEM chamber. The schematic of the stage is shown in figure 5-2. It consists of a X-Y manipulator, and the silicon chip with the microdevice is glued onto the manipulator. A tungsten probe is attached to a piezoactuator, which in turn is glued to a Z-manipulator attached to a L-channel. Using the X-Y and Z manipulators (manual linear positioners from National Apertures Inc.), the probe is brought close to the pushing head of the device. The piezoelectric actuator or piezoactuator (Thor labs, maximum displacement is 17.4 μm at 150 V) is used to apply displacement loading to the device, through a stiff tungsten probe. The size of the stage is small enough to fit it into standard SEM chambers, and is vacuum compatible. It can be used to apply controlled displacement loading with high resolution (less than 100 nm). The high resolution of the manipulators (1 μm) allows for fine positioning of the probe with respect to the device. Figure 5-3 shows an image of the fabricated stage with electrical leads for piezoelectric actuation. In the next section, the procedure for the tensile experiments of nanowires is explained.

5.3 Experimental Procedure for Tensile Experiments at Nanoscale

The nanowires were manipulated onto the jaws of the microdevice by the pick-and-place technique (described in section 4.3). Then, the silicon chip with the microdevice was attached to the SEM straining stage, and the tungsten probe was aligned with the pushing head of the device, under an optical microscope. Later, the stage was transferred to a SEM chamber.
Figure 5-2: Schematic of SEM Stage.

Figure 5-3: Customized SEM Stage for In-situ Experiments.
The piezoactuator was actuated by applying a voltage (Agilent 6010A Autoranging DC power source), which in turns loads the device. At different stages of loading, the verniers were imaged to measure the displacements of the buckling beams or force sensing beams. Figure 5-4 shows images of the verniers at different stages of loading.

![Vernier Images at Different Stages of Loading.](image)

The displacement of the buckling beams or force sensing beams were used to estimate the force and displacement of the nanowire (details in Chapter 3). The dimensions of the nanowire (measured from SEM images) were used to calculate the stresses and strains on the specimen, and obtain a stress-strain plot. In addition to tensile experiments, cantilever bending experiments were also performed to measure the Young’s modulus of nanowires, and the procedure for these experiments is discussed in the next section.
5.4 Experimental Procedure for Cantilever Bending Experiments

The zinc oxide nanowires grown by VLS (vapor-liquid-solid) mechanism generally occurred as clusters, and individual nanowires are required for the cantilever bending experiments. Individual zinc oxide nanowires were manipulated to the edge of a chip of a silicon wafer (coated with 100 nm thick gold film to improve imaging in SEM), as shown in figure 5-5 A. The nanowires were manipulated by a tungsten probe, using the direct pick-and-place technique (described in section 4.3). The nanowire was oriented perpendicular to the edge of the silicon wafer.

The end of the nanowire was ‘glued’ on to edge of the silicon wafer by platinum deposition, using a focused ion beam (FEI Quanta 3D 200 FIB/SEM), as shown in figure 5-5 B. The inset in figure 5-5 B shows the platinum deposition or ‘glue’ on the nanowire near the edge of the silicon wafer.
To study the effect of boundary conditions (at the clamped end of the nanowire), another specimen preparation technique was used for cantilever bending experiments. The technique has been previously employed by Ding et al. [1] to obtain individual boron nanowire specimens. A Transmission Electron Microscope (TEM) grid (2000 Mesh Gilder Grid from Ted Pella Inc.) was cut into two halves using a razor blade. The cut grid was gently brushed on a silicon sample with nanowire growth (VLS growth). The nanowires get deposited on the grid, and some of them are protruding out from the TEM grid, as shown in figure 5-6 (there are 2 nanowires protruding out).

Figure 5-6: Zinc Oxide Nanowires Protruding from a TEM Grid.
The boundary condition for nanowire bending, without any external clamping (attached to the TEM grid), was ascertained in the SEM. The nanowire was deflected with a tungsten probe (Omniprobe) inside a FIB chamber, and the base of the nanowire, lying on the substrate, was observed. In most of the cases, no motion in the base of the nanowire was observed, implying that the boundary condition of the nanowire can be assumed to be that of clamped boundary condition. The firm gripping of the nanowire can be attributed to the roughness of the TEM grid and static charges induced on the nanowire, during rubbing of the grid with the silicon samples.

The nanowire cantilever specimens were transferred to the FIB chamber. Bending loads were applied to the nanowires using an Atomic Force Microscope (AFM) cantilever, with a known spring constant. The AFM cantilever (MikroMasch, CSC12) was mounted on the tungsten probe tip, which is a three-axis piezoelectric actuator in the FIB-SEM (figure 5-7 A, probe is not shown in image). The SEM image plane is the X-Y plane. Then, the probe was tilted in-situ such that the tip face is aligned perpendicular to the viewing screen, parallel to the Z axis (figure 5-7 B). This will ensure that the loading direction is in the desired plane (X-Y plane). The SEM stage was rotated about the Z axis to align the longitudinal axis (length) of the nanowire parallel to the length of the AFM cantilever (figure 5-8 A). This ensures that the central axis of the nanowire and AFM tip are parallel before loading. Then, stage was tilted about the X axis to verify that the nanowire is completely in the X-Y plane. After ensuring that the nanowire and the AFM tip are aligned, cantilever bending experiment was performed in-situ inside the SEM. The schematic of the bending experiment is shown in figure 5-8 A.
Figure 5-8 A is not to scale, and in reality, the nanowire is thinner than the AFM cantilever. Figure 5-8 B shows the in-situ bending experiment inside the SEM (two different loading steps). The AFM cantilever moves vertically downwards (negative Y direction) to vertically load the nanowire, and the deflection of the AFM cantilever and nanowire tip were assumed to be the same. The stiffness of the nanowire can be estimated from the deflections of the AFM cantilever base and nanowire tip. Figure 5-8 C shows the spring equivalent of the loading experiment. From this diagram, the stiffness of the nanowire is given by

\[ k_{nw} = k_{tip} \left( \frac{y_{base}}{y_{nw}} - 1 \right). \]  

(5.1)
The assumptions for the cantilever bending experiments are

1. clamped fixed end,
2. small strains, and
3. small nanowire tip deflections.

Based on these assumptions, the stiffness of the nanowire in terms of the Young’s modulus and geometry of the nanowire is given

\[ k_{nw} = \frac{3EI}{l^3}, \]  

(5.2)
where $E$ is the Young’s modulus of the nanowire (along the longitudinal direction or growth direction), $I$ is the area moment of inertia of the nanowire (about $Z$ axis), and $l$ is the length of the nanowire. The deflections of the nanowire and AFM cantilever base were estimated from processing the SEM images during the bending experiment. Thus, using the deflection values of the AFM cantilever base and nanowire tip and equations 5.1 and 5.2, the Young’s modulus of the nanowires was estimated. The stress ($\sigma$) and strain ($\varepsilon$) on the nanowire, during the cantilever bending, are given by

$$\sigma = \frac{k_{\text{tip}} (y_{\text{base}} - y_{\text{nw}})l}{2I},$$

$$\varepsilon = \frac{3y_{\text{nw}}d}{2l^2},$$

(5.3)

where $d$ is the radius of the nanowire. Alternatively, the Young’s modulus of the nanowire can be calculated from the stress-strain plot.

In the next chapter, the results on fracture strain and Young’s modulus of zinc oxide nanowires are presented, along with discussions on the experimental observations.

5.5 References

Chapter 6

Results and Discussions

6.1 Fracture Strain of Zinc Oxide Nanowires

The experimental technique discussed in section 5.1 was used to estimate the fracture strain of zinc oxide nanowire specimens. Some of the nanowire specimens fractured close to the ends, where the nanowires were clamped. The failure at the ends implies that either the loading of the nanowire was not purely tensile or the nanowire failed at the ends due to stress concentration. Hence, the experimental data was considered for only those nanowire specimens that fractured close to the center of the wires. The length of the nanowire just before fracture was measured from the Scanning Electron Microscope (SEM) images, and compared with initial length of the nanowire to estimate the fracture strain. Hence, the values reported in this thesis are the lower limit on fracture strains.

Figure 6-1 shows the plot for fracture strain of the nanowire versus diameter of the wires with error bars. The resolution of the experimental data is limited by the pixel resolution of the SEM images. The pixel resolution for the SEM images was 12 nm, and this value was assumed to be the error in calculation of diameters and strains. Zinc oxide, which is a ceramic material on the bulk scale (fracture strains expected to be less than 1%), exhibits high fracture strains as one-dimensional nanowires.
Hoffman et al. [1] and Chen and Zhu [2] have measured the fracture strain of zinc oxide nanowires to be 4 – 8 % and 4 – 7 %, respectively, which are comparable to the values estimated in this research. Researchers have also estimated fracture strains for carbon nanotubes by tensile loading to be 2 – 6 % [3] and 3.5 – 13 % [4]. There is no data available on the fracture strain of bulk zinc oxide. During the measurement of fracture strain of zinc oxide nanowires in this research, no necking (reduction in diameter) or ductile phenomenon was observed during the failure of zinc oxide nanowires. This implies that the fracture of zinc oxide nanowires is a brittle failure, and is in agreement with observation by other researchers [1, 2] on the failure of zinc oxide nanowires. From

![Figure 6-1: Fracture Strain versus Diameter for Zinc Oxide Nanowire.](image-url)
figure 6-1, it can be also seen that the fracture strain of the nanowire increases with decreasing diameter, which was not observed by other researchers.

One of the most probable reasons for higher fracture strains at the nanoscale is that the number of defects is reduced at the nanoscale, assuming defect density remains constant. Since fracture occurs due to crack nucleation and propagation at a defect (or defects), the probability of failure is reduced as the number of defects is lower. The Transmission Electron Microscope (TEM) images of zinc oxide nanowires confirm the presence of very few defects. Also, the bottom-up synthesis process of the zinc oxide nanowires leads to fewer number of defects, compared to the top-down fabrication processes, where bulk machining can introduce defects. Another possible explanation for high fracture strains is that as the diameter decreases, the fraction of surface atoms increases, and the properties of surfaces begin to influence overall behavior of the material. Computational analysis on the structure of surfaces in zinc oxide show that the free surfaces of zinc oxide undergo significant relaxation characterized by bond length contractions [5-7]. In a recent study, Sun et al. [8], proposed a theory for size effect on mechanical properties called bond-order–bond-length–bond-strength (bond-OLS) correlation mechanism. In this theory, they suggested that bond relaxation on the surface atoms occurs due to imperfect co-ordination number, i.e. the number of neighboring atoms is different for the surface atoms (lesser than bulk atoms). The relaxation of bond-length (bond-length contraction) results in strengthening of the bond. Hence, the binding energies of surface atoms tend to be higher than bulk atoms.

In the next section, the experimental results on the modulus of zinc oxide nanowires are presented, and compared with existing results.
6.2 Young’s Modulus of Zinc Oxide Nanowires Measured by Tensile Loading

The zinc oxide nanowires were manipulated to the microdevices, (described in sections 3.3, 3.8 and 3.9) using the pick-and-place technique (elaborated in section 4.3). The initial experiments were performed using microdevices, whose designs were based on the post-buckling phenomenon (device design described in sections 3.3 and 3.8), and later experiments were performed with microdevices consisting of linear springs (device design described in 3.9). Uniaxial tensile loading was applied on the nanowires to obtain the stress-strain values (the experimental details discussed in section 5.3), and the Young’s modulus was estimated. Figure 6-2 shows a stress-strain plot with error bars for a nanowire that was tested using a linear spring microdevice. The resolution of the experimental data is primarily limited by the pixel resolution of the SEM images, which was assumed to be 12 nm. The SEM images were used to measure displacements of buckling beams and force sensors, nanowire dimensions, and microdevice dimensions. In microdevices with buckling beams, there are additional source of errors due to inaccurate modeling of the post-buckling deformation. A more detailed error analysis in measurement of Young’s modulus is presented in appendix C. The Young’s modulus for nine nanowires was 26 ± 9 GPa and one nanowire was 78 GPa (table 6-1). The diameters of the nanowires ranged from 192 to 423 nm, and the Young’s modulus was not diameter dependent, i.e. there was no trend in variation of the modulus with diameter. The error in estimation of modulus is 10 – 15 % (based on pixel resolution), which is mainly due to the error in measurement of diameter of the wire. Imperfect modeling of the post-buckling mechanics results in additional error of approximately 10 % in the microdevice
design, based on buckling beams. The variation in Young’s modulus values is on the order of errors in measurement of modulus.

Table 6-2 shows the modulus values of zinc oxide nanostructures determined experimentally by other researchers. In this thesis, for the first time a stress-strain plot for single crystal zinc oxide is presented. In all of studies in table 6-2, the growth of zinc oxide nanostructure was along the same direction ([0001] direction), and the modulus of the wire or belt was estimated along the length ([0001] direction).

Figure 6-2: Stress-strain Plot for a Nanowire in Tensile Loading.
The first four rows correspond to experimental results on zinc oxide nanobelts (rectangular cross section), and the rest of the rows correspond to experiments on nanowires (hexagonal or circular cross-section). In the experimental study in the sixth row (marked with *), researchers observed diameter dependence for the modulus, where the modulus increased from 140 GPa (bulk value according to Kobiakov [9]) to 210 GPa, as the diameters of the nanowires decreased from 550 nm to 20 nm. Most of the other researchers observed that the modulus of zinc oxide nanostructure is less than bulk zinc oxide, and the modulus of the nanostructure is not dependent on diameter of the nanowire (or the critical dimension in case of nanobelt). The range of size for which the nanostructures were tested in literature was between 20 nm and 550 nm.

Table 6-1: Measured Young’s modulus of ZnO nanowires of Different Dimensions.

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Length (µm)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>217</td>
<td>3.1</td>
<td>19</td>
</tr>
<tr>
<td>250</td>
<td>32</td>
<td>21</td>
</tr>
<tr>
<td>287</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>299</td>
<td>1.5</td>
<td>25.5</td>
</tr>
<tr>
<td>333</td>
<td>15.9</td>
<td>25</td>
</tr>
<tr>
<td>366</td>
<td>12.2</td>
<td>19</td>
</tr>
<tr>
<td>366</td>
<td>52.9</td>
<td>49</td>
</tr>
<tr>
<td>400</td>
<td>11.7</td>
<td>24.5</td>
</tr>
<tr>
<td>423</td>
<td>10.4</td>
<td>46</td>
</tr>
<tr>
<td>364</td>
<td>2.9</td>
<td>78</td>
</tr>
</tbody>
</table>
One of the prime reasons for the scatter in modulus values of zinc oxide nanostructures in literature is the difference in techniques used to estimate the modulus. Wang et al. [10], Chen et al. [14], Huang et al. [15] and Zhou et al. [17] have measured the modulus of nanowire or nanobelt using the resonance technique (details described in section 2.1.4), and hence, have effectively measured the dynamic modulus of zinc oxide. According to Nowick and Berry [19], due to anelastic relaxation in crystalline solids the Young’s modulus decreases with time, and settles to a final value ($E_R$, relaxed modulus) after a finite time. The dynamic modulus is the unrelaxed modulus ($E_U$, unrelaxed modulus). In dynamic experiments, the time period of motion of the nanowire is lower than the relaxation time (especially at nanoscale, where frequencies are on the order of megahertz), and hence, the modulus values estimated during dynamic experiments tend

<table>
<thead>
<tr>
<th>Young’s Modulus (GPa)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>TEM Resonance</td>
<td>[10]</td>
</tr>
<tr>
<td>38.2</td>
<td>AFM Bending</td>
<td>[11]</td>
</tr>
<tr>
<td>31.3</td>
<td>Nanoindentation</td>
<td>[11]</td>
</tr>
<tr>
<td>55, 108</td>
<td>Nanoindentation</td>
<td>[12]</td>
</tr>
<tr>
<td>29 ± 8</td>
<td>AFM Bending</td>
<td>[13]</td>
</tr>
<tr>
<td>140 – 210 *</td>
<td>SEM Resonance</td>
<td>[14]</td>
</tr>
<tr>
<td>58</td>
<td>TEM Resonance</td>
<td>[15]</td>
</tr>
<tr>
<td>90 – 100</td>
<td>Nanoindentation</td>
<td>[16]</td>
</tr>
<tr>
<td>106±25</td>
<td>Optical Microscope Resonance</td>
<td>[17]</td>
</tr>
<tr>
<td>97 ± 18</td>
<td>Tensile Loading</td>
<td>[1]</td>
</tr>
<tr>
<td>117, 229, 454</td>
<td>Measured Critical Buckling Load</td>
<td>[18]</td>
</tr>
</tbody>
</table>
to be higher than the values estimated during static or quasi-static experiments \((E_U > E_R)\).

Another explanation for the increase in measured modulus during dynamic experiments is that, in these experiments, an oscillating electric field is applied to the nanowire to vibrate the nanowire. The electric field induces charges on the nanowire surface, and the nanowire is deflected by electrostatic forces. Zheng and Zhu \[20\] have analytically shown that due to presence of induced charges on the surface, the measured modulus in presence of electric fields is higher than the actual modulus of the material. The increase in measured modulus is due to the fact that the electrostatically stiffened surface contributes to the measured modulus. The extent of overestimation of modulus increases with increasing aspect ratio of the nanowire, because the quantity of charges on the surface is higher. For instance, Zheng and Zhou \[20\] estimated that for aspect ratios of around 100 for copper nanowires, the measured modulus is 1.5 times the actual modulus. As a result, the modulus values measured during dynamic experiments, where the nanowire deflection is induced by electric fields, tend to be the overestimated modulus values.

In case of nanoindentation of nanowires or nanobelts, the measured modulus is the bulk modulus of material, while in case of resonance based, bending or tensile experiments the Young’s modulus (along the [0001] direction) is measured. As a result, the modulus values might be different due to difference in the nature of the modulus value that is being measured. In nanoindentation, a small volume of the material is deformed (details of the procedure in section 2.1.3). Hence, the measured modulus is a result of a localized deformation as opposed to other modulus measurement techniques, where the whole structure is deformed. Feng et al. \[16\] estimated the modulus of the
nanowires from the hardness values of the nanowires, which were measured during nanoindentation. In order to estimate the hardness of the nanowire, they had to make assumptions about the elastic properties of the nanoindenter tip and the nanowire material. In their experiments, they assumed that the elastic properties of bulk zinc oxide are applicable to zinc oxide nanowires, and this may have influenced the final estimated modulus value of the nanowire. The interpretation of experimental data during nanoindentation of nanostructures is not sufficiently developed, and is susceptible to ‘substrate effects’. Another possible reason for the differences in modulus values between different techniques is that the loading conditions are different. In uniaxial tensile loading, i.e. the loading conditions in this research and in the study by Hoffman et al. [1], the material is homogeneously deformed. However, in most of the other studies (AFM bending and resonance based), the deformation of surfaces dominate during flexural loading. In flexural based deformations (bending), surfaces of the material carry highest stresses and strains while in uniaxial tension loading, the stresses and strains are homogenously distributed throughout the bulk of the material. As a consequence, for nanowires with same diameters, the contribution of surface elasticity to measured mechanical properties is more significant in case of flexural based techniques. Another technique that was used to measure the modulus of zinc oxide nanowires was by measurement of critical buckling load, during nanoindentation of vertically grown nanowires [18]. This technique is susceptible to measurement errors inherent in the nanoindentation technique. In addition, since the experiment was not performed in-situ, the exact boundary conditions were unknown, and the uncertainty in boundary conditions could influence the measured modulus. The final technique used to measure the modulus
of zinc oxide nanowires was by tensile loading of the nanowire and measurement of the Young’s modulus at fracture [1]. Assuming no plastic deformation in zinc oxide (which is a reasonable assumption considering zinc oxide is ceramic), the modulus at fracture and the modulus at lower strains are expected to be identical. However, the modulus values reported by Hoffman et al. [1] are different from values reported in this research (tensile loading), and one of the reasons could be the difference in boundary conditions, specifically the technique of clamping the ends of the nanowires.

From the previous discussion, it can be concluded that the observed scatter in measured modulus of zinc oxide nanostructures is due to difference in experimental techniques. The deformation characteristics and the boundary conditions influence the measured modulus at the nanoscale, and their effects on the measurement need to be considered while estimating the actual modulus of the material. The salient features of the modulus value reported in this research are as follows:

- The modulus value was estimated from stress-strain data (only instance of stress-strain data on zinc oxide nanostructure), and hence, the linearity of the stress-strain data was ensured, while computing the Young’s modulus.
- The experiments were performed \textit{in-situ}, inside a SEM, that enabled for visual verification of the boundary and loading conditions.
- Since the loading was uniaxial, the measured modulus value had no contributions from strain gradients, which are present in flexural loading (the popular loading technique for measurement of modulus of zinc oxide nanostructures).
Also, the loading during the tensile experiments were quasi-static, and hence, the measured modulus values is not influenced by electrostatically stiffened surfaces, as is the case in resonance based techniques for modulus measurement.

Although researchers have not observed any diameter dependence of modulus of zinc oxide nanostructures (except Chen et al. [14]), the modulus of zinc oxide nanostructures is less than the modulus of bulk zinc oxide in [0001] direction. Most of the researchers attribute the change in modulus from bulk to nano scale to surface effects, and hence, the influence of surfaces to measured modulus is discussed in detail in the next section.

6.3 Surface Effects on Measured Modulus at Nanoscale

The surface atoms have a lower co-ordination number compared to bulk atoms, i.e. they have fewer neighbors [8]. As a result, the charge density in the vicinity of the surface is redistributed. Correspondingly, the nature of chemical bond and the equilibrium interatomic distances at the surface are different from that inside the bulk [21]. From the point of view of mechanical properties, the difference in chemical nature and length of interatomic bonds leads to surface stresses and surface energy. Hence, the mechanical properties of surfaces are different from that of bulk material. As the size of material decreases to nanoscale, the percentage of surface atoms increases. Since the number of surface atoms is higher at the nanoscale, the properties of surfaces significantly contribute to overall behavior of the material; this is called surface effect.

Researchers have incorporated the surface effect on mechanical properties of
nanoscale materials in several ways (refer to section 2.3.1 for a detailed literature review). To quantify the effect of surfaces on measured modulus, the concept of surface stresses that evolved from continuum theories will be used. Initially, Cammarata [22] had defined surface stresses to have contributions from surface energy density and its derivative with respect to strain. This definition of surface stress was refined by Miller and Shenoy [23] such that the equation for surface stress was analogous to the constitutive equation for bulk stresses. The linear constitutive equations for surface stresses ($\tau_{\alpha\beta}$) and bulk stresses ($\sigma_i$) are as follows:

\[
\tau_{\alpha\beta} = \tau_{\alpha\beta}^0 + S_{\alpha\beta} \epsilon_{\beta} \\
\sigma_i = C_{ij} \epsilon_j,
\]

where the Voigt notation has been adopted for the reducing the number of indices, $i, j$ go from 1 to 6 and $\alpha, \beta$ go from 1 to 3. The elastic constants (bulk) are denoted by $C_{ij}$, $\tau_{\alpha\beta}^0$ is the surface stress in externally unstrained material, $S_{\alpha\beta}$ is the surface elastic constant and $\epsilon$ is the strain in the material. It is to be noted that the unit of surface stress is N/m.

At the bulk scale, surface area is small compared to bulk volume, and only the second part of equation 6.1 is used to describe material deformation. However, at the nanoscale the surface area is comparable, and both the constitutive equations are required to explain the deformation behavior. As a result, the measured modulus at nanoscale has contributions from bulk elastic properties ($C_{ij}$) and surface elastic properties ($\tau_{\alpha\beta}^0$ and $S_{\alpha\beta}$), while at the bulk scale the measured modulus is defined by bulk elastic constants only. Young’s modulus of zinc oxide nanowires has been primarily measured by tensile or flexural loading at the nanoscale. Incorporating the effect of surface stresses in the
mechanics of deformation (using equation 6.1 for surface stresses), the measured modulus (in the [0001] direction) during tensile and flexural loading is given by

\[
E_{\text{measured}} = E_{\text{bulk}} + \frac{1}{d} \left( 8S_{\alpha\beta} + f \left( E_{\text{bulk}}, S_{\alpha\beta}, \tau_{\alpha\beta}^0 \right) \right) - \text{Flexural}
\]

\[
E_{\text{measured}} = E_{\text{bulk}} + \frac{1}{d} 4S_{\alpha\beta} - \text{Tensile}
\]

where \(d\) is the critical size of the material (in case of a wire \(d\) is the cross-sectional diameter), \(E_{\text{measured}}\) is the measured modulus, \(E_{\text{bulk}}\) is the Young’s modulus at bulk scale (a function of \(C_{ij}\)), \(\tau_{\alpha\beta}^0\) and \(S_{\alpha\beta}\) are the surface elastic constants, and \(\alpha = 1\) and \(\beta = 1\) in the required direction of measurement. The details of the derivation and the function \(f\) are provided in appendix D. It can be seen from the above equation that the measured modulus is greatly influenced by the surface elastic constants when size of the material \((d)\) is small.

From equation 6.2, the measured modulus of the material should be a function of diameter \((d)\) at small length scales. However, for zinc oxide nanowires, most of the researchers have not observed any diameter dependency of the Young’s modulus. This implies that the surface effect is not a significant factor contributing to the reduction in the modulus of zinc oxide nanowires compared to bulk zinc oxide. This claim can be further justified by quantifying the effect of surface stresses on the measured modulus using equation 6.2. In all the experiments for measurement of Young’s modulus, the zinc oxide nanostructures were grown in the [0001] direction, and the modulus was measured in [0001] direction. Using the elastic constant values of bulk zinc oxide (determined experimentally by Kobiakov [9]), the Young’s modulus in [0001] direction is 140 GPa, i.e. \(E_{\text{bulk}} = 140\) GPa. There is no data available in literature regarding the surface elastic
constants of zinc oxide. Shenoy [24] and Dingreville et al. [25] have determined the surface elastic constants for several metals using atomistic simulations, and similar calculations have to be performed for zinc oxide to estimate the surface elastic properties. In this research, the surface elastic constants were estimated using semi-empirical techniques. Jiang et al. [26, 27] proposed a model for the surface stresses in semiconductor (zinc oxide is also a semiconductor) that is given by

\[ f = \sqrt{\frac{3\gamma_{sl}d_{bond}B}{4}}, \quad (6.3) \]

where \( \gamma_{sl} \) is the solid liquid interface energy, \( d_{bond} \) is the equilibrium bond length for zinc oxide (1.973 Angstroms), and \( B \) is the bulk modulus of zinc oxide. The equation for surface stress was established based on thermodynamic consideration of the size dependence of solid - liquid interface energy, under an assumption that the solid - liquid interface of a particle immersed in surrounding liquid disappears, when almost all atoms of the particle are located on its surface [27]. The solid liquid interface energy (\( \gamma_{sl} \)) can be related to the surface energy of \( 0110 \) surface of zinc oxide, which is the typical surface of zinc oxide nanowires. Using the value of surface energy of \( 10\overline{1}0 \) zinc oxide [7], \( \gamma_{sl} \) was estimated as 0.258 J/m\(^2\). Using equation 6.3, the surface stress (\( f \)) for \( 10\overline{1}0 \) face of zinc oxide is 2.312 N/m. The surface stress is assumed to be the stress at zero strain, and \( \tau_{11}^0 = f = 2.312 \) N/m. To estimate the strain dependent surface elastic constant of zinc oxide (\( S_{11} \)), the equivalence between zinc oxide and a material with known surface elastic constants is considered. The magnitude of surface stresses can be related to the interatomic bond strength and distance, and the arrangement of the atoms (inferred from discussion on origin of surface stresses by Haiss [21]). The bulk modulus (\( B \)) of a
material is a function of the interatomic bond strength and distance, and hence, platinum can be considered to be equivalent to zinc oxide in that sense; for platinum $B = 144$ GPa and for zinc oxide $B = 143$ GPa. The surface elastic constants of platinum have been estimated using atomistic simulation by Shenoy [24]. From point of view of atomic arrangements, the (111) crystal face of platinum (fcc metal) is equivalent to (10̅10̅) face of zinc oxide, since they both belong to the plane point group, 6mm. As a result, the surface elastic constant, $S$, for zinc oxide is equivalent to $S_{1111}$ or $S_{11}$ (reduced indices notation) of (111) face for platinum; for zinc oxide $S_{11} = -12.67$ N/m (the relaxed surface elastic constant is considered).

The values of surface and bulk elastic constants from the previous paragraphs are substituted in equation 6.2, and the effect of surface stresses on the measured modulus ($E_{0001}$) during tensile and flexural loading (cantilever bending) is quantified in figure 6-3. The measured modulus is estimated for nanowire diameters ranging from 20 nm to 550 nm, which represents the range of diameters of nanowires experimentally characterized in literature and this research. It can be seen from the plot that the influence of surface stresses is much greater in flexural loading, and this is in agreement with Miller and Shenoy [23], who computationally estimated the effect of surface stresses on Young’s modulus. In tensile loading, the modulus measurement is negligibly influenced by surface stresses, and for nanowires with diameters as low as 20 nm the Young’s modulus slightly decreases from 140 GPa (bulk value) to 137.5 GPa. Even in case of flexural loading, the modulus decrease, due to surface effect, is not significant enough to explain the experimentally observed decrease in modulus of zinc oxide nanostructures. For instance, for 40 nm diameter nanowire (most of the nanowires tested in literature have a larger
diameter), the modulus in flexural loading is approximately 130 GPa, which is still much larger than the experimentally measured modulus. This implies that the effect of surface stresses, in isolation, cannot be used to explain the significant decreases in modulus of zinc oxide nanowires.

![Figure 6-3: Effect of Surface Stresses on Measured Modulus.](image)

Also, from the plot (figure 6-3) and equation 6.2, it can be inferred that the Young’s modulus at the nanoscale should be a function of diameter of the wire. However, researchers have not observed any diameter dependence of Young’s modulus, which is another indication that surface effect is not a dominant factor to explain size effects in modulus of zinc oxide nanostructures.
The inset in figure 6-3 shows the variation in measured modulus during flexural loading of nanowires with diameters less than 20 nm. For nanowires with diameters less than 14 nm, the Young’s modulus becomes negative implying that continuum mechanics is no longer valid at this length scale. However, for a 14 nm diameter nanowire the modulus estimated during tensile loading is 136 GPa. Therefore, tensile loading is the preferred technique for mechanical characterization of materials (measurement of fundamental properties), due to the minimal influence of surface properties. Figure 6-3 also illustrates that at nanoscale the measurement technique used to estimate mechanical properties influences the measured value. Due to surface effects (figure 6-3), the modulus of zinc oxide decreases with decreasing size, because the surface elastic constant ($S$) is negative. Hence, the sign of surface elastic constant determines the direction of change in modulus as the size of the material is reduced to nanoscale. It is to be noted that surface elastic constants can assume a negative value as opposed to bulk elastic constants, which are always positive [24]. Thus, the magnitude of the surface elastic constants determine the rate of change of modulus with size due to surface effects, and the sign of surface elastic constants determine the direction of change. In conclusion, the analysis in the preceding paragraphs shows that difference in Young’s modulus values between nanoscale and bulk zinc oxide cannot be explained by considering surface effects in isolation. In the previous discussion, the effect of intrinsic surface stresses was considered. However, similar arguments can be used to study the effect of surface stresses due to other factors (such as synthesis process induced stresses) on mechanical properties of nanoscale materials. In the next section, the results of cantilever bending experiments on zinc oxide nanowires are presented.
6.4 Young’s Modulus of Zinc Oxide Nanowires Measured by Cantilever Bending

It can be inferred from the preceding analysis that surface effect cannot explain the decrease in modulus of zinc oxide nanowires compared to bulk zinc oxide, even in the case of flexural (bending) deformation. However, most of the experimental techniques (AFM bending and resonance based) used to estimate the modulus of nanowires consists of flexural deformations, and hence, other factors such as boundary conditions could influence the measured modulus. Another advantage of performing bending experiments is characterization of the nanowire deformation for low strains. Due to buckling instabilities in the microdevice design and low displacement resolution in microdevices with linear springs, the stress-strain data is not accurate in the early deformation (low strain) of the nanowires. However, for relatively larger deflections of the nanowire during flexural deformations, the strain values are lower, because the strain is proportional to inverse of aspect ratio, i.e. proportional to \( \frac{d}{l} \) (section 5.4.) Since the aspect ratios of nanowires are very large, the strains in the nanowire during bending are small. Hence, to investigate the low-strain deformation of nanowires and explore the effects of boundary conditions, the experimental technique discussed in section 5.4 was used to measure the Young’s modulus of zinc oxide nanowires by cantilever bending. The modulus values of the nanowires (5 specimens) that were picked and placed ranged from 35 GPa to 44 GPa, and the diameters of the wires ranged from 350 nm to 750 nm (first specimen preparation technique in section 5.4). In the second type of nanowire specimens (prepared by brushing a TEM grid, section 5.4), the modulus of the nanowires varied from 18 GPa to 27 GPa (4 nanowire specimens), and the range of diameters was from 190 nm to 330 nm.
Figure 6-4 shows the stress-strain plot with error bars (based on pixel resolution of SEM images) for a zinc oxide nanowire that was picked and placed. The stress and strain in the plot are the maximum values of the stress and strain that occur at the surface of the nanowire.

![Stress-strain Plot for a Nanowire in Cantilever Bending Experiment](image)

The SEM images were used to measure displacements and dimensions of nanowires and AFM cantilever. A detailed error analysis in measurement of Young’s modulus during cantilever bending is presented in appendix C. The error in estimation of modulus is 21% (based on pixel resolution), which is mainly due to the error in measurement of diameter.
of the wire and error in measurement of the thickness of the AFM tip. The variation in Young’s modulus values is on the order of errors in measurement.

The modulus of zinc oxide nanowires measured in this research by cantilever bending is comparable to experimental results on Young’s modulus measured by other researchers using quasi-static flexural loading (38 GPa [11] and 29 ± 8 GPa [13]). However, the modulus of zinc oxide nanowires is still less than modulus of bulk zinc oxide, and shows no diameter dependency, which is consistent with discussion in previous section on the effect of surfaces on modulus of zinc oxide nanowires. Another observation from the cantilever bending experiments was that the modulus values are different for the nanowire specimens prepared by the two techniques. In the first technique, the nanowire was glued to the substrate using platinum deposition to ensure firm clamping of the nanowire. As a result, the boundary condition for cantilever bending of zero slope and zero deflection at the clamped end is satisfied (perfect clamping). In the second technique, the nanowires were not externally clamped, but the boundary condition was visually verified in the SEM. Hence, the clamped end in the second type of nanowire specimens might have a finite torsional stiffness. The presence of torsional deformation at the clamped end will lead to apparent softening of the material and reduction in the measured modulus, which is consistent with the above observation. However, during platinum deposition external stresses might be induced in the nanowire, which might influence the measured modulus. In the next section, the different factors influencing the modulus measurement during bending experiments (including ion beam induced stresses) are discussed.
6.5 Different Factors Influencing Measured Modulus in Bending Experiments

During specimen preparation for the cantilever bending experiments, it was observed that the nanowires permanently deformed due to exposure to the ion beam in FIB-SEM (Focused Ion Beam – Scanning Electron Microscope), i.e. stresses were induced in the nanowires. In case of nanowire specimens prepared by clamping using platinum deposition, the nanowires are exposed to the ion beam. To quantify the effect of ion beam exposure only, nanowires were manipulated to the substrate in a cantilever configuration, and exposed to a low dose of ion beam (30 kV, 30 pA, for approximately 60 seconds), and the deflection of the nanowire tip was measure \textit{in-situ} inside the SEM. For small deflection assumption, the moment curvature relation can be written as \cite{28} (pg 514)

\[ \frac{d^2 y}{dx^2} = \frac{M}{EI}, \quad (6.4) \]

where $M$ is the bending moment, $E$ is the Young’s modulus of the nanowire ($E_{0001}$) and $I$ is the area moment of inertia. The loading due to ion beam induced stresses is assumed to be equivalent to constant force per unit length loading ($q$) on the nanowire. For such a loading, the deflection of the nanowire tip ($\delta_{\text{end}}$) is given by \cite{28} (pg 531)

\[ \delta_{\text{end}} = \frac{ql^4}{8EI}. \quad (6.5) \]

From the tip deflection and nanowire geometry, the unit force loading ($q$) can be estimated using equation 6.5. The maximum stress due to $q$ is given by,

\[ \sigma_{\text{max}} = \frac{ql^2d}{4I}. \quad (6.6) \]
During the cantilever bending experiments, it was observed that when the AFM tip is brought close to the nanowire, the nanowire snaps to the tip due to adhesion forces (figure 6-5). By measuring the snap-in distance, the adhesion force can be quantified. For small deflection assumption, the equation for deflection of the nanowire tip due to a point force ($F$) acting at a distance of $l_{contact}$ from the fixed end of the nanowire is given by [28] (pg 531),

$$\delta_{end} = \frac{Fl_{contact}^2(3l - l_{contact})}{6EI}. \quad (6.7)$$

If the snap-in distance is considered as the deflection of the nanowire tip ($\delta_{end}$), then equation 6.7 can be used to compute the adhesion force ($F_{adhesion}$) between the nanowire and the tip ($F = F_{adhesion}$).

Figure 6-5: Nanowire Snap-in in presence of AFM Tip.
In cantilever bending experiments, another factor that needs to be accounted for is the effect of friction forces. The AFM tip slides over the nanowire during loading, because the AFM tip is constrained to move in the Y-direction only; figure 6-6 illustrates the sliding of the tip.

In figure 6-6, the initial contact of the AFM tip with the nanowire is at point A. As the tip deflects the nanowire by moving in the vertical direction the new point of contact is B. Hence, the tip slides on the nanowire from point A to point B during loading. The sliding will cause a friction force \( F_r \) to be present between the tip and the nanowire. The deformation of the nanowire is influenced by the adhesion and friction forces, in addition to the force exerted by the AFM tip. Figure 6-7 shows the different forces acting on the nanowire during cantilever bending. The ion beam induced stresses is modeled by a force per unit length loading \( (q) \). \( F_{\text{adhesion}} \) represents the adhesion force between the tip and nanowire, \( F_{\text{tip}} \) is the force exerted by the AFM tip, and \( F_r \) is the friction force between the tip and nanowire.
In case of bending of beams with very large radius of curvature ($\rho$) (beam is almost straight initially) and regular cross-section (like circular cross-section of the nanowire), the neutral axis of bending coincides with the centroidal axis of the cross-sectional area. The neutral axis of bending is defined as the axis where the resultant moment due to bending stresses is zero. However, during nanowire bending the friction force on the surface offsets the neutral axis from the centroidal axis; this offset is called bending eccentricity ($e$). $e$ is given by

$$F_r = \frac{E}{\rho} \int ydA$$

$$e = \frac{\rho F_r}{AE} \text{ for circular cross-section}$$

Figure 6-7: Forces acting on the Nanowire during Cantilever Bending.
The integration in the above equation is carried out over the cross-sectional area. The moment curvature relation with respect to loading condition in figure 6-7 and accounting for $e$ can be expressed as

$$\frac{d^2 y}{dx^2} = \frac{M}{EI}$$

$$\frac{d^2 y}{dx^2} = \frac{1}{EI} \left( -\frac{q(l - x)^2}{2} + \left( F_{\text{adhesion}} - F_{\text{tip}} \right) (l_{\text{contact}} - x) \right)$$

$$x \leq l_{\text{contact}}$$

$$= \frac{1}{EI} \left( -\frac{q(l - x)^2}{2} \right)$$

$$x > l_{\text{contact}}$$

where $\theta$ is the slope of the cantilever at $x = l_{\text{contact}}$, and $r$ is the radius of the nanowire.

From the previous discussion, it can be inferred that ion beam induced stresses, adhesion forces and friction forces influence the observed deformation during cantilever bending experiments. The magnitudes of these forces generally are expected to be low and hence, difficult to quantify. However, during experiments on nanowires with very high aspect ratios (length by diameter ratio, $l/d$), these forces are comparable to the applied loading. In order to estimate the additional stresses and forces, cantilever bending experiments were performed on nanowires with very high aspect ratios (about 350), which have cantilever bending stiffness on the order of $10 - 50$ pN/µm. The nanowires were initially exposed to a low dose of ion beam, and the tip deflection was measured inside the SEM. Using equations 6.5 and 6.6, the average unit force loading $(q)$ was 3 pN/µm, and the maximum stress was approximately 10 MPa. Then, the AFM tip was brought close to the nanowire, and the snap-in distance of the nanowire was measured. From equation 6.7, the average adhesion force was estimated to be 0.1 nN.
The AFM tip was used to apply cantilever bending load on the nanowire, and SEM images of the nanowire were recorded at each loading step. For ultra-low stiffness nanowires, the bending loads are very small and difficult to quantify, because the AFM tip deflections are very small (beyond the resolution of SEM images). Hence, indirect techniques were used to estimate the applied bending loads and friction forces. From equation 6.9, it can be seen that, for the loading condition shown in figure 6-7, the nanowire deformation profile can be represented by a fourth degree polynomial of the form, \( ax^4 + bx^3 + cx^2 \). For different loading steps, the fourth degree polynomial was fitted to the actual nanowire profile, and the two unknown forces, applied load \( F_{\text{tip}} \) and the friction force \( F_r \), were estimated from the fitting parameters. The average friction force was approximately 10 nN.

Therefore, if the applied loads or bending stresses in the nanowire are comparable to the ion beam induced stresses, adhesion force and/or friction force, the influence of these factors on the measured mechanical properties cannot be neglected. For instance, suppose the force and stress values for these factors are assumed to be the same as estimated in the previous paragraphs. Then, for cantilever bending experiments on nanowires with stiffness on the order of 30 pN/\( \mu \)m, the estimated modulus is 45 \% lower than the actual modulus, if the ion beam induced stresses, adhesion force and friction force are neglected. It is to be noted that the estimates obtained for the stresses and forces are approximate, and more detailed experiments are required to quantify the influence of the stresses and forces on the measured mechanical properties. The friction force estimated is high (10 nN) compared to the applied loads (on the order of 0.1 to 1 nN). However, such large friction forces have been observed in literature, when the contacting
areas are nanoscopic [29-32]. A detailed discussion on the origin of these large friction forces is provided in appendix E.

Another factor that needs to be considered during bending experiments is the validity of the assumption of small deflections. Since the fracture strains of nanowires are very high, the nanowires can be subjected to large deflections without failure. Small deflection assumption for straight beams implies that the slope of the nanowire profile is negligible (<< 1), and the approximate form of the moment curvature relation (equation 6.4) is valid. However, during cantilever bending experiments, the nanowires were subjected to large deflections, and the more accurate form of moment curvature relation is given by

\[
\frac{d^2 y}{dx^2} = \frac{M}{EI} \left( \frac{dy}{dx} \right)^2 \left( 1 + \left( \frac{dy}{dx} \right)^2 \right)^{3/2},
\]

(6.10)

If the effect of ion-beam induced stresses, adhesion force and friction are ignored, for applied load at the tip of the nanowire, the equation 6.10 can be written as

\[
\frac{d^2 y}{dx^2} = \frac{-F(l_{contact} - x)}{EI} \left( \frac{dy}{dx} \right)^2 \left( 1 + \left( \frac{dy}{dx} \right)^2 \right)^{3/2},
\]

(6.11)

where \( l_{contact} \) is the distance of the point of contact of the AFM tip from the fixed end.

To estimate the Young’s modulus of the nanowire for large deflections, the following procedure is adopted. The applied load (\( F \)), the area moment of inertia of the nanowire (\( I \)) and \( l_{contact} \) are the known parameters. The non-linear differential equation
(equation 6.11) is solved for different values of $E$, and the solution is matched to the actual bending profile of the nanowire. The value of $E$ that gives the closest match of the solution to the actual profile is the Young’s modulus of the nanowire. Figure 6-8 shows the best-fit non-linear differential equation solution and the actual nanowire profile for a particular loading step, in one of the cantilever bending experiments. The inset in figure 6-8 shows SEM image of the actual nanowire, loaded by the AFM tip. The dashed line in the plot represents the expected profile of the nanowire, under the assumption of small deflections (equation 6.4). The Young’s modulus estimated from the non-linear differential equation solution was 22.3 GPa, and the modulus calculated from the small deflection assumption (linear solution, dashed line) was 17.8 GPa. Although the difference between the two modulus values is not significant, ignoring the effect of large deflections might result in large errors in measured modulus for other cantilever bending experiments. For the experiment in figure 6-8, the maximum deflection was 4 $\mu$m for a 7 $\mu$m long wire.

In conclusion, ion beam induced stresses, adhesion and friction forces and the small deflection assumption influence the measured value of modulus during cantilever bending experiments. Hence, the observed decrease in modulus of zinc oxide nanowires could be an artifact of neglecting these factors, and not necessarily a size effect. In the bending experiments performed in this research, only the small deflection assumption was considered while interpreting the experimental results. The influence of other factors will be significant for ultra-low stiffness nanowires. However, the nanowire specimens for the cantilever bending experiments were relatively stiff.
The applied forces on the nanowire were approximately hundreds of nano-Newton, and the bending stresses were roughly hundreds of mega-Pascal. As a result, the effects of ion beam induced stresses, adhesion and friction forces on the estimated modulus are expected to be negligible. Another factor that could result in errors in estimates of Young’s modulus during bending experiments is the effect of bending eccentricity ($e$). Generally $e$ is considered to be zero, but the presence of surface stresses and forces results in a non-zero value for $e$. 

Figure 6-8: Large Deflection Deformation of Nanowire.
Until now, effects of surfaces and boundary conditions on the measured modulus of zinc oxide nanowires were analyzed. These effects cannot explain the large decrease in modulus of zinc oxide nanowires compared to bulk zinc oxide, and alternative theories are explored, which analyze the size effect from an atomistic point of view. In the next section, one of these alternative theories is discussed, which considers the strain induced charge variation in a zinc oxide bond.

### 6.6 Strain Induced Charge Redistribution

Fundamental properties, such as bulk modulus, can be related to the atomic arrangement, bond energy and bond distances [33-36]. For instance, Cohen [34] derived an expression to calculate the bulk modulus for the whole class of tetrahedral compounds (group IV, III-V and II-VI) in terms of the interatomic distances. For zinc oxide nanowires (II-VI tetrahedral compound), Transmission Electron Microscope (TEM) analysis confirms that the lattice constants (hence interatomic distances) for zinc oxide nanowires are same as those for bulk zinc oxide. This implies that the bulk modulus values are expected to be the same for nano and macro scales. However, the Young’s modulus of zinc oxide nanowires and not bulk modulus was measured during experiments, and the atomistic origin of Young’s modulus will be explored in zinc oxide. In tetrahedrally coordinated compounds such as diamond, the interatomic forces can be resolved into bond stretching and bond bending forces [35, 36]. In ionic tetrahedrally coordinated compounds such as zinc oxide, there is an additional contribution to the bond
force from the coulombic (electrostatic) interactions due to the effective charge on the oppositely charged ions [35].

The modulus of a material can be related to the bond energy and hence, the interatomic bond forces. For instance, the bulk modulus of a material can be written as [34, 37],

\[ B = V \left( \frac{d^2 U}{d(d_{\text{bond}}^3)} \right)^2 \frac{d(d_{\text{bond}})}{dV} \], \hspace{1cm} (6.12)

where \( B \) is the bulk modulus of the material, \( U \) is the bond energy, \( d_{\text{bond}} \) is the length of the bond, and \( V \) is volume of the bond. Hence, the modulus of a material can be derived from the bond deformation behavior (stretching and bending) and coulombic interactions.

Researchers have derived expressions for elastic constants \( (c_{ij}) \) in zinc blende (ZB) type crystals in terms of the bond deformation constants and the effective charge on the bond [35, 38]. The ZB crystal structure has a cubic crystal structure, and is similar to the diamond structure where the atoms are tetrahedrally bonded to each other, i.e. one cation is tetrahedrally connected to four anions and \textit{viceversa}. ZB crystal structure has three independent elastic constants, and the expressions for the elastic constants are [35, 38] as follows:
where \( \alpha \) and \( \beta \) are force constants corresponding to bond stretching and bond bending, \( d_{\text{bond}}^0 \) is the equilibrium bond length, \( s \) denotes the contribution due to coulombic (electrostatic) forces, and \( \zeta \) is an internal strain parameter defined by Kleinman [39]. Martin [35] defined \( s \) as

\[
s = s'C_0 \]
\[
s' = \frac{e^*}{\chi}, \]
\[
C_0 = \frac{(e^0)^2}{4\pi\varepsilon_0 d_{\text{bond}}^0} \]

where \( e^* \) is the effective charge (in atomic units) on the bond due to the ionic nature of the bond, \( \chi \) is the electronic dielectric constant, \( \varepsilon_0 \) is the permittivity of vacuum, and \( e^0 \) is the charge on a electron. Since ZB crystal structure is anisotropic, the Young’s modulus will be different in different directions, and can be estimated using the expressions for elastic constants in equations 6.13 and 6.14.
From equations 6.13 and 6.14, it can be seen that the elastic constants in ZB crystal structure are a function of the effective charge, $e^*$. For certain compounds such as zinc oxide, Phillips and Vechten [40] have shown that the effective charge ($e^*$) changes (or redistributes) with strain, i.e. when the bond is stretched, and the expression for charge redistribution is given by,

$$e^*(r) = e_0^* \left( \frac{d_{\text{bond}}}{d_{\text{bond}}^0} \right)^b$$

(6.15)

where $e_0^*$ is the effective charge at zero strain, $d_{\text{bond}}^0$ is the bond length at zero strain (equilibrium bond length), $d_{\text{bond}}$ is the bond length at some finite strain, $e^*$ is the effective charge for that strain, and $b$ is the charge redistribution index. Since $e^*$ contributes to coulombic force constant ($s$, equation 6.14), $s$ changes as the material is strained, and the strain dependence of $s$ is given by (using equations 6.14 and 6.15)

$$s = \frac{e^*}{\kappa d_{\text{bond}}^4} \left( \frac{d_{\text{bond}}^0}{d_{\text{bond}}^0} \right)^{2b-4} = s_0 \left( \frac{d_{\text{bond}}}{d_{\text{bond}}^0} \right)^{2b-4},$$

(6.16)

where $s_0$ is the coulombic force constant at zero strain ($d_{\text{bond}} = d_{\text{bond}}^0$). If the strain in the bond is assumed to be same as the strain in the material, then the strain ($\varepsilon$) can be related to the bond length as,

$$\frac{d_{\text{bond}}}{d_{\text{bond}}^0} = 1 + \varepsilon.$$

(6.17)

Combining equations 6.13, 6.16 and 6.17, it can be seen that the elastic constants of the ZB crystal structure ($c^{ZB}$) are dependent on strain in the material, because the coulombic force constant changes with strain, and can be briefly expressed as
The expressions in previous paragraph for strain dependent elastic constants are valid for ZB structure. However, zinc oxide generally occurs as a solid with wurtzite (Wu) crystal structure. Similar expressions for strain dependent elastic constants can be derived for Wu structure by considering the geometric equivalence between Wu and ZB structure. The wurtzite structure can be considered as two interpenetrating hexagonal close packed (hcp) lattices, and it has 6 independent elastic constants ($c_{ij}$). Martin [41] derived expressions for transforming the three independent elastic constants from ZB structure ($c_{\text{ZB}}$) to the six elastic constants in Wu structure ($c_{\text{Wu}}$). The underlying assumptions for the transformation are that both the crystal structures can be constructed from tetrahedral building blocks, and the two inequivalently oriented tetrahedra in Wu structure can be related to the standard orientation of ZB tetrahedron by a rotation transformation [42]. The transformation equations are as follows [41, 43]:

$$c^{\text{ZB}} = f(\varepsilon).$$ (6.18)
Using expressions for elastic constant transformation (equation 6.19) and strain dependence of elastic constants of ZB structure (equation 6.18), expressions for strain dependence of elastic constants in Wu crystal structure can be derived, and briefly expressed as,

\[ c^{\text{Wu}} = P c^{\text{ZB}} - D \]

where

\[ P = \frac{1}{6} \begin{bmatrix} 3 & 3 & 6 \\ 2 & 4 & 8 \\ 1 & 5 & -2 \\ 2 & 4 & -4 \\ 2 & -2 & 2 \\ 1 & -1 & 4 \end{bmatrix}, \quad D = \begin{bmatrix} \frac{\Delta^2}{C_5^{\text{Wu}}} \\ 0 \\ -\frac{\Delta^2}{C_5^{\text{Wu}}} \\ 0 \\ \frac{\Delta^2}{C_1^{\text{Wu}}} \\ \frac{\Delta^2}{C_5^{\text{Wu}}} \end{bmatrix} \]

\[ \overline{C}_i^{\text{Wu}} = \sum_{j=1}^{3} P_{ij} c_j^{\text{ZB}}, \quad \Delta = Q c^{\text{ZB}} \quad \text{and} \quad Q = \left( \frac{1}{3\sqrt{2}} \right) \begin{bmatrix} 1 & -1 & -2 \end{bmatrix} \]

Using expressions for elastic constant transformation (equation 6.19) and strain dependence of elastic constants of ZB structure (equation 6.18), expressions for strain dependence of elastic constants in Wu crystal structure can be derived, and briefly expressed as,

\[ c^{\text{Wu}} = f(\varepsilon). \]
The growth direction of the zinc oxide nanowires is [0001], and the modulus is measured along the growth direction. For wurtzite crystal structure, the Young’s modulus along the [0001] direction ($E_{0001}$) can be expressed in terms of the elastic constants as

$$E_{0001} = c_{33} - \frac{2c_{13}^2}{c_{11} + c_{12}}.$$  \hspace{1cm} (6.21)

From equations 6.20 and 6.21, it can be seen that the Young’s modulus is a function of strain because of the strain dependent elastic constants. To explain the differences in Young’s modulus values between nano and bulk scale, the differences in measurement techniques at different length scales is considered. The elastic constants of zinc oxide [9] bulk crystals are measured by wave propagation techniques. In these techniques, the strains on the material are negligible, and the effect of strain induced modulus variation can be ignored. Hence, the modulus values of bulk zinc oxide represent the modulus at zero strain ($E_0$). However, during experiments on nanowires, the strains on the nanowire are significantly higher (upto 10 %). The fracture strains in nanowires are much higher than bulk materials, because the number of defects is reduced as the size of the material decreases to nanoscale. Since the strains in nanowires are much higher than bulk and the modulus is a function of strain (decreases with strain as shown in the next paragraph), the modulus of zinc oxide nanowires is lower than the modulus of bulk zinc oxide. The effect of charge redistribution on the Young’s modulus of nanowires is summarized in figure 6-9. The effect of Young’s modulus dependency on strain will be quantified for zinc oxide (ZnO), and compared with zinc sulphide (ZnS). The reason for choosing zinc sulphide is that, like zinc oxide, it can exist in wurtzite and zinc-blende crystal structures. Also and more importantly, researchers have observed a decrease in modulus for zinc sulphide
nanobelts [44] from bulk value (from 118 GPa to 43 - 64 GPa) and observed no size dependence of modulus at the nanoscale. It is to be noted that the elastic constants of bulk zinc sulphide were measured with wave propagation techniques [45], similar to zinc oxide.

Initially, the effect of strain on the coulombic force constant ($s$) is computed using equations 6.16 and 6.17. The values of $s_0$ can be computed from equation 6.16 and data in a paper by Martin [35]. The values of $s_0$ and $b$ for ZnS and ZnO are shown in table 6-3. Using values from the table, the variation of $s$ with strain is plotted for ZnS and ZnO (figure 6-10) using equations 6.16 and 6.17.
In the plot, the coulombic force constant values are normalized ($\bar{s} = s / s_0$) for both compounds so that at zero strain $\bar{s} = 1$. The coulombic force constant decreases with increasing strain, due to the negative value of $b$, and the effect of charge redistribution is
higher in case of zinc oxide, since it has a higher $b$ (magnitude). To compute the effect of strain on Young’s modulus, the contribution of strain induced change in $s$ to the elastic constants in ZB structure ($c^{ZB}$) is estimated using equations 6.13 to 6.17. Then $c^{ZB}$ is transformed to the elastic constants of equivalent Wu structure ($c^{Wu}$) using transformation equation 6.19. Finally, the strain dependence of Young’s modulus in [0001] direction ($E_{0001}$) is computed using equation 6.21. To compare the effect of strain induced modulus change on both materials (ZnO and ZnS), the normalized value of $E_{0001}$ with respect to the modulus value at zero strain ($E_0$) is plotted, such that $E = 1$ at zero strain. The plot for variation of modulus with strain is shown in figure 6-11.

Figure 6-11: Strain Dependence of Young’s Modulus.
The Young’s modulus decreases with strain (due to negative value of $b$), and the reduction is more significant in zinc oxide (because of a higher magnitude of $b$).

The phenomenon of strain induced charge redistribution gives rise to piezoelectricity in different compounds such as zinc oxide and silicon carbide (SiC) [40, 46]. From the previous discussion, the charge redistribution also gives rise to strain dependent modulus. To observe these phenomena in other piezoelectric single crystals, the experimental values of modulus of a compound in the bulk scale and nanoscale are compared in table 6-4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bulk (GPa)</th>
<th>Nanoscale (GPa)</th>
<th>$b$ [40]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>118 [45]</td>
<td>43 - 64 [44]</td>
<td>-0.37</td>
</tr>
<tr>
<td>SiC</td>
<td>423 [47]</td>
<td>610 - 660 [48]</td>
<td>8.88</td>
</tr>
</tbody>
</table>

From the table 6-4, it can be seen that charge redistribution is one of the possible mechanisms to explain the observed size effect for modulus in piezoelectric single crystals, and the sign of $b$ indicates the direction of change in modulus from bulk scale to nanoscale.

Strain dependent modulus implies that the stress-strain curve is non-linear, but the tensile experiments yielded linear stress-strain response for almost all the nanowires within experimental errors.
Figure 6-12: Idealized and Experimental Stress-strain Plots for Zinc Oxide.
Figure 6-12 A shows the expected stress-strain curve for zinc oxide based on charge redistribution mechanism, while figure 6-12 B shows the experimental stress-strain curve obtained by tensile loading of the nanowire. There are several possible explanations for discrepancy between idealized and experimental stress-strain responses. The errors in experimental data might prevent the non-linear effects from manifesting. In the analysis of charge redistribution, the force constants ($\alpha$ and $\beta$) are assumed to be constant up to large strain values, which might not necessarily be true. According to charge redistribution mechanism, the expected modulus values for 5% and 10% strains are approximately 98 GPa and 70 GPa, respectively. However, the modulus values observed in literature and in this research are lower than expected values, according to charge redistribution mechanism. The prime reason for this discrepancy is that the charge redistribution mechanism was analyzed assuming an ideal crystal, and the crystal does not fracture. However, in actual experiments the nanowires are not perfect, and fracture at finite strains during tensile experiments. The effect of charge redistribution on the Young’s modulus might be affected, when the role of defects in the mechanical deformation of material becomes significant (near fracture). In spite of its limitations, the charge redistribution mechanism can be used to qualitatively explain the difference in modulus values for zinc oxide and other materials, between bulk and nano scale.

Another possible reason, for the inability of the charge redistribution mechanism to quantitatively explain the size effect in modulus, is that the effect of the mechanism was explored from an atomistic view point. The expressions for strain dependency of elastic constants were developed by considering the effect of strain induced charge redistribution on the elastic constants. The charge redistribution expression
(equation 6.15) is valid at the atomistic level, i.e. for an isolated zinc oxide bond, and the influence of zinc oxide crystal structure is not considered in the equation for charge redistribution. This could result in deviation of the expected behavior of zinc oxide bulk material from the expected behavior based on the charge redistribution phenomenon. Hence, a macroscopic description of the effect of charge redistribution is desirable to explain the mechanical response of zinc oxide. Charge redistribution phenomenon is responsible for piezoelectricity or electromechanical coupling in zinc oxide [40], which has a macroscopic or phenomenological description. Hence, a theory based on the electromechanical coupling is discussed in the next section to explain the observed size effect for modulus values in zinc oxide nanowires.

6.7 Influence of Electromechanical Coupling on Measured Modulus

Intrinsic material properties, such as the Young’s modulus, are generally discussed within a purely mechanics framework. However, it is important to recognize that zinc oxide is a highly piezoelectric material [10, 49, 50], and the effect of the strong electromechanical coupling on mechanical properties cannot be ignored. In fact, for bulk materials, the Young’s modulus measurement technique (IEEE Standard on Piezoelectricity) is carefully designed to address the issue of electromechanical coupling in piezoelectric materials [51]. However, at the nanoscale, it is challenging to characterize the material in accordance with the IEEE standard, and hence, the effect of electromechanical coupling needs to be considered. To study the effect of
electromechanical coupling, a spring-mass model of zinc oxide is considered, in presence of an electric field.

The macroscopic properties of materials can be estimated based on the microscopic behavior [34-36]. The zinc oxide at the microscopic level can be modeled as two masses, representing the cation and anion and connected by a spring of spring constant $k$, which can be related to the Young’s modulus (figure 6-13 A). Suppose a force, $F$, is applied to stretch the spring a distance $x$, then $k = F/x$. In addition to the force, an electric field ($E$) is applied directed from the anion to the cation (figure 6-13 B). Since zinc oxide has a partly ionic nature [52], the electric field also exerts an electrostatic force on the spring-mass system. In this case, spring constant $k = (F - qE)/x$, where $q$ is the charge on the ions. Thus, the electric field tends to reduce the measured value of $k$ for a positive value of $E$.

![Figure 6-13: Effect of Electric Field on Measured Spring Constant.](image-url)
The spring constant can be related to the macroscopic modulus of the material \([35, 36]\), and hence, the presence of an electric field leads to apparent softening of the material. As a result, low strain and high frequency mechanical characterization techniques are recommended by IEEE \([51]\) to minimize or suppress the influence of internally induced electric fields in piezoelectric materials.

The internal electric fields are induced in zinc oxide during straining, due to the highly asymmetric wurtzite crystal structure and ionic nature of the bond \([53, 54]\). The electromechanical coupling results in inter-dependency between electric polarization \((P_i)\) or electric field \((E_i)\) and mechanical strain \((e_i)\), and the relations can be expressed as

\[
\begin{align*}
P_i &= e_{ijk} e_{jk}, \\
e_{ij} &= d_{ijk} E_k,
\end{align*}
\]

(6.22)

where \(e_{ijk}\) and \(d_{ijk}\) are third rank piezoelectric tensors \([51, 55]\). The Einstein convention for summation has been adopted, and the indices \(i, j\) and \(k\) go from 1 to 3 to indicate the three co-ordinate axis. It is to be noted that the phenomenon of piezoelectricity in crystals exists because of the strong electromechanical coupling at the microscopic level. However, the relations in equation 6.22 are phenomological expressions, and \(e_{ijk}\) and \(d_{ijk}\) are macroscopic quantities. For zinc oxide nanowires, the growth direction is \([0001]\), which corresponds to 3-direction and the direction of tensile loading (figure 6-14). The relevant physical quantities in equation 6.22 for 3-direction can be written as

\[
P_3 = e_{33} e_3 \quad \text{and} \quad e_3 = d_{33} E_3.
\]

(6.23)
For purpose of illustration, strains, electric fields and polarization have been neglected in the transverse direction, and a more compact notation (Voigt notation) has been used by reducing the number of indices [51, 55]. The quantities $e_{33}$ and $d_{33}$ have been analytically [40] and computationally [56] proven to be positive for zinc oxide, and also experimentally verified in bulk single crystal zinc oxide [9]. Positive piezoelectric constant, $e_{33}$, implies that the electric polarization induced due to tensile strain is positive (first part of equation 6.23). Polarization is defined as the electric dipole moment per unit volume (product of charge per unit volume and charge separation). Hence, a positive polarization implies that the charges tend to separate (assuming no additional charges are externally added). Similarly, a positive value of $d_{33}$ means that the induced electric field tends to separate the charges or stretch the bond. This in turn implies that the induced electric field in zinc oxide acts in the direction as shown in figure 6-13 B, and reduces the measured value of Young’s modulus.

To quantify the effect of electric field on measured modulus, the piezoelectric constitutive equations relating stress ($\sigma$), strain ($\varepsilon$) and electric field ($E$) are used and they are given by [51, 55]
The equation 6.24 is re-written in the desired direction ([0001]), and a more compact notation is adopted for the indices; thus,

\[ \sigma_{ij} = c_{ijkl} \varepsilon_{kl} - \varepsilon_{ijk} E_k. \]  

(6.24)

where \( E_{0001} \) is the Young's modulus in the growth direction. The equation in the 3-direction reduces to a simpler form, because some of the material constants are zero due to \( 6mm \) crystal symmetry of zinc oxide [55]. It can be seen from equation 6.25 that for a positive electric field the resulting stress in the material is reduced, and hence, the measured modulus is lower. In nanoscale mechanical characterization experiments, the influence of electromechanical coupling is not considered, and hence, the measured modulus is different from the actual modulus. Equation 6.25 can be rearranged to relate the measured modulus of the material to the actual modulus, due to the electromechanical coupling, as

\[ E_{0001}^{\text{measured}} = E_{0001} - \frac{\varepsilon_{33} E_3}{\varepsilon_3}. \]  

(6.26)

The actual electric field generated internally depends on the electrical boundary conditions and the surrounding dielectric media, and is difficult to quantify. To illustrate the effect of electromechanical coupling, certain approximations are made to estimate the field and its effect on the measured modulus. From equation 6.22, the electric polarization \( P_3 \) is related to the tensile strain \( \varepsilon_3 \) (considering the effect of transverse strains) as
\[ P_3 = (e_{33} - 2e_{31})\varepsilon_3, \]  

where the transverse strains are assumed to be on the same order as tensile strain, and \( e_{31} \) is the transverse piezoelectric constant. The electric field is proportional to the polarization, and can be expressed as

\[ E_3 = K_{EP} \frac{P_3}{\varepsilon_0}, \]  

where \( \varepsilon_0 \) is permittivity of vacuum, and \( K_{EP} \) is a proportionality constant. Combining equations 6.26, 6.27 and 6.28, the expression for the measured modulus is given by

\[ E_{0001}^{\text{measured}} = E_{0001} - K_{EP} \frac{e_{33}(e_{33} - 2e_{31})}{\varepsilon_0}. \]  

The values of the elastic and piezoelectric constants of zinc oxide nanowire are assumed to be same as bulk zinc oxide, and are listed in the table 6-5 [9].

<table>
<thead>
<tr>
<th>Material Constant</th>
<th>Value (GPa or C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_{11} )</td>
<td>207.0</td>
</tr>
<tr>
<td>( c_{33} )</td>
<td>209.5</td>
</tr>
<tr>
<td>( e_{12} )</td>
<td>117.7</td>
</tr>
<tr>
<td>( e_{13} )</td>
<td>106.1</td>
</tr>
<tr>
<td>( e_{33} )</td>
<td>0.96</td>
</tr>
<tr>
<td>( e_{31} )</td>
<td>-0.62</td>
</tr>
</tbody>
</table>

Substituting the material constants values from table 6-5 in equation 6.29, the measured modulus of zinc oxide nanowires is given by
where the units for modulus values are in giga-Pascal. An accurate estimate of the influence of the internal electric field on measured modulus would require an accurate value of $K_{EP}$, which depends on the electrical boundary conditions. However, the first-principal calculations and experimental estimates of $K_{EP}$ are within the scope of future work of this research. The range of values that $K_{EP}$ can assume is between 0 and 0.6. The upper limit of the range ensures that the measured modulus due to electromechanical coupling is positive. Table 6-6 lists the values of the measured modulus for some of the $K_{EP}$ values, using equation 6.30.

Table 6-6: Measured Modulus for different values of $K_{EP}$.

<table>
<thead>
<tr>
<th>$K_{EP}$</th>
<th>$E_{0001}^{measured}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>116.1</td>
</tr>
<tr>
<td>0.2</td>
<td>92.3</td>
</tr>
<tr>
<td>0.3</td>
<td>68.4</td>
</tr>
<tr>
<td>0.4</td>
<td>44.6</td>
</tr>
<tr>
<td>0.5</td>
<td>20.7</td>
</tr>
</tbody>
</table>

For purposes of illustration, the definition of electric polarization is used to obtain an estimate of $K_{EP}$, as a specific case. From the definition, the polarization along the axial direction can be expressed as (pages 68 and 69 of [55])

$$P_3 = \chi_0 (\chi_3 - 1) E_3,$$

(6.31)
where $\chi_3$ is the dielectric constant of zinc oxide in the 3-direction, and is equal to 11.26 [9]. From equations 6.28 and 6.31, and using the value of $\chi_3$, $K_{EP} = 0.097$. Using equation 6.30, the measured modulus due to the internal electric field is approximately 117 GPa.

The analysis in the previous paragraphs shows that the presence of electric field reduces the measured modulus during tensile experiments on zinc oxide nanowires, due to the strong electromechanical coupling in zinc oxide. Most of the modulus values in table 6-6 are still larger than the values reported in this research (26 ± 9 GPa), and this is mainly because of the several approximations made in the analysis of the influence of electromechanical coupling. One of the significant approximations is the expression for the internal electric field, and hence, the uncertainty in the value of $K_{EP}$. The linear piezoelectric constitutive equations used in the previous discussion are valid only for small strains, but some of the nanowires sustained strains as high as 10 %. Also, the material properties are not expected to be constant upto large values of strains. Bester et al. [57] computationally showed that the piezoelectric coefficients for III-V semiconductors, such as gallium arsenide, are strain dependent. Hence, a more accurate estimation to account for large strain deformations would involve second order effects at the expense of quantitative characterization of the higher order parameters. In the previous analysis, it has also been assumed that the piezoelectric constants are not size-dependent. However, Fu et al. [58] measured the converse piezoelectric constant ($d_{33}$) to be large for microtubular zinc oxide crystals compared to bulk zinc oxide. Also, the effect of surrounding dielectric media, such as air and silicon, is neglected, which makes the quantification of boundary conditions more challenging.
Nevertheless, the previous discussion illustrates how the electrical and mechanical boundary conditions can influence the measurement of purely mechanical properties of piezo-electric materials such as zinc oxide. For bulk piezoelectric materials, static tests are not recommended for materials with low permittivity, such as zinc oxide, due to difficulty in maintaining controlled electrical boundary conditions [51]. The pronounced effect of electromechanical coupling on the measured modulus of nanostructures is also supported by the experimental observations of reduction in Young’s modulus for zinc sulphide nanowires [44], which are piezoelectric and no change in modulus for silicon nanowires [59, 60], which are non-piezoelectric. In the next section, the effect of electromechanical coupling in flexural deformation due to flexoelectric effect is discussed.

6.8 Flexoelectric Effect

In the previous section, the discussion on electromechanical coupling was related to the uniaxial tensile deformation of zinc oxide nanowires. However, similar arguments can be extended to flexural deformation of nanowires during three-point and cantilever bending experiments. The main difference between tensile and flexural deformation is that in the latter case the deformation is not homogeneous and there are strain gradients present in the material. Figure 6-15 shows an image of a zinc oxide nanowire in a cantilever bending experiment (flexural deformation). Figure 6-15 B shows the schematic of a section of the nanowire in bending. The dotted line represents the neutral axis, where the bending strain is zero. The strains are maximum at the outermost surfaces ($\varepsilon_{\text{max}}$),
where $e_{\text{max}}$ is a function of nanowire geometry and deflection (equation 5.3). If $r$ is the radius of the nanowire, then a strain gradient of magnitude $e_{\text{max}}/r$ is introduced in the nanowire during bending.

The presence of strain gradients induces additional polarization due to the flexoelectric effect [61, 62] in piezoelectric materials, which relates the electric polarization to the strain gradients as

$$P_i = e_{ijk} e_{jk} + \mu_{ijkl} \frac{\partial^2 u_j}{\partial x_k x_l}. \quad (6.32)$$

Here $e_{ijk}$ is the third rank piezoelectric tensor, $\mu_{ijkl}$ is the fourth rank flexoelectric tensor and $u_j$ is the deformation of the material. The Einstein convention for summation has been adopted, and the indices $i, j, k$ and $l$ go from 1 to 3 to indicate the three co-ordinate axis. Equation 6.32 is re-written in the [0001] direction, adopting a more compact notation for the indices, as

$$P_3 = e_{33} e_3 + \mu_{33} \frac{\epsilon_3}{r} + \ldots, \quad (6.33)$$

where the additional terms of transverse strains are not shown for purpose of illustration. The effect of flexoelectricity is expected to be more significant at nanoscale compared to bulk, because the strain gradients at nanoscale are approximately six orders larger than bulk. The reason for large strain gradients is because of the inverse relation between strain gradients and radius of the nanowire. There have been no computational or experimental studies on the flexoelectricity in zinc oxide.
Kogan [63] suggested the following relation to get approximate estimates of the flexoelectric constant:

\[
\mu = \frac{\chi e^0}{a},
\]

(6.34)

where \(\chi\) is the dielectric constant, \(e^0\) is the electronic charge \((1.6 \times 10^{-19} \text{ C})\), and \(a\) is the lattice constant of the material. For zinc oxide, \(\chi = 8.81 [9]\) (along 3-direction), and \(a = 3.25\) Angstroms, and hence, \(\mu \approx 5 \times 10^{-9} \text{ C/m}\). The contribution of flexoelectric effect to
the total strain induced polarization is on the order of $\mu / r$, where $r$ is the radius of the nanowire. It can be seen from equation 6.33 that flexoelectric term will dominate piezoelectric term for smaller diameter nanowires. The piezoelectric constant ($e_{33}$) along the 3-direction is approximately 1 C/m$^2$. The flexoelectric term is approximately one-tenth of the piezoelectric term, when the nanowire diameter is 100 nm. Hence, the flexoelectric effect should be considered for interpreting results of electromechanically influenced modulus measurement in cantilever bending and three-point bending experiments on thin piezoelectric nanowires (diameters less than 100 nm). In the next section, the effect of boundary conditions in tensile loading experiments is discussed.

### 6.9 Boundary Conditions in Tensile Loading

Experimental data in tensile loading is interpreted under the assumptions of perfect boundary conditions. In this section, the effects of three of these conditions on the measured modulus of the nanowire are analyzed. The nanowire specimen is placed on the top of the jaws of the microdevice during tensile experiments, as shown in figure 6-16 A. As a result, the force applied by the nanowire on the force sensing beam is at the top of the beam. In the present discussion, the linear spring design is considered (section 3.9), but similar arguments can be extended to the device design with buckling beams (sections 3.3 and 3.8). Figure 6-16 B shows the SEM micrograph of the force sensing beam and the direction and location of the force applied by the nanowire. In the figure, force is applied in the X direction. Since the force is applied at the top of the beam (and not center of the depth), the nanowire also applies a twisting moment about the Z axis to
the force sensing beam. Figure 6-16 C shows the schematic of a part of the force sensing beam and the direction of force \((F)\) and twisting moment \((T)\). When calculating force on the nanowire, the twisting of the force sensing beam is neglected, and this could result in errors in estimation of the force.

In order to quantify the influence of twisting of the beam on the measured force, the relative stiffness of the bending and twisting of the force sensing beam is calculated. Let \(2a\) be the thickness of the beam in the X direction \((2 \mu m)\), \(2b\) be the depth of the beam in the Y direction \((20 \mu m)\), and \(2l\) be the length of the beam in the Z direction \((1000 \mu m)\). The bending stiffness of the beam is assumed to be the spring constant of the force sensing beam while calculating force on the nanowire, and is given by

\[
k_{bending} = \frac{32a^3bE_{Si}}{l^3}, \quad (6.35)
\]

where \(E_{Si}\) is the Young’s modulus of silicon \((170 \text{ GPa})\). For the beam dimensions described above \(k_{bending} = 0.4352 \text{ N/m}\). The twisting or torsional stiffness of the beam is neglected while calculating the force on the nanowires, and is given by

\[
k_{torsion} = \frac{2KG_{Si}}{lb^2} \quad \text{where} \quad K = ab^3 \left[ \frac{16}{3} - 3.36 \frac{b}{a} \left(1 - \frac{b^4}{12a^4}\right) \right], \quad (6.36)
\]

where \(G_{Si}\) is the shear modulus of silicon \((52 \text{ GPa})\). For the beam dimensions described above \(k_{torsion} = 58.18 \text{ MN/m}\). The torsional stiffness of the force sensing beam is 7 orders greater than the bending stiffness, and hence, the deflection of the beam due to bending is approximately 7 orders larger than the deflection of beam due to twisting. As a result, the contribution of beam twisting to the total deflection is negligible, and the error due to neglecting of beam twisting is very small.
The second source of error with respect to the boundary conditions is the compliance of the platinum deposition (grip compliance), which is used to attach the nanowire to the device. In tensile loading experiments, it is assumed that the fixed ends of the nanowire are infinitely stiff. However, the mechanical properties of the grip (platinum in this case) result in finite stiffness at the ends, and this could influence the measured mechanical properties. The platinum deposited on the nanowire is approximately a cube of 1 μm, and the bulk modulus of platinum is 144 GPa. The stiffness of the deposited platinum is approximately 144 KN/m, which is approximately
three orders higher than the stiffness of the nanowires. Hence, the deformation of the platinum bond is three orders lower than the displacement of nanowire, and can be neglected while interpreting experimental data on nanowires. However, the nanowire could also be sliding within the platinum bond. The nanowire sliding was not visually observed during the tensile experiments. In order to quantify the sliding, the exact lengths of the nanowire during different loading steps were measured along with displacements of the verniers. The measurements of nanowire displacement based on vernier displacements include the effects of grip compliance, while the exact nanowires length measurements preclude any grip compliance. Hence, by comparing the nanowire displacement data estimated by the two techniques, the grip compliance was estimated to be approximately 0.5%. The strains on the nanowires are much higher (upto 10%), and the effect of grip compliance can be neglected. It is to be noted that the measurement of exact change in length of the nanowire is challenging due to resolution of SEM, and the estimate for grip compliance obtained is approximate. Also, no length dependence of the measured Young’s modulus was observed in tensile loading of zinc oxide nanowires, which implies that grip compliance is not a significant factor influencing the measurement of strains on the nanowire.

The third boundary condition effect that is considered is the nature of clamping of the nanowire by the platinum deposition. Ideally, the nanowire is assumed to be completely clamped by the platinum as shown in figure 6-17 A. The diagonal black line pattern on the cross-sectional view of the nanowire end shows the area of the nanowire that is clamped. In ‘perfect clamping’, the whole area is clamped. However, during actual deposition of platinum only the circumference of the nanowire cross-section is bonded to
the substrate (figure 6-17 B). As a result, due to ‘imperfect clamping’, only half the circumference is clamped. The imperfect clamping leads to deformation of the end of the nanowire, and this deformation might influence the measured mechanical properties during nanowire tensile experiments. The effect of clamping was studied by simulating both, the perfect and imperfect clamping, in ANSYS (finite element analysis, FEA software) for a nanowire with Young’s modulus of 30 GPa and aspect ratio of 50. The tensile experiment was simulated, and the force at the clamped ends was measured. For 10 % strain, the force in the clamped end for imperfect clamping was 3 % less than the force for perfect clamping.

Figure 6-17: Ideal and Actual Clamping Conditions during Tensile Experiments.
This implies that the modulus value will be underestimated by approximately 3\%. The clamping condition minimally influences the mechanical deformation of the nanowire because of the high aspect ratio of the wire. However, the effect of imperfect clamping could be significant in tensile testing of low aspect ratio nanowires. In the next section, the analysis of size effect on modulus of zinc oxide nanowires is summarized along with final comments.

6.10 Final Remarks on the Size Effect for Modulus

In this research, the Young’s modulus along the [0001] direction for zinc oxide nanowires was measured by uniaxial tensile experiments. The Young’s modulus was measured to be 26 ± 9 GPa, which is comparable to the modulus values reported by other researchers experimentally, but less than the modulus of bulk zinc oxide. The diameters of the nanowires are not small enough for surface effects due to intrinsic surface stresses to manifest, and this hypothesis was quantitatively justified. Since most of the experimental technique for measurement of Young’s modulus of zinc oxide nanostructures involve flexural loading, cantilever bending experiments were performed on the zinc oxide nanowires. The average modulus for externally clamped nanowires was 40 GPa, and that for intrinsically clamped nanowires was 22 GPa. The effects of boundary conditions, fabrication induced stresses, adhesion and friction forces, and non-linear deformation of nanowires were considered as possible factors influencing the measured modulus at the nanoscale. The strain induced charge redistribution at the atomistic level for zinc oxide results in strain dependent modulus. In spite of the
approximations involved in the analysis, the charge redistribution mechanism can qualitatively explain the difference in modulus values between nanostructures and bulk solids of the same material, on the basis of the high fracture strains at nanoscale. The charge redistribution is an atomistic phenomenon, and it macroscopically results in piezoelectricity or strong electromechanical coupling in zinc oxide. Hence, the effect of electromechanical boundary conditions on the measured mechanical properties was analyzed, and shown to reduce the measured modulus in case of zinc oxide nanowires. In case of flexural deformation, additional electromechanical coupling might be present due to presence of high strain gradients at nanoscale via the flexoelectric effect.

The effect of boundary conditions in uniaxial tensile experiments was analyzed in the form of twisting of force sensing beam, grip compliance and imperfect clamping. These boundary conditions were shown to minimally influence the measured modulus of zinc oxide nanowires. The scatter observed in experimental values of Young’s modulus of zinc oxide nanostructures is mainly due to the differences in measurement techniques. The boundary conditions such as electromechanical coupling and clamping conditions are different in different experimental techniques, mainly because it is challenging to control the experimental conditions at nanoscale. Since the modulus measurements are significantly influenced by boundary conditions at nanoscale, the measured modulus values are not consistent. In this research, the results on uniaxial compression experiments are not reported. Although the microdevices can be used to perform compression experiments, the low critical buckling load of the nanowire (because of the high aspect ratio) causes the nanowire to buckle rather than compress axially.
It is to be noted that at the bulk scale for anisotropic single crystals such as zinc oxide, uniaxial tensile technique is not the preferred technique for mechanical characterization. The main reason for the non-preference is that the properties of the crystal are different in different directions, and the elastic constants of the crystal are measured by wave propagation techniques. Hence, the Young’s modulus along the [0001] direction measured in this research is a structural property rather than a material property of zinc oxide nanowires. This argument is valid from a scientific viewpoint, where the focus is on the effect of size on the elastic constants of the material. However, the zinc oxide nanowires synthesized in this research (and by other researchers) always grow in the [0001] direction. Hence, the properties of the nanowire along the [0001] direction are important from a technological point of view. Applications of zinc oxide nanowires involving mechanical deformation are primarily governed by properties in the longitudinal direction ([0001]). As a result, the basic definitions of mechanical properties need to be revised when describing behavior of one-dimensional objects such as nanowires. In the next chapter, the present research is summarized and directions for further research are discussed.

### 6.11 References


Chapter 7

Conclusions and Directions for Further Research

In this research, the size effects on the mechanical properties of nanowires were studied. Zinc oxide was chosen as a representative material because of its technological significance. The zinc oxide nanowires were synthesized using the vapor-liquid-solid process (VLS). In order to perform uniaxial tensile experiments, microdevices were designed and fabricated. The microdevices exploited the stiffness attenuation and displacement amplification in the post-buckling deformation of slender columns to achieve very high force and displacement resolution (nano-Newton and nanometer respectively). Specimen preparation techniques were developed for nanoscale mechanical characterization. The fracture strains of zinc oxide nanowires were measured to be between 4 % and 14 %, and increased with decreasing diameter of the wires. The high fracture strains in nanowires were attributed to reduced number of defects and increasing contribution of surfaces. The Young’s modulus of the nanowires along the growth direction ([0001]) was measured to be $26 \pm 9$ GPa by uniaxial tensile experiments and 18 – 44 GPa by cantilever bending experiments. The Young’s modulus values were comparable to modulus values estimated by other researchers on zinc oxide nanostructures, but significantly lower than the modulus of bulk zinc oxide (140 GPa). Several theories for the observed size effect were analyzed such as surface effects, strain induced charge redistribution, piezoelectric and flexoelectric effects, and non-ideal
boundary conditions. In the next section, the scientific and technological contributions of the research are summarized.

7.1 Contributions of the Thesis

7.1.1 Scientific Contributions

Researchers generally attribute the size effect in material properties to surface effects. The effects of surfaces on the mechanical properties of materials were analyzed, and constitutive equations were developed to relate the measured modulus of the material to the actual material modulus and surface elastic constants. An empirical procedure was used in this thesis to estimate the surface elastic properties of zinc oxide. The experimental results on Young’s modulus of zinc oxide nanowires in this research and other studies confirm that the modulus values are not diameter dependent, but different from bulk values. This implies that there exist some phenomena unique to the nanoscale and not influenced by surface effects, which is a diameter dependent phenomenon. The effects of boundary conditions in tensile and cantilever bending experiments were analyzed theoretically, computationally and experimentally. Although most of the boundary conditions minimally influenced the measured modulus in this research, their effects could be significant during experiments on other nanostructures. Atomistic origin of size effect in Young’s modulus of zinc oxide was studied by considering the strain induced charge redistribution mechanism. This mechanism results in strain-dependent modulus, and since the strains during experiments on nanoscale and bulk specimens are
different, the modulus values are expected be different. Since zinc oxide is highly piezoelectric, the effect of electromechanical boundary conditions on the Young’s modulus was analyzed. It was shown that the electromechanical coupling results in lowering of the measured modulus in zinc oxide. Principles of macro-scale characterization techniques for measuring mechanical properties were analyzed in the framework of nanoscale characterization experiments such as interpretation of experimental data.

7.1.2 Technological Contributions

A novel application of post-buckling mechanics was analyzed and used in design of microdevices for performing tensile experiments. Different types of micro-devices for performing uniaxial tensile experiments were developed. The salient features of the microdevices are as follows:

- High resolution force and displacement sensing and actuation.
- Ability to perform in-situ experiments in electron microscope chambers.
- Adaptability of the microdevices for different applications such as life-sciences studies or coupled-field investigations.

Different specimen preparation techniques were explored that are generic, robust, reliable and/or less cost and time intensive. Experimental techniques for nanoscale mechanical characterization (uniaxial tensile and cantilever bending) were developed, and procedures for extracting data from the experiments were also discussed. These experiments were performed in-situ in electron microscope chambers. Synthesis process for growth of zinc
oxide nanowires was developed, and the growth parameters were analyzed with reference to the binary phase diagram of gold-zinc. In the next section, directions for further research are discussed.

7.2 Directions for Further Research

Due to the piezoelectric nature of zinc oxide, the measured modulus of zinc oxide nanowires is reduced. Experiments need to be designed to specifically study the electromechanical coupling or piezoelectricity in zinc oxide nanowires. The microdevices developed in this thesis are suited for performing these types of coupled-field studies. The experimental data resolution in the initial deformation region of nanowires during tensile experiments needs to be improved. There are several advantages of superior data resolution in the lower strain regions such as loading-unloading stress-strain curves for the nanowires. Also, the initial deformation of the nanowires can be studied to capture any non-linearity in the stress-strain curve, as predicted by strain-induced charge redistribution mechanism. Researchers have observed that in single crystals, due to slipping of planes (governed by Schmid’s law), the stress-strain curves have two distinct slopes [1-5]. This could explain the reduced modulus in zinc oxide nanowires, because the stress-strain data is computed for larger strains. To confirm the slipping activity in nanowires, the tensile experiments need to be performed inside a Transmission Electron Microscope (TEM). *In-situ* experiments inside the TEM would also improve the resolution of experimental data. Experimental procedures need to be developed to perform tensile and bending experiments on the same nanowire specimen without fracturing or
manipulating the nanowire. Such experiments in conjunction with the equations for influence of surface stresses, developed in this research, could be used to experimentally measure surface and bulk elastic constants. The interpretation of experimental data in nanoscale mechanical characterization needs to be developed to minimize the influence of boundary conditions and experimental techniques on the measured mechanical properties. Specimen preparation techniques such as on-site growth and co-fabrication with the microdevices should be developed to increase the yield of experimental techniques. Also, research in specimen preparation techniques will aid in mass-manufacturing of nanostructure based functional systems. Quantum mechanical (QM) calculations such as Hartree-Fock simulations need to be performed to calculate the material constants of zinc oxide. Most of the atomistic simulations for studying the properties of nanowires use potential functions, whose parameters are fitted based on experimental data on bulk materials. QM calculations in conjunction with experimental data on nanowires can results in better computational analysis of the behavior of nanowires.

7.3 References


Appendix A

Force and Displacement on a Column with Initial Imperfection

The elastica model is used to derive analytical expressions for force and displacement of a column with initial imperfection. It is assumed that the length of the column is fixed (i.e. negligible axial strain), and the contribution of shear to deflection is negligible. The schematic of a single column with initial imperfection is shown in figure A-1.

![Figure A-1: Schematic of Column with Initial Imperfection.](image)

The general expression for bending is given by

\[
\frac{M}{EI} = \frac{1}{\rho} - \frac{1}{R_0}, \quad (A.1)
\]
where $M$ is the bending moment, $\rho$ is the radius of curvature and $R_0$ is the initial radius of curvature. The bending moment at any cross section is given by

$$M = -M_0 - Py,$$  \hspace{1cm} (A.2)

where $P$ is the axial load, $M_0$ is the initial moment in the fixed-fixed column, ‘$y$’ represents the final shape of buckled column, and ‘$y_0$’ represents the initial shape or undeformed shape. For a column with initial imperfection, the shape is initially an obtuse triangle. The equation of the column after buckling ($y$) is given by

$$y = D\sin(\omega s),$$  \hspace{1cm} (A.3)

where $\omega = 2\pi/L$, and $D$ is the maximum value of the lateral displacement. Equation of the column before buckling ($y_0$) is given by

$$y_0 = \frac{\xi s}{L} \text{ where } s < \frac{L}{2},$$

$$y_0 = \frac{\xi (L-s)}{L} \text{ where } s > \frac{L}{2},$$ \hspace{1cm} (A.4)

$$y_0 = \xi \text{ where } s = \frac{L}{2}$$

where ‘$s$’ is the co-ordinate defined at the central axis of the column along the length (along the path of the column). The final curvature is given by

$$\frac{1}{\rho} = \frac{y''}{\sqrt{1-(y')^2}},$$ \hspace{1cm} (A.5)

and the initial curvature is given by

$$\frac{1}{R_0} = \frac{y_0''}{\sqrt{1-(y_0')^2}}.$$ \hspace{1cm} (A.6)
The unknown variable in the moment equation is the initial moment in the fixed-fixed column, $M_0$. The symmetry of the problem implies that the column has points of inflexions, $C_1$ and $C_2$, at distances $L/4$ away from the supports (the points of inflexion are at a distance slightly less than $L/4$ from the supports, but since the horizontal angle is very small this assumption is valid). At the points of inflexion, the internal moments vanish. The expressions for shape of $C_1C_2$ before and after application of the load $P$ are given by A.3 and A.4, respectively. Substituting for $\rho$ and $R_0$ in A.1 using A.3 and A.4, and from A.2, the following expression can be derived:

$$\frac{-Py}{\kappa} = \frac{y''}{\sqrt{1-y'^2}} - \frac{y_0''}{\sqrt{1-y_0'^2}},$$  \hspace{1cm} (A.7)

where ‘$\kappa$’ is the flexural rigidity ($EI$). Equation A.7 consists of derivatives of $y_0$, but the triangular shape of the column is not continuous at $s = L/2$. Hence, the initial curvature (initial deformation) is expressed in terms of a Fourier sine series expansion, which allows for existence of derivatives of $y_0$, as

$$y_0 = \xi \left[ \frac{8}{\pi^2} \sum_{n=1,3,5}^{\infty} \frac{(-1)^{n-1}}{n^2} \sin\left(\frac{n\pi s}{L/2}\right) \right].$$  \hspace{1cm} (A.8)

Only the first three terms are expanded, and the approximate expression for the initial profile of column is given by (defined along $C_1C_2$),

$$y_0 = \xi \left[ \frac{8}{\pi^2} \left( \sin\left(\frac{\pi s}{L/2}\right) - \frac{1}{9} \sin\left(\frac{3\pi s}{L/2}\right) + \frac{1}{25} \sin\left(\frac{5\pi s}{L/2}\right) \right) \right].$$  \hspace{1cm} (A.9)

Equation A.7 reduces to
Substituting expressions for \( y \) and \( y_0 \) from A.3 and A.9 in equation A.10, multiplying both sides by \( \sin(\omega s) \), and integrating with respect to ‘\( s \)’ from 0 to \( L/2 \), the following expression for force can be derived:

\[
-\frac{Py}{\kappa} = \frac{y''}{\sqrt{1 - y''^2}} - \frac{y_0''}{\sqrt{1 - y_0''^2}} = y''(1 + \frac{1}{2} y''^2) - y_0''(1 + \frac{1}{2} y_0''^2).
\]  (A.10)

Hence, the force on the column and axial displacement of the column with an initial imperfection can be estimated from the lateral displacements, using expressions A.11 and A.12, respectively.
Appendix B

Calibration of Microdevice with Buckling Beams

Fabrication uncertainties, during lithography and etching, may result in the actual device dimensions being different from design (expected) values. Therefore, it is very important to have a calibration scheme for the devices, and the scheme is illustrated with a representative device. In this research, the devices are fabricated without the specimen. The dimensions of the device are shown in table B-1.

Table B-1: Dimensions of the Representative Microdevice.

<table>
<thead>
<tr>
<th>Device Parameter</th>
<th>Value (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the Longer Column</td>
<td>500</td>
</tr>
<tr>
<td>Length of the Shorter Column</td>
<td>490</td>
</tr>
<tr>
<td>Width of the Columns</td>
<td>3</td>
</tr>
<tr>
<td>Depth of the Columns</td>
<td>15</td>
</tr>
<tr>
<td>Initial Imperfection</td>
<td>3</td>
</tr>
</tbody>
</table>

The device is loaded without any specimen, and force on the specimen is estimated from the measurement of the lateral displacements of the buckling columns (equation 3.4). In the absence of any specimen, this force is ideally zero. However, this force might not be zero in the actual experiment due to errors in measurement of lateral displacements,
which is determined by the resolution of Scanning Electron Microscope (SEM) images. The lateral displacements of the columns are estimated by processing the SEM images. The error in force measurement is computed due to the resolution limit of SEM images, using analytical expressions for force on the specimen (equation 3.4). This value of error in force is the minimum force \( F_{\text{min}} \), estimated by the analytical expressions in the absence of any specimen. The force on the specimen is related to the lateral displacements of the columns via the cross-sectional moments of inertia of the columns \( (I_l \text{ for the longer columns and } I_s \text{ for the shorter columns}) \) and the initial imperfection \( (\zeta) \).

The area moments of inertia and initial imperfections of the columns are varied and the force is re-estimated, maintaining the same values of lateral displacements. The inertia and initial imperfection values are varied such that the force estimated is nearly equal to \( F_{\text{min}} \). The effective moments of inertia (‘effective I’) and the effective initial imperfection, for which the force is nearly zero \( (F_{\text{min}}) \), are taken as the calibrated values for the device, and are used in further experiments on nanowires. Table B-2 shows the nominal values (design values) for the device parameters and the calibrated values.

<table>
<thead>
<tr>
<th>Device Parameter</th>
<th>Nominal Value</th>
<th>Calibrated Value</th>
<th>Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_l ) (( \mu m^4 ))</td>
<td>33.75</td>
<td>37.13</td>
<td>10</td>
</tr>
<tr>
<td>( I_s ) (( \mu m^4 ))</td>
<td>33.75</td>
<td>32.83</td>
<td>2.7</td>
</tr>
<tr>
<td>( \zeta ) (( \mu m ))</td>
<td>3</td>
<td>3.08</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Appendix C

Error Analysis in Tensile and Bending Experiments

C.1 Tensile Experiments

In tensile experiments, the Young’s modulus is estimated using the following expression:

\[ E = \frac{\sigma}{\varepsilon} = \frac{F/A}{\delta/L}, \]  \hspace{1cm} (C.1)

where,

\( E \): Young’s modulus of the nanowire
\( \sigma \): Stress on the nanowire
\( \varepsilon \): Strain on the nanowire
\( F \): Force on the nanowire
\( A \): Cross-sectional area of the nanowire
\( \delta \): Elongation in the nanowire
\( L \): Length of the nanowire.

From equation C.1, the fractional error in modulus estimation can be written as

\[ \frac{\partial E}{E} = \left| \frac{\partial F}{F} \right| + \left| \frac{\partial A}{A} \right| + \left| \frac{\partial \delta}{\delta} \right| + \left| \frac{\partial L}{L} \right|. \]  \hspace{1cm} (C.2)

Since the cross-sectional area of the nanowire is proportional to square of the diameter of the wire, the fractional error in area estimate is given by
where $d$ is the diameter of the nanowire. Error in estimation of diameter and length of the nanowire is limited by the pixel resolution of the Scanning Electron Microscope (SEM) images, which is assumed to be 12 nm. For an average nanowire diameter of 300 nm, the fractional error in estimate of cross-sectional area is 0.08. For an average nanowire length of 10 $\mu$m, the fractional error in length estimate is $1.2 \times 10^{-3}$. The error in estimation of force is governed by the error in estimation of dimensions of the buckling beams or force sensing beams, and error in measurement of lateral displacement ($D$) of buckling beams or displacement of the force sensing beams ($\delta_{beams}$). The error in estimation of dimensions of the beam is determined primarily by measurement of the smallest dimension of the beam, i.e. width of the beam ($w$). Hence, fractional error in force estimate can be written as

$$\frac{\partial F}{F} \approx \frac{3}{w} \frac{\partial w}{w} + \frac{2}{D} \frac{\partial D}{D}, \quad \text{buckling beams}$$

$$\frac{\partial F}{F} \approx \frac{3}{w} \frac{\partial w}{w} + \frac{\partial \delta_{beams}}{\delta_{beams}}, \quad \text{linear springs} \quad (C.4)$$

The factor of three for fractional error in width is present, because the force is proportional to cube of the width (same explanation for factor of 2 in fractional error in $D$). If 3 $\mu$m is the average value of the width of the columns or beams, the fractional error, due to width, is 0.018. The errors in measurement of lateral displacements or beam displacements depend on nanowire strain, and are larger for smaller strains. As a result, the average values of the error are calculated. For buckling beam design, the fractional error in lateral measurement of displacements is $4.8 \times 10^{-3}$. For the linear spring design,
the fractional error in measurement of beam displacements is $2.4 \times 10^{-3}$. The error in measurement of nanowire strains is determined primarily by the errors in measurement of nanowire displacements. These errors are greatly reduced for microdevice with buckling beam design because of the measurement of amplified lateral displacements. The fractional error in measurement of nanowire displacement in buckling beam design is on the order of error in measurement of lateral displacements in force estimate, i.e. $4.8 \times 10^{-3}$.

For linear spring design, the average nanowire displacements are 250 nm and the fractional error in measurement of nanowire displacements is 0.048. Thus, the error in measurement of Young’s modulus is 10 % for buckling beam design and 15 % for linear spring design. The error is mainly because of the error in measurement of diameter of the nanowire. In case of linear spring design, the other source of significant error is the measurement of direct displacements of the nanowire as opposed to measurement of amplified distances in case of buckling beam design. There are additional errors in buckling beam design due to imperfection in modeling of the non-linearity (details in section 3.5). These errors result in approximately 10 % error in estimation of Young’s modulus. The fractional error in estimation of modulus during tensile experiments can be written as (considering only the terms with significant contributions)

$$
\frac{\partial E}{E} \approx 2 \frac{\partial d}{d} + \text{error in modeling} \quad \text{buckling beam design}
$$

$$
\frac{\partial E}{E} \approx 2 \frac{\partial d}{d} + \frac{\delta_{nw}}{\delta_{nw}} \quad \text{linear spring design}
$$

(C.5)
C.2 Bending Experiments

In bending experiments, the Young’s modulus is estimated using the following expression

\[ E = \frac{\sigma}{\varepsilon} = \frac{k_{\text{tip}} y_{\text{tip}} L r}{ \frac{I}{3 y_{\text{nw}} r} \frac{L^2}{L^2} } \]  

(C.6)

\( E \): Young’s modulus of the nanowire
\( \sigma \): Maximum stress on the nanowire (surface of the nanowire)
\( \varepsilon \): Maximum strain on the nanowire (surface of the nanowire)
\( k_{\text{tip}} \): Spring constant of the AFM tip
\( y_{\text{tip}} \): Deflection of the AFM tip
\( y_{\text{nw}} \): Deflection of the nanowire
\( I \): Area moment of inertia of the nanowire
\( L \): Length of the nanowire
\( r \): Radius of the nanowire.

An expression similar to fractional error in measurement of Young’s modulus during tensile experiments (equation C.5) will be developed, considering only significant sources of error. One of the most significant sources of error is the measurement of radius of the nanowire \((r)\). The other source of error is the measurement of deflection of the nanowire and AFM tip, which are on the same order. The last significant source of error is the measurement of thickness of the AFM tip \((t_{\text{tip}})\), which is used to calculate the spring
constant of the tip ($k_{tip}$). Hence, the expression for fractional error in measurement of Young’s modulus during bending experiments is given by,

$$\frac{\partial E}{E} \approx 3 \frac{\partial t_{tip}}{t_{tip}} + 4 \frac{\partial d}{d} + 2 \frac{\partial y_{nw}}{y_{nw}}.$$  \hspace{1cm} (C.7)

The multiplication factors appear in the above equation, because $k_{tip} \propto t_{tip}^3$, $I \propto d^4$, and the order of errors are the same for nanowire and AFM tip deflections. The errors are limited by the pixel resolution of SEM images, which is assumed to be 12 nm. Average value of $t_{tip}$, $d$ and $y_{nw}$ are 1 $\mu$m, 300 nm and 2 $\mu$m, respectively. Hence, the error in estimation of Young’s modulus during bending experiments is approximately 21%.
Appendix D

Effect of Surface Stresses to Measured Modulus

The linear constitutive equation for surface stress is given by [1]

\[ \tau_{\alpha\beta} = \tau_{\alpha\beta}^0 + S_{\alpha\beta} \epsilon \beta , \]  

(D.1)

where the Voigt notation has been adopted for the reducing the number of indices, and \( \alpha, \beta \) go from 1 to 3. \( \tau_{\alpha\beta}^0 \) is the surface stress in externally unstrained material, \( S_{\alpha\beta} \) is the surface elastic constant, and \( \epsilon \) is the strain in the material. The units of surface stresses are N/m. The effect of surface stresses is incorporated in the equations for flexural deformations. Consider a beam, subjected to a bending moment, as shown in figure D-1. Although the cross-section is shown as rectangular, the analysis is valid for any cross-section that is symmetric about Y axis. The bending moment, \( M_b \), is assumed to be constant throughout the length, and hence, this is the case of pure bending of beams. The neutral surface in a beam subjected to bending moment is the surface about which the moment due to bending stresses is zero. In figure D-1, the origin of the co-ordinate axis is assumed to be at the neutral surface and at a point symmetric about the Y axis. In pure bending, the shear stresses \( \tau_{xy} \) and \( \tau_{xz} \) are equal to zero [2] (pg 422). The beam is assumed to be slender, and hence, the transverse stresses are negligible, i.e. \( \sigma_y = \sigma_z = \tau_{yz} = 0 \). The only significant stresses are the bending stresses, \( \sigma_x \) and surface stresses, \( \tau \). For beam in pure bending, the following expression for strain in X direction can be derived [2] (pg 421):
where $\rho$ is the radius of curvature. Using the expression for strain (equation D.2), the following expressions for bending and surface stresses can be derived:

$$\varepsilon_x = -\frac{y}{\rho}, \quad (D.2)$$

$$\sigma_x = E\varepsilon = -\frac{E_y}{\rho},$$

$$\tau = \tau_0 + S\varepsilon = \tau_0 - \frac{S_y}{\rho}, \quad (D.3)$$
where $E$ is the Young’s modulus in the X direction. Considering the force equilibrium in the X direction and the moment equilibrium about the Y and Z axis, the following expressions can be derived:

\[ \Sigma F_x = 0 \Rightarrow -\frac{E}{\rho} \int ydA + \tau_0 P - \frac{S}{\rho} \int ydl = 0 \]  
\[ \Sigma M_y = 0 \Rightarrow -\frac{E}{\rho} \int zydA + \tau_0 \int zdl - \frac{S}{\rho} \int zdyl = 0 \]

and,

\[ \Sigma M_z = M_b \Rightarrow \frac{E}{\rho} \int y^2 dA - \tau_0 \int ydl + \frac{S}{\rho} \int y^2 dl = M_b \, , \]  
\[ (D.6) \]

where $P$ is the perimeter of the cross-section, and $\int dl$ indicates a line integral over the perimeter of the cross-sectional area. Since the area is symmetric about Y axis, \[ \int zydA = \int zdl = \int zdyl = 0 \, . \] Generally, in bending of beams without any surface stresses, the neutral axis coincides with the centroidal axis. However, due to the presence of surface stresses (or any asymmetrical force or stress about the XZ plane), the centroidal axis is offset with respect to the neutral axis, and this offset is called bending eccentricity ($e$). The convention for sign of $e$ is that $e$ is positive when the centroidal axis lies below the neutral axis (along the Y direction); the positive direction of $e$ is shown in figure D-1.

The nanowires have approximately a circular cross-section. For circular cross-section, the expressions for the integrals in terms of $e$ are given by

\[ \int ydl = 2\pi r e, \quad \int y^2 dl = \pi r^3 + 2\pi r^2 e \]
\[ \int ydA = \pi r^2, \quad \int y^2 dA = \frac{\pi r^4}{4} + \pi r^2 e^2 \, , \]  
\[ (D.7) \]
where \( r \) is the radius of the cross-section. Combining equations D.4 and D.7, the expression for \( e \) in case of a circular cross-section is given by

\[
e = \frac{2\tau_0\rho}{Er + S}.
\]  

Using D.6 and D.7, the expression for bending moment can be derived as

\[
M_b = \frac{\pi r^4 E}{4\rho} \left[ 1 + \frac{4}{r} \left( \frac{S}{E} \right) \left( 1 + \left( \frac{2e}{r} \right)^2 \right) \right].
\]  

(D.9)

During experiments involving flexural deformations, the expression used for bending moment is given by,

\[
M_b = \frac{\pi r^4 E_{\text{measured}}}{4\rho}
\]  

(D.10)

where Young’s modulus is denoted by \( E_{\text{measured}} \), because the effect of surface stresses are ignored. Comparing equations D.9 and D.10, the expression for measured modulus during bending (flexural) experiments is given by

\[
E_{\text{measured}} = E + \frac{4}{r} S + f(E, S, \tau_0)
\]  

where

\[
f(E, S, \tau_0) = E \left( \frac{2e}{r} \right)^2 + \frac{4}{r} S \left( \frac{2e}{r} \right)^2.
\]  

(D.11)

The effect of surface stresses on measured modulus during tensile experiments has been derived by Miller and Shenoy [1] to be

\[
E_{\text{measured}} = E + \frac{2S}{r}.
\]  

(D.12)
References


Appendix E

Mechanism of Friction between Nanowire and AFM Tip

In the cantilever bending experiments on zinc oxide nanowires, the friction forces between the nanowire and AFM tip (made of silicon) were measured to be on the order of 10 nN. However, the forces applied by the AFM tip on the nanowire (i.e. the normal forces) were on the order of 0.1 to 1 nN. Considering the Amonton’s law of friction, i.e. the friction forces are proportional to normal forces, yield friction coefficients as 10 to 100, which are extremely high in conventional sliding between two solids. The reason for the unusually high friction coefficients is that the Amonton’s law is applicable for two macroscopic surfaces in contact. In nanowire sliding, the two surfaces involved are nanoscopic. Such large friction forces have been observed in literature, when the contacting areas are nanoscopic, such as AFM tips or carbon nanotubes [1-4]. According to the literature, at the nanoscale there are several possible contributions to mechanisms of friction such as fluctuating electromagnetic fields, phononic excitation, conservative van der Waals interaction, localized plastic deformations and surface roughness. The surfaces involved in the present study, zinc oxide nanowire and AFM tip, are too small for surface roughness to contribute to friction forces, and too large for fluctuating electromagnetic fields and phononic excitation to cause frictional forces. The high friction forces are possibly due to the local van der Waals interactions between molecules of zinc oxide nanowire and silicon AFM tip. The friction forces can be modeled as the forces required to overcome these interactions; these types of friction forces are also
called as static adhesional frictional forces [2]. The local van der Waals interactions between the AFM tip and nanowire can be represented by figure E-1.

![Figure E-1: Adhesional-friction Mechanism.](image)

When the tip is close to the nanowire, adhesive interatomic bonds (due to van der Waals forces) are formed between the molecules of the nanowire and tip (the left side of figure E-1). As the tip slides, these bonds are broken, and new bonds are again formed (the right side of figure E-1). The force required to break these localized bonds is represented by $F$ in the figure, and is called the static adhesional friction. The origins of these local van der Waals interactions can be traced to electrostatic interactions between molecules; a detailed explanation of the mechanism of adhesional friction is provided by Dedkov [2]. This mechanism of friction can also be expressed in the form of Bowden-Tabor theory of dry sliding without ploughing [5], i.e. $F_{\text{friction}} = \tau A_{\text{contact}}$.

Generally van der Waals forces are considered to be acting at very small distances (on the order of tens of Angstroms). However, in cantilever bending experiments the snap-in distance between the nanowire and AFM tip was a few microns, and this snap-in
was attributed to adhesion or van der Waals forces. It is to be noted that van der Waals force is a loose, generic term to explain electrostatic interactions between materials (Hellman-Feynman theorem) [6]. At large distances (such as snap-in distance between the nanowire and AFM tip), the main contribution to van der Waals interaction is due to coulombic (electrostatic) forces, which can be represented by

$$F_{coulomb} = \frac{Q_1 Q_2}{4 \pi \varepsilon_0 r_{\text{snap}}^2}, \quad (E.1)$$

where $Q_1$ and $Q_2$ are the charge on nanowire and AFM tip, and $r_{\text{snap}}$ is the snap-in distance. At close distances, the dominant mechanism for van der Waals forces is the interaction of the electron clouds between the molecules, represented by

$$F_{\text{electroncloud}} = \frac{C_{\text{electroncloud}}}{r_{\text{electron}}^5}, \quad (E.2)$$

where $r_{\text{electron}}$ is the interaction distance between the electrons, and the parameter $C_{\text{electroncloud}}$ depends on the interacting materials. To calculate $Q_1 Q_2$, an approximation that the charges on nanowire and tip can be represented by point charges is used. For the observed snap-in distance in nanowire bending experiment, $Q_1 Q_2$ is 6.6e-32 C$^2$; for comparison the $Q_1 Q_2$ for a pair of electrons is 2.6e-38 C$^2$. At large snap-in distances, $F_{\text{electroncloud}}$ will be small, since it is a short-range interacting force.

References


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