ABSTRACT

CHANG, TZU-HSUAN. In-situ Scanning Electron Microscopy Mechanical Characterization of Crystalline Nanowires using MEMS Devices. (Under the direction of Dr. Yong Zhu).

The nanostructures such as nanoparticles, nanowires (NWs), nanotubes and graphene are important building blocks for a broad spectrum of nanotechnology applications including energy harvesting and storage, nanoelectromechanical systems (NEMS), flexible electronics and stretchable electronics, where the ultrahigh strength is of direct relevance. Therefore, it is of important to accurately characterize their mechanical response. Microelectromechanical systems (MEMS) is the reliable platform while performing the in-situ characterization of nanostructure. It can measure not only the mechanical properties of nanomaterials but also other significant physical properties such as electrical or thermomechanical. In this thesis, we conduct the MEMS tensile stage to study the mechanical behaviors of two important NWs: Si NWs and Ag NWs.

We start with an overall review on recent advances in experimental techniques conducting MEMS devices for nano-mechanical testing. Such platforms have been used for basic tensile testing, fatigue, thermomechanical testing, multiphysical testing, and true displacement-controlled testing via feedback control. A large number of nanostructures have been characterized including carbon nanotubes, crystalline NWs, metallic glass NWs, and polymer nanofibers.

For the Si NWs, we focus on the study of temperature effect on the mechanical properties. A brief review on brittle-to-ductile (BDT) transition of single crystalline silicon is presented. A clear trend of size effect on BDT is demonstrated in the literatures, which shows the decreasing of BDT temperature with the reduction of sample size. On the other hand,
ambiguous results on either brittle or ductile failure of Si NWs are found, which are going to be clarified in this report. A novel temperature controllable MEMS tensile platform for NWs characterization is therefore designed and carefully calibrated. Multiphysics finite element analysis (coupled electrical-thermal-mechanical) was carried out to optimize the structure design and minimize undesired thermal displacement during heating. The simulation results of temperature distribution on MEMS device are confirmed by the in-situ Raman spectroscopy. The Si NW clamped on the MEMS tensile platform is able to be heated up close to 600 K.

Using this device, we thoroughly study the thermomechanical properties of Si NWs. Both Young’s modulus and fracture strength of the Si NWs decrease with the increasing of the temperature. In addition to the experimental finding, a new approach in order to assess the BDT of crystalline Si NWs is proposed in this report. The activation volumes of dislocation in crystalline Si NWs acquired from in-situ SEM tensile testing and thermal activation analytical model show a clear deformation mechanism transition. The dislocation nucleation induced shear band and diameter reduction were confirmed by TEM postmortem imaging which strongly support that the Si NWs were undergoing plastic deformation at temperature of 600 K.

Ag NWs is another significant nanostructure since they possess the highest electrical conductivity among all kinds of 2D nanomaterial. They recently received even more attention due to their excellent mechanical properties compared to the bulk counterpart. As a result, they have been widely utilized in soft conductor and stretchable electronics. However, their elasticity size effect remains not well understood due to the large discrepancy in the reported experimental and simulation results. In this thesis, we report an experimental effort
to address the discrepancy about the size-dependent Young’s modulus of penta-twinced Ag NWs. Two independent experiments on the same NW, in-situ resonance test and tensile test in a scanning electron microscope, were used to measure the Young’s moduli. The cross-sectional shape of the Ag NWs was found to transit from pentagon to circle with decreasing NW diameter, which can modify the Young’s modulus as much as 8% (for resonance test) and 19% (for tensile test) for the tested diameter range. This work confirmed that the Young’s modulus of penta-twinced Ag NWs increases with decreasing NW diameter.
In-situ Scanning Electron Microscopy Mechanical Characterization of Crystalline Nanowires using MEMS Devices

by

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DEDICATION

To my family in Taiwan.
BIOGRAPHY

Tzu-Hsuan was born in Taipei, a city in northern Taiwan. It is the capital, economic center and the largest city of Taiwan. He received his B.S. degree in Civil Engineering on 2007 from National Taiwan University, which is ranked as the No.1 university in Taiwan. He continued his study as a master student in Civil Engineering at National Taiwan University and graduated on 2009 under the advisory from Dr. Chuin-Shan Chen and co-advisory from Dr. Long-Sun Huang at Institute of Applied Mechanics. During his master study, he measured and characterized the alkanethiols absorption behaviors on a gold-coated MEMS cantilever. After finishing the mandatory military service as Taiwanese citizenship, he started his PhD program at NC State under the advisory of Dr. Yong Zhu in August 2012. His PhD research focuses on the mechanical properties characterization of crystalline nanowires.

Outside of work, T-H spends time on baseball, video game and playing guitar.
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Chapter 1.

Introduction

Recent advance in nanotechnology has brought forth a host of nanostructures, such as nanoparticles, nanowires (NWs), nanotubes and graphene that exhibit ultrahigh mechanical strength (e.g., sample-wide stress > 1/10 of their ideal strengths) [1]. Such nanostructures are important building blocks for a broad spectrum of nanotechnology applications including energy harvesting and storage [2–4], nanoelectromechanical systems (NEMS) [5,6], flexible electronics [7,8] and stretchable electronics [9–11], where the ultrahigh strength is of direct relevance. It is known that electronic band gaps change with elastic strain, so do phononic band gaps, thermal transport and other physical and chemical properties. Therefore, the ultrahigh strength offers unprecedented opportunities to tune the functional properties of nanostructures through the elastic strain engineering [1]. As an example, Si NWs were found to exhibit an enormous range of elastic strain (e.g., > 10%) [12], which is promising for future semiconductor engineering such as field effect transistor built via Si NW arrays [13,14].

In addition to the important technological applications, the ultra-strength materials provide an excellent platform to study fundamental mechanical behavior at the nanoscale. It is known that size dependent mechanical properties and deformation mechanisms arise as the characteristic dimension of single-crystalline nanostructures approaches 100 nm or so [15,16]. This has greatly motivated the mechanics of materials community to investigate
nanoscale mechanical behavior from both computational and experimental perspectives. Indeed, recent rapid advance in nanoscale manipulation/mechanical testing [17,18] and in-situ characterization tools such as electron microscopies [19,20] has enabled real-time observation of deformation and defect dynamics. As the number of atoms in these nanostructures comes increasingly within the reach of the state-of-the-art computational modeling capabilities, direct comparison between nano-mechanical tests and atomistic simulations side by side has become closer to reality and hold great promises for important new discoveries in materials science.

Among these, Si NWs and Ag NWs are two of the most applied nanomaterials since they can be massively produced with high quality and are mechanically, electrically and thermally outstanding [21,22]. For Si NWs, clear evidences of enhancement on mechanical behavior have been reported by various approaches [12,23–25]. In contrary, the thermal-mechanical response of Si NWs still remains inconsistency due to the experimental difficulty in performing in-situ mechanical testing with various temperatures for such small specimens. One particular interest from engineering view is the temperature range for triggering brittle to ductile transition (BDT) of Si NWs. It is of important because Si NWs have been considered as the building blocks of future NEMs sensors and anodes for Li battery [3] where high temperature will be often involved.

Ag NWs possess the highest electrical conductivity among all kind of 2D nanomaterials and thus have been widely used for soft electrode and stretchable electronics [26,27]. Compared to the single crystalline Ag NWs, penta-twinned Ag NWs is relatively easy and scalable to be synthesized based on solution phase [28] and thus become the majority in
research and application aspect. For the studies on mechanical response, increased Young’s modulus and yield strength with decreasing NW diameter have been recently discovered via tension [29,30] and bending [31,32]. However, the elasticity size effect of penta-twinne Ag NWs was found to be more pronounced under bending than tension and resulted in ambiguous conclusions in literatures. Understanding the origin of size effect will not only provide the guidance for the application design but also help to probe the fundamental physics.

Therefore, in this thesis, we are going to address these important mechanical issues mentioned above of Si NWs and Ag NWs. For Si NWs, we developed an integrated MEMS platform that can perform mechanical testing with various temperatures inside a SEM and combined in-situ tensile testing with ex-situ TEM observation of dislocation activities to unveil the BDT of Si NWs. For the Ag NWs, we conducted two independent experiments on the same NW, in-situ resonance test and tensile test in a SEM, to measure the Young’s moduli in order to compare the difference under different loading mode and solve the discrepancy in the literatures.

1.1. Silicon nanowires

Silicon is widely employed in the small scale applications. In the micrometer scale, silicon is the most fundamental materials in semiconductor and MEMS industry. When it acquires a 1D shape, namely nanowire, silicon exhibits some unique properties in the aspect of mechanical, electrical and optical [21,33]. It has shown promising demonstrations in
oscillators [5], mechanical sensor [34], field effect transistors (Figure 1-1(a)) [35,36], photovoltaics [37] and lithium batteries [3,38]. In addition, because of the extremely high surface to volume ratio combined with excellent ion sensitivity, Si NWs became a great candidate of chemical and biochemical sensors as well (Figure 1-1(b))[14].

![Figure 1-1](image_url)

Figure 1-1 (a) Illustration of Si NW-based thin film transistor on a plastic substrate [35]. (b) Schematic illustrating the conversion of NW-based FET into a pH sensor [14].

1.1.1. Synthesis

Numbers of synthesis techniques nowadays exist to fabricate Si NWs. In general, these can be classified into bottom-up and top-down methods. The top-down approach usually involves in lithography, etching, and deposition, which utilize to pattern bulk materials to small scale. One of the most attraction ways to prepare large area arrays of nanowires via etching-based of top-down strategy was demonstrated by Zhu and co-workers [39,40], and extensively developed by others later [41,42]. The way of fabrication is based on silver-
induced excessive local oxidation and dissolution of a silicon wafer substrate in HF/Fe(NO$_3$)$_3$ solution. Such method was utilized previously to prepare porous silicon. Details of fabrication are schematically shown in Figure 1-2(a). First of all, Si wafer was electroless deposit silver (Ag) nanoparticle layer. The distribution of Ag particles on the Si surface determines the density and size of the Si NWs after etching. The Si wafer covered by Ag particles is then immersed in an aqueous HF/Fe(NO$_3$)$_3$ solution at 50 °C. In general, the etching process of normal Si wafer in HF/Fe(NO$_3$)$_3$ is very time consuming. But with the assist of Ag nanoparticles, etching speed is enhanced and the whole process can be finish in 30 mins. In addition to the capability of massive production of well-aligned NWs in one time, different crystallographic orientations can be promptly fabricated by the selection of Si wafers, where (100), (110) and (111) are all commercially available. Minamisawa et al. demonstrated that the single crystalline Si nanowire fabricated via top-down method can sustain elastic strain up to 4.5% [43]. Compare to its bulk counterpart which usually fractured at strain level around 1%, the Si nanowires show the capability to endure high stress that approach the scenario of ultra-strength materials [1].
Figure 1-2 Schematic elucidations of the formation mechanism of SiNWs arrays via: (a) metal-assisted chemical etching [41]; (b) VLS growth [33].

On the other hand, the bottom-up method is usually a physical/chemical adatoms process, much like the way that builds up complicated structure or building, layer by layer. Physical and chemical properties, such as diameter, length, growth direction, density and doping can be readily controlled during synthesis. The most prominent way to synthesis NWs using bottom-up approach might be the vapor-liquid-solid mechanism (VLS), which were usually utilized to synthesis group IVA, III-V and II-VI NWs (i.e. Si, GaAs and ZnO) [44–46]. In the case of Si NWs, VLS synthesis was first demonstrated as early as 1960s, when Wagner and Ellis first used this approach to fabricate Si whiskers with size from sub-micron
to millimeter [47]. VLS synthesis requires a catalyst on the grown substrate, which usually were liquid gold (Au) nanoclusters. Then the target material compound (i.e. SiH$_4$ for Si NWs [48]) is introduced in gas phase to saturate nanoclusters. Once reaching supersaturation, the nanocluster started displaced from the surface of the substrate and sat on the top of growing nanowires, as illustrated in Figure 1-2(b). The nanowire diameter is mainly determined by the size of nanocluster and the length can be simply tuned by controlling the exposure time.

1.1.2. Mechanical characterization

Silicon NWs so far is one of the most studied semiconductor materials since it is the fundamental building block for nanoelectronic and nanoelectromechanical devices. A particular concern is the size effect on mechanical properties, such as Young’s modulus, failure strain and stress, which highly affect the reliability and performance of device. One predicament scientists have encountered was uncertain growth direction of the NWs and hard to characterize before test. They could be randomly grown along either [100], [110], [111], or [112]-oriented even using the same synthesis method on the same substrate [48–50]. Anisotropic material properties further increased the difficulty for researchers to interpret the equivocation in nano-scale.

Zhu et al. reported the first quantitative mechanical data of VLS synthesis Si NWs with diameter from 15 to 60 nm by in situ SEM tensile testing [12]. All of the important mechanical properties, including Young’s modulus, failure stress and strain, demonstrated a strong size dependent effect in the report. The Young’s modulus dropped significantly from
bulk value while the diameters of NWs are below 30 nm, and the smallest value was around 80 GPa. Meanwhile, the elastic strain of NW was keeping increase and could sustain fracture strain as high as 12%. Although the authors did not characterize the growth direction for every NWs in the report, compare to bulk value, the softening in the Young’s modulus of Si NWs is clear no matter what the growth direction is. The results are most likely due to the surface effect, which was correlated with the surface reconstruction that lead to bond saturation, bond contraction or elongation, and loss of bonding neighbors.

Steighner et al. developed a method to pick and mechanical test a single NW with desired orientation [51]. The NWs were first placed on the lacey carbon TEM grid and the growth orientation was defined by TEM. The chosen NW was then picked up from grid and transfer to a MEMS tensile test stage inside SEM by pick and place method. They test seven NWs with diameters range from 268 to 840 nm, and three different growth direction, which are [110], [111], and [112]. A similar size dependent strength was found in these NWs. In addition, the growth direction dependent strength has been discovered as well. The failure stress and strain increased with the decrease of NW diameters, while [112]-oriented NWs possessed the highest failure strain and stress, followed by [110], and the smallest one is [111]. Besides, in both reports, all of the stress-strain behavior showed only linear without potential plastic deformation.

Because many of silicon-fabricated components are now being required to perform at middle to high temperature, it is of important to carefully characterize thermomechanical response. One of the major concerns is the brittle-to-ductile transition (BDT) of single crystalline silicon at nano scale, where controversial results have been reported. However, to
in-situ test nanowires with elevated temperature is still a challenge. In Chapter 3, we design a
temperature controllable MEMS device which is able to perform in-situ SEM/TEM material
colorization. In Chapter 4, we will first briefly review the current studies on the BDT of
single crystalline silicon, and then conduct in-situ tensile testing to unveil thermomechanical
properties of single crystalline Si NWs using the MEMS device we fabricated in Chapter 3.

1.2. Silver nanowires

Face-center-cubic (FCC) metal NWs, including gold, silver and copper play especially
important role in the field of stretchable and flexible electronics due to their extraordinary
electrical conductivity and mechanical ductility [11]. Among all these materials, silver has
the highest conductivity. As such, Ag NWs became the most extensively studied and utilized
metal nanostructures as conductors. In addition to its advantage on electrical conductivity,
Ag NWs also possess a noticeable surface plasmon resonance property [52,53], which makes
them become the great candidate of biosensor [54] and plasmonic waveguiding [55].

1.2.1. Synthesis

The most widely utilized method to synthesis Ag NWs was developed by Xia and co-
workers via a solution-phase approach, self-seeding process that used PVP (poly(vinyl
pyrrolidone)) as the coordination reagent [56,57,28]. In this method, the multiply twinned
decahedra structure of Ag (or Pt) nanoparticles was first formed by reducing AgNO₃ (PtCl₂)
with ethylene glycol (EG) heated to 160 °C. The reason of forming a decahedra shape is due to the most thermodynamically stable seed, since it is bound entirely by the lower energy \{111\} facets [58]. These Ag/Pt nanoparticles could serve as seeds for the heterogeneous nucleation and growth of crystalline Ag NWs. Since the twin boundaries possess the highest energy on the surface of nanoparticles, silver atoms will tend to crystallize on those sites. As a result, the decahedra nanoparticle will elongate into a pentagonal nanowire with five-fold twinned grain boundary running along the length direction. The processes are illustrated in Figure 1-3(a).

Martin and co-workers developed a method called “template synthesis” for fabricating micro/nano structures via membrane-based synthesis [59]. This method involves synthesis of the nanostructures within the pores of a nanoporous membrane. Two types of membranes, track-etch polymeric and porous alumina membranes, are the most often carried out to fabricate nanostructures. The most advantage of this method is easy to synthesis various types of materials in addition to silver [60], including other metals [61,62], semiconductors, ceramics and organic polymers. Figure 1-3(b) illustrates an overall process to synthesis Cu nanopillars using PMMA layer as a template. The only restriction of sample selection is the desired material must be able to load into the pores based on vapor-phase sputtering, liquid-phase injection, or solution-phase chemical or electrochemical deposition.

Richter et al. recently developed a bottom-up method that utilizing physical vapor deposition (PVD) to grow single crystal metal nanowires [63–68]. A small fragment of silicon cut from silicon wafer is served as grown substrate. The silicon substrate was first coated with a thin (~30 nm) carbon layer by magnetron sputtering. Then the materials are
deposited under ultra-high vacuum condition (<2 × 10⁻10 mbar) by molecular beam epitaxy. Substrate temperatures are controlled case by case for each material, e.g., 650 °C for cupper and 680 °C for gold. The deposition rate was set to be 0.05 nm/sec for all materials. Using this method, they have successfully grown high aspect ratio single crystalline nanowires of Cu [63], Au [65], Pd [64], Ag [67] and Au-Ag nanotubes [68]. Figure 1-3(c) shows a SEM image of single crystalline Cu nanowires grown on the Si substrate.

Figure 1-3 (a) Schematic drawing of the process that synthesis silver nanowires via a Pt-seeded polyol method [57]. (b) Schematic illustration of the fabrication process for metal nanowires through membrane-based synthesis [62]. (c) SEM image of Cu nanowires grown on the Si substrate [63].
1.2.2. Mechanical characterization

The mechanical behavior of crystalline metals in small scale had received lots of interest over fifty years started from pioneering works which were done S. S. Brenner during 1950s [69–71]. Since then, numerous studies tried to approach by either tensile, compressed or bending experiments, and a few dedicated reviews had been published recently for experiments [15] and simulations [16].

In the field of nanoscale, the most well addressed material probably is penta-twinned Ag NWs since it is much more accessible with high quality and quantity than others. Early reports on mechanical testing of penta-twinned Ag NWs usually carried out an AFM-bending [32,31] test or nanoindentation [72,73] because they are easy to be manipulated. All of the above studies found a strong size dependent Young’s modulus in penta-twinned nanowires. For instance, for the NWs with large diameters (> 70nm), the Young’s modulus is close to the bulk value of 84 GPa. But the modulus increases with the decrease of size, which could be higher than 160 GPa. Recently, Zhu et al. [29] and Filleter et al. [30] reported the similar stiffening effect of increased Young’s modulus and yield strength with decreasing NW diameter. These NWs can sustain tensile stress as high as 2.64 GPa without apparent plastic deformation, which was close to the theoretical tensile strength of silver in the <110> direction based on the Schmid factor analysis of {111}/<112> system (3.5 GPa) [29].

In addition to the ultra-high strength, there are a few interesting mechanical response of penta-twinned Ag NWs have been reported. Filleter et al. discovered a unique strain
hardening and multiple necking deformation mechanism via in-situ TEM observation [30]. With the assist of molecular dynamics (MD) simulations, they found out that the whole process was controlled by dislocation nucleation from a local stress concentrator, which leads to the formation of a linear chain of stacking fault decahedrons. Twin boundaries along the NW length can cause the formation of stacking fault decahedron chain and confine dislocation activities that locally harden the NW, resulting in enhanced flow stress and ductility. Narayanan et al. later reported a similar size dependent strain hardening effect through stress-strain relationship of both in-situ SEM tensile testing and MD simulation, as shown in Figure 1-4(a) [74].

Another unique behavior of penta-twinned Ag NWs recently reported by Qin et al. is time-dependent mechanical response [67]. They discovered an unusual, fully reversible plasticity, which does not exist in single-crystalline Ag NWs. In situ SEM and TEM tensile testing was performed including several steps as shown in Figure 1-4(b). A specimen was first stretched to a given strain. When the actuator was held constant, the load on the specimen decreased with time, while the specimen was elongated simultaneously. After the relaxation step, the specimen was gradually unloaded until the actuator was turned off (the specimen was still elongated but under compressive stress). At the recovery step, complete strain recovery was observed. MD simulations revealed that the observed behavior originates from the surface nucleation, propagation and retraction of partial dislocations. More specifically, vacancies reduce the dislocation nucleation barrier, facilitating stress relaxation, while the twin boundaries and their intrinsic stress field promote retraction of partial dislocations, resulting in full strain recovery. In situ TEM directly observed the interaction
between dislocations and existing twin boundaries during the relaxation step and the dislocation annihilation during the recovery step. Since the relaxation strain is rather small, a highly stable testing system (e.g. the MEMS platform used) is the key to observing such a fine behavior. Other testing systems such as those involving a nanomanipulator might not work due to the inevitable drift of the nanomanipulator. Similar recoverable plasticity on penta-twinned Ag NWs has been reported in terms of athermal manifestation [75].

Although there is a general consensus regarding size effect elasticity of penta-twinned Ag NWs, the reported values were showing conflict in a certain degree. In Chapter 5, we will carefully address the discrepancy through a thorough literature review and cross-sectional TEM experiments.

Figure 1-4 Stress-strain curve for penta-twinned Ag NWs: (a) For various diameters. Inset shows the microstructure of penta-twinned built by MD simulation [74]. (b) During loading, relaxation, unloading and recovery [67].
1.3. Thesis outline

This thesis is divided into four major sections and organized as follow: In Chapter 2, we first review recent advances in experimental techniques conducting MEMS devices for nano-mechanical testing. In Chapter 3, a novel MEMS device for thermomechanical testing is designed and carefully calibrated by finite element analysis and Raman spectroscopy. It consists of a comb-drive actuator, capacitive load sensor and resistive heater. Chapter 4 starts with a brief review on brittle-to-ductile transition of single crystalline silicon, followed by a systematic study of thermomechanical response of Si NWs. With a combination of in-situ tensile testing, thermal activation model and TEM observation, we are able to quantify and qualify the dislocation nucleation in Si NWs. In Chapter 5, we will try to solve the discrepancy about the size-dependent Young’s modulus of penta-twinned Ag NWs. Two independent experiments on the same NW, in-situ SEM resonance test and tensile test, were used to measure the Young’s moduli. In addition, the cross-sectional shape of the Ag NWs was measured as a function of the NW diameter, which was found to transit from pentagon to circle with decreasing NW diameter. Finally, in Chapter 6 we summarize the major contribution in the thesis and outline the future challenge.
Chapter 2.

Review of Microelectromechanical Systems for Nanoscale Mechanical Characterization

Characterizing mechanical properties of individual one-dimensional (1D) nanostructures is still challenging because of the following requirements: (1) constructing appropriate tools to manipulate, position and align specimens, (2) applying and measuring forces with nano-Newton resolution, and (3) measuring local deformation with nanometer resolution. Existing experimental methods for mechanical characterization of 1D nanostructures include vibration/resonance in scanning or transmission electron microscopes (SEM or TEM) [76–80], bending using an atomic force microscope (AFM) in different operation modes [81–86], tension/bending/buckling in an SEM with the aid of a nanomanipulator [63,29,87–90] as well as nanoindentation [72,91]. Among all these methods tensile testing is the most straightforward one and it can measure a full spectrum of mechanical properties such as elasticity, plasticity and fracture.

However, the above in-situ SEM tensile testing systems are difficult to capture the effect of loading rate and not possible for the effects of temperature and environment. A reliable, multifunctional tensile testing apparatus becomes necessitated in order to further understand the mechanical behaviors of 1D nanostructures. Microelectromechanical systems (MEMS) consist of micrometer scale components but they offer nanometer displacement and nano-Newton force resolutions. MEMS actuators and sensors can be integrated on a chip [92]. As
such, MEMS have been employed in various nanotechnology-related applications ranging from nanomanufacturing [93] to cell manipulation [94]. Similarly, MEMS could have potential to impact the nanomechanical characterization through controlled actuation, high-resolution force/displacement measurements, integrated multi-functions and tiny size for in-situ electron microscopy testing. Zhu and Espinosa have developed an integrated nanoscale testing system using MEMS technology [95–98]. In the past decade, there has been extensive interest in developing MEMS-based instrumentation for experimental nanomechanics that will be reviewed in this article.

In this Chapter, we summarize the recent advances in the field of mechanical characterization of 1D nanostructures using MEMS platforms. We start with three commonly used device configurations and other design considerations such as actuation and load sensing mechanisms, device fabrication, sample preparation and displacement/strain measurement. After that, representative MEMS platforms are reviewed in accordance with the device configurations. Such platforms have been used for basic tensile testing, fatigue, thermomechanical testing, multiphysical testing, and true displacement-controlled testing via feedback control.

### 2.1. MEMS tensile testing platform: Actuator and sensor

Tensile test is the most unambiguous testing method to measure mechanical properties. For bulk materials a number of testing machines are commercially available such as those from MTS and Instron. The testing machines typically consist of three parts: a servohydraulic
(MTS) or screw-driven (Instron) actuator, a load cell (sensor), and a pair of grips. The same concept prevails at the small scale. There have been considerable efforts in developing instrumentation for micro/nano-scale tensile testing. However, the methods for actuation, sensing and even sample gripping are much different from the large-scale ones. In this section, we present brief review of utilizing MEMS devices as tensile testing platforms for 1D nanomaterials.

A number of actuation mechanisms have been implemented in MEMS including electrostatic actuation, thermal actuation, piezoelectric actuation, and shape memory alloy actuation [99,100], among which the former two have been widely used for MEMS-based mechanical testing due to their compatibility with conventional microfabrication techniques.

An electrostatic actuator is based on the attraction of two oppositely charged plates. In particular, a comb-drive-type electrostatic actuator makes use of a large number of interdigitated “fingers” that are actuated by applying a voltage between them [101,102] (Figure 2-1(a)). A comb drive actuator can generate relatively large travel range (~ 10 µm or more). A distinctive feature of the comb drive actuator is that the electrostatic force is nearly constant over the travel range at a given voltage. The comb drive actuator has been widely used in the MEMS field. However, an undesirable feature as an actuator for mechanical testing is that it requires a large actuation voltage (often > 50 V), which might cause instability (pull-in) of the comb structure.

A thermal actuator relies on thermal expansion of the structural materials. Thermal actuators in a variety of configurations have been exploited for achieving in-plane motion, including U-shaped [103], V-shaped [95,104] and Z-shaped actuators [105,106]. For these
actuators, when electric current passes across the freestanding beams, Joule heating results in thermal expansion, leading to linear forward motion in the cases of V-shaped (Figure 2-1(b)) and Z-shaped (Figure 2-1(c)) actuators. A V-shaped actuator is very stiff and can provide a quite large force (~ 10 mN) at a relatively low actuation voltage, while a Z-shaped actuator is much more compliant and could be used as a sensor simultaneously. Both types of thermal actuators are typically limited in terms of travel range (~ 1 – 2 µm). A critical challenge for using thermal actuators in nanomechanical testing is the undesired heating of the specimen. To mitigate this problem, Zhu et al. introduced heat sink structures to dissipate heat and hence decrease the temperature rise at the specimen region to below 5 °C [95,107], without adding complexity in the fabrication process (e.g., extra steps to introduce a heat isolation structure between the actuator and the specimen). In vacuum the more the heat sink beams between the thermal actuator and the specimen, the more the heat dissipation is [95,107]. In air a larger distance between the actuator and the specimen also helps (even without the heat sink beams) due to the heat dissipation to the air [108]. Abbas et al. designed a cascaded thermal actuator that was able to provide >10 µm displacement (at reduced stiffness) while the temperature near the specimen could remain as low as 50 °C [109].
Figure 2-1 Schematics of common in-plane mechanical actuators. (a) Comb drive actuator, (b) V-shaped thermal actuator, (c) Z-shaped thermal actuator. The black and grey colors represent anchors and moveable parts, respectively.

A load sensor typically consists of a flexible member, so the load is measured as the sensor displacement multiplied by the sensor stiffness. Displacement sensing mechanisms commonly used in MEMS include capacitive sensing, piezoresistive sensing, piezoelectric sensing and tunneling sensing [99,100]; the former two have been used for MEMS-based mechanical testing, again due to their compatibility with conventional microfabrication techniques.
Capacitive sensing is perhaps the most popular sensing mechanism in MEMS with commercial chips available for data acquisition. In principle any structure consisting of two plates separated by a gap is a capacitor. It is very difficult to measure the absolute capacitance in MEMS and the capacitance change does not readily correlate with the sensor displacement due to the presence of parasitic capacitances and stray capacitances. So typically a differential capacitive sensor is used in a MEMS testing platform. Capacitive sensors are typically insensitive to temperature. For these reasons, differential capacitive sensor have been widely used in many MEMS devices such as accelerometers [109]. Parasitic capacitances can be mitigated by a commercially available sensing module (MS3110, MicroSensors) [96,110,111]. In addition, the MEMS package is suggested to be placed as close as possible to the sensing module in order to diminish stray capacitance and electromagnetic interference [96].

Piezoresistive effect is a change in the electric resistivity of a semiconductor when mechanical strain is applied. The gauge factor (the ratio between relative resistance change and strain) can be as large as 200 for diffused semiconductors. Si is a common piezoresistive material including single-crystalline and polycrystalline Si, therefore piezoresistive sensing is widely used in MEMS devices [112]. Piezoresistive sensors are typically sensitive to temperature, though methods like Wheatstone bridge can be used to cancel out the temperature effect.
2.2. Sample preparation

A key step in nanoscale mechanical testing is to position specimens at desired locations with nanometer resolution and high throughput. For tensile testing, this step becomes even more challenging compared to other types of testing methods as the specimens must be freestanding, aligned with the loading direction and clamped at both ends. Methods for manipulation and positioning of nanostructures onto MEMS devices mainly include “pick-and-place” by nano-manipulation [96] and dielectrophoresis [113,114] in addition to co-fabrication and direct synthesis. Here we briefly discuss these sample preparation methods, while more details can be found elsewhere [17,115].

A widely used method for mounting nanostructures onto MEMS devices is “pick-and-place” by nanomanipulation introduced by Zhu and Espinosa [96]. In this method, a nanomanipulator is employed to pick and transfer a desired sample from the substrate to a target location inside a SEM or a dual-beam (SEM/FIB). Electron Beam Induced Deposition (EBID) of residual hydrocarbon in a SEM chamber or a precursor gas (e.g., platinum), is commonly used for clamping the samples. This method has been used successfully for a wide range of nano-structures [12,64,116–120]. Admittedly this method is tedious. The carbon- or platinum-containing materials could form amorphous contamination on the sample surface. There is also concern if the clamping mechanism is sufficiently rigid and reproducible. Gianola and co-workers recently reported artifacts in the strain measurement directly between the clamps due to compliance and permanent deformation of the clamps [121]. Zhu and co-workers also found the measured Young’s modulus of a NW (using the resonance
method) depends on the clamping [78]. But they pointed out true Young’s modulus can be measured if the critical clamp size is reached. The critical clamp size is a function of the NW diameter and modulus ratio of the clamp material and the NW. Note that their work was for resonance (or bending). Further investigation on the effect of clamping on mechanical behavior measured under tension is warranted. Meanwhile, displacement markers deposited along the NW length have been used for local displacement measurement [67,120,121]. To alleviate the issues of EBID, adhesives (e.g., epoxy) have been used to clamp polymer nanofibers [122], CNTs [123] and Au nanobeams [124]. With adhesives manipulating individual specimen can only be done in air under optical microscope, which might limit this method to relatively large specimen size. Compliance of the adhesives could also be of potential concern.

Dielectrophoresis has been used to mount CNTs [113] and GaN NWs [114] onto MEMS devices. While this method is more scalable than the “pick-and-place” one, the yield is typically low and contamination during the process is quite common.

Directed synthesis is a promising method that could potentially eliminate the issues with the “pick-and-place” approach. The boundary conditions are supposed to be robust. Mass production could be possible that avoid the tedious manipulation process. However, so far only limited materials have been synthesized, including Si NWs [34] and Ge NWs [125] between microfabricated Si posts. In addition, no direct synthesis into movable MEMS devices has been reported. Co-fabrication is another method while the materials that can be co-fabricated are typically limited. C_{60} NWs [126], Au NWs [116], and Pt ultra-thin films [109] has been successfully co-fabricated with MEMS devices for in situ tensile testing.
2.3. Displacement/strain measurement

Accurate and non-contact displacement/strain measurement is critical in mechanical testing of nanostructures. The simplest method is to compare images of two markers on the specimen before and after the deformation. For 1D nanostructures, the markers can be made by EBID of carbon or platinum on the specimen surface [67]. The gap between the actuator and the load sensor can also be used to measure specimen displacement without the local markers, provided that there is no sliding between the specimen and the MEMS device. Since the nanomechanical testing is typically conducted inside SEM or TEM, high-resolution images of the specimen can be readily obtained. The displacement resolution can be as high as half pixel.

The manual operation of image correlation, however, can be tedious. In order to increase the yield as well as improving the resolution, digital image correlation (DIC) algorithm can be used. DIC is a method based on comparing images of an area with random features on the specimen before and after the deformation. This method has been widely used for measuring displacement/strain using optical images [127–129] and recently extended to SEM images [130–132]. Correction schemes have been developed to account for issues like spatial distortion, time-varying distortion (drift distortion) and random step changes (image shift) in SEM images. In addition, high beam current and long dwell time were recommended to minimize inherent noise of electron beam [133]. The recommendations might extend from
the microscale to the nanoscale with the caution that high electron beam could introduce radiation damage to nanostructures.

Naraghi et al. obtained the specimen displacement and strain by measuring the displacements of the MEMS structures (not directly of the specimen) using DIC of optical images [134]. FIB milling was used to introduce the random features on the otherwise smooth surface of the MEMS structures. Yilmaz and Kysar used the same DIC method but with SEM images [116]. Gianola et al. applied DIC directly on a single NW, where the natural contrast along the length of the NW, presumably from a carbonaceous layer that had formed as a result of SEM imaging, was used as the random features [135]. In this case, DIC can provide displacement/strain information along the entire NW, which could be useful to indicate if the strain is uniform or if there exists localized necks or slip lines. The accuracy of DIC can reach 1/8 of a pixel or better.

Both methods above require a series of images capturing the specimen deformation. For the in-situ SEM/TEM testing, microscopy imaging at low magnification is needed to obtain the specimen displacement and sometimes the load, which might sacrifice the opportunity to observe deformation mechanisms at high magnification or at least requires switching between the magnifications and related electron beam conditions. The imaging rate is generally low. And it is time-consuming to analyze a large number of images for image correlation. In some other cases, ex-situ testing is required or in-situ testing is unnecessary, e.g., to study the fatigue behavior under a controlled environment. Therefore, electronic readout of the displacement/strain without the need of imaging becomes desirable. Espinosa et al. first developed a MEMS platform with two capacitive sensors [98]; difference of the
displacements measured by the two sensors is the specimen displacement. Pierron and co-workers implemented such a two-sensor scheme to study Ni nanobeams [111] and later applied on fatigue behavior study of nanostructures, both in situ and ex situ [124].

### 2.4. MEMS device configurations

MEMS devices can be outlined as three typical configurations for tensile testing: 1) without a direct load sensor, 2) with a direct load sensor and an external actuator, and 3) with a direct load sensor and an on-chip actuator, which comprises a complete material testing system.

For the first configuration, a specimen is positioned between the actuator and a fixed post. Before the specimen is positioned (or after it is failed), the actuator displacement $\delta_0$ is recorded as a function of the applied voltage. During the testing, another set of displacement $\delta (=L' - L)$, which should be smaller than $\delta_0$ due to the finite stiffness of the specimen, is recorded as a function of the same applied voltage. Both specimen displacement (elongation) and load (thus strain and stress) can be measured based on $\delta$ and $\delta_0$ that can be obtained from images or other methods – the elongation is equal to $\delta$, while the load can be calculated based on $\delta$ and $\delta_0$ provided the stiffness (or spring constant) $K_A$ of the actuator is known, i.e., $F = K_A \times (\delta_0 - \delta)$.

Lu et al. developed a MEMS platform consisting of a custom-made thermal actuator [122]. The platform was used to test template carbon nanotubes that were mounted onto the platform using dielectrophoresis [136]. Kiuchi et al. [137] developed a MEMS platform
consisting of a comb drive actuator (1000 – 5000 pairs of combs) using the SOI process. A unique feature of this platform is a cantilever that serves as an amplification system for measuring tensile displacement of the specimen. The amplification system was able to magnify actuator displacement over 90 times. Using optical microscopy, a resolution of 30 nm in cantilever deflection was acquired, translating to 0.29 nm in the actuator displacement.

Of particular note is the “push-to-pull” concept that has been applied to the MEMS platforms. Such a platform typically involves an existing transducer (e.g., nanoindenter) and a micro-fabricated structure that can convert compression from the transducer to tension on the nanostructure. Hysitron developed a push-to-pull platform that can be used together with their TEM nanoindentation holder to perform in-situ TEM tensile testing [138]. As shown in Figure 2-2(a), the platform consists of a fixed part and a freestanding part that is supported by four folded beams. While an indenter head pushes the freestanding part from the left-hand side, the gap between the fixed and freestanding parts expands and applies a tensile load to the specimen that is bridged across the gap. Guo et al. employed this platform to study phase transition of VO$_2$ NWs by in-situ TEM [120,139]. Lu et al. developed another type of push-to-pull MEMS platform that coverts compression from a nanoindenter to tension in the orthogonal direction inside SEM and TEM, as shown in Figure 2-2(b) [140]. This device further developed the concept of Theta-like specimen [141,142] that was used for mechanical testing of micro-fabricated small-scale structures.
Figure 2-2 (a) SEM image of the push-to-pull platform by Hysitron for in-situ TEM testing [120]. A nanoidenter head pushes the movable part from the left side. (b) SEM image of the push-to-pull platform by Lou and co-workers [140]. A nanoidenter header pushes from the top.

For the second configuration, the stage consist of an external actuator and a direct load sensor, which is supported by spring leafs and gripping pad. An external actuator can be either hooked [143] or glued [144] to the gripping pad to impose the displacement, while a specimen is positioned between the load sensor and the gripping pad. The load applied on the specimen is equal to that on the load sensor; i.e., \( F = K_S \times \delta \), where \( K_S \) is the stiffness of the load sensor and \( \delta \) is the load sensor displacement. Naraghi et al. have developed a MEMS platform that is actuated by an external piezoelectric actuator [144], see Figure 2-3(a). The platform includes a leaf-spring load sensor, a gripping pad and a gap in between to mount the specimen. A tipless AFM cantilever connects the three-axis piezo-actuator and the gripping
pad. Both load and elongation of the specimen were obtained from optical images of the MEMS platform using DIC, as shown in Figure 2-3(b).

Haque and Saif introduced a MEMS platform to characterize nanoscale thin films inside SEM and TEM [143,145,146]. The platform was actuated by an external piezo-actuator in the “pulling” direction. A U-shaped structure was co-fabricated in the platform to help mitigate the misalignment between the actuator and the specimen. Later Desai and Haque developed a platform using the push-to-pull mechanism [147], with an independent load sensor, to study 1D nanostructures, as shown in Figure 2-3(c). When the platform is pushed by an external piezo-actuator, the specimen across the movable jaw and fixed jaw is stretched. The authors introduced an interesting design that is based on buckling of sensing beams (columns). The load on the specimen is the difference of the forces on the longer columns and shorter columns, while the specimen elongation is also related to the lateral displacement of the buckled beams. The lateral displacement of a sensing beam (1,000, 2 and 10 μm in length, width and thickness, respectively), when buckled, is about 40 times larger than the specimen elongation. The large amplification makes it possible for an optical microscope to measure specimen elongation and the load on the specimen.
Figure 2-3 (a) The MEMS platform consisting of a loadcell, actuated by an external actuator for nanofiber testing [148]. (b) DIC displacement measurement [144]. (c) The push-to-pull MEMS platform by Haque and co-workers. An external piezo actuator pushes from the left side [143].

The third device configuration consists of both on-chip load sensor and actuator. The load and displacement of the specimen are measured similar to those discussed for the second device configuration. The major difference is involvement of an on-chip actuator – both comb drive actuators [97,149] and thermal actuators [95] have been used. Generally speaking, comb drive actuators can provide force-control loading condition while thermal actuators is displacement control assuming the comb drive has low stiffness while the
thermal actuator has large stiffness. Displacement control and force control are the two common options available for large-scale machines.

Using the third device configuration, Zhu and Espinosa have developed a MEMS platform that includes an on-chip actuator and an electronic load sensor with a gap in between [42]. Two types of MEMS actuators were used, thermal actuator for displacement control as shown in Figure 2-4(a) and comb-drive actuator for force control as shown in Figure 2-4(b). A major advance in their work was the introduction of a capacitance load sensor that measures displacement electronically based on differential capacitive sensing rather than microscope imaging. Since then, a large number of MEMS platforms using this configuration have been reported. For instance, Steighner et al. fabricated a platform that includes a V-shaped thermal actuator and a capacitive load sensor for in-situ SEM tensile testing of Si NWs [51], as shown in Figure 2-4(c).

Figure 2-4(d) shows a MEMS platform developed by Zhang et al., which consists of a comb-drive actuator and a simply folded beam that serves as the load sensor [119]. A three-beam structure, as shown in inset of Figure 2-4(d), was fabricated near the specimen gap to capture specimen elongation and load sensor displacement in one image. Chen et al. has reported a platform that employed the similar structure for mechanical testing of Pd NWs [64]. The platform consists of a V-shaped thermal actuator, a load sensor comprised of folded beams, and a comb structure adjacent to sample that is attached to the platform and the substrate (similar to the three-beam structure mentioned above). This platform was developed as part of the Sandia Discovery Platforms.
Figure 2-4 A MEMS platform including a thermal actuator (a) or comb drive actuator (b), a capacitive load sensor and a specimen in between (fabricated by Poly-MUMPs) [97]. (c) A platform consisting of a thermal actuator, a specimen gap, and a capacitive load sensor (fabricated by SOI-MUMPs) [150]. (d) A platform including a comb drive actuator and a beam load sensor [119]. Inset shows a magnified view of the three-beam structure, which is attached to the device in the boxed area.

2.5. Platforms for Multiphysical Testing

1D nanostructures have been demonstrated as the building blocks of next-generation electronics and sensors. For device applications it is inevitable for nanostructures to experience different temperatures. Thus, it is of relevance to characterize their
thermomechanical behavior. Chen et al. integrated their MEMS platform inside a vacuum cryostat including a heater, a cooling channel with liquid nitrogen circulation and a PID temperature controller [151]. The vacuum chamber has a fused silica window on top so that the MEMS platform inside can be viewed by an optical microscope. The experimental setup is shown schematically in Figure 2-5(a). Their setup is capable of achieving temperature range from 77 to 475 K, with the largest 0.035 K/min drift. Defect-free <110> Pd NWs were tested to demonstrate the capability of the setup. Temperature dependent stress-strain behavior was found in these Pd NWs.

Kang and Saif developed a novel MEMS platform for in situ uniaxial test of micro/nanoscale samples at high temperature [152]. Fabricated out of SiC, this platform was able to sustain temperature up to 700 °C, which is much higher than those made of Si. Based on the design by Haque and Saif earlier [153], Joule heating mechanism and a local bi-metal type temperature sensor were incorporated for heating and temperature measurement, respectively, as shown in Figure 2-5(b). Of note is that microfabricated heaters have been used in thermomechanical testing platforms for microscale films [154].
Figure 2-5 (a) Schematic of the vacuum cryostat system for temperature control [151]. (b) Schematic of a MEMS thermomechanical platform made of SiC including a co-fabricated temperature sensor [152].

It is of fundamental and technological importance to understand how mechanical strain can alter other physical properties including charge carrier transport and phonon transport among others – so-called elastic strain engineering. Nanostructures typically exhibit ultrahigh mechanical strength, thus offer unprecedentedly large room for elastic strain engineering. Bernal et al. has developed a MEMS platform using MUMPs-PLUS to characterize electromechanical coupling of NWs, by integrating four-point electric measurement and tensile loading [155]. Based on the original design that consists of a thermal actuator, a specimen gap and a capacity load sensor, four conductive support beams were added to form electrical paths to the interconnects on the device shuttles where the specimen is positioned, as shown in Figure 2-6(a) and (b). Penta-twinned Ag NWs and Si NWs were tested representative of metallic and semiconductor NWs, respectively.
Zhang et al. [156] fabricated an electromechanical MEMS platform based on standard SOI process, but with a SiO$_2$ layer beneath the structural layer for insulation, as shown in Figure 2-6(c) and (d). Piezoresistivity of Si NWs was reported. Kiuchi et al. fabricated an electromechanical MEMS platform based on their previous mechanical platform [157]. An external Kelvin bridge method was used for resistance measurement.

Murphy et al. have studied thermal conductivity of Si NWs as a function of tensile strain [158]. While the MEMS platform was used to apply tensile strain to the specimen, Raman spectroscopy was used to measure its thermal conductivity. Using photoluminescence and Raman spectroscopy, optomechanical behavior of direct-bandgap NWs has been investigated [125,159,160]. Of note is that most MEMS-based in-situ testing has been performed inside SEM or TEM. Integration of MEMS platforms with other types of microscopy or spectroscopy could offer exciting opportunities for multiphysical testing of nanostructures especially strain engineering.
Figure 2-6 (a) SEM image of a MEMS platform with four-point electric measurement of single NW [155]. (b) Interconnects sit on the silicon nitride shuttle provided electrical connection (magnified view of the box in panel a). (c) Schematic of a MEMS platform with two-point electrical measurement [156]. (d) 3D schematic of the platform showing buried oxide layer beneath the device serving as mechanical connection and electrical isolation.

2.6. Conclusion

In this chapter, we have reviewed the exciting advances in the field of mechanical characterization of 1D nanostructures, especially using MEMS platforms in the past decade. A large number of nanostructures have been characterized including carbon nanotubes, crystalline NWs, metallic glass NWs, and polymer nanofibers. Representative references are list in Table 2-1 below. These MEMS platforms and related nanomechanics studies have contributed tremendously to our understanding of the nanoscale mechanical behaviors.
Table 2-1 Summary of MEMS platforms for tensile testing of 1D nanostructures.

<table>
<thead>
<tr>
<th>Device type</th>
<th>Fabrication method</th>
<th>Thickness (μm)</th>
<th>Actuator type</th>
<th>Strain measurement</th>
<th>Load sensing</th>
<th>Tested materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st SOI</td>
<td>35 Electrostatic</td>
<td>Optical image</td>
<td>Optical image with cantilever amplifier (0.3 nm)</td>
<td>Carbon[137]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly-MUMPS</td>
<td>3.5 Thermal</td>
<td>SEM image (40 nm)</td>
<td>SEM image</td>
<td>Carbon NF[161], GaN[114]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>5 Indenter</td>
<td>SEM DIC</td>
<td>Nanoindentor readout</td>
<td>VO₂[120,139], MO[162]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>9.5 Indenter</td>
<td>Nanoindentor readout</td>
<td>Nanoindentor readout</td>
<td>Carbon NT[123], Ni[163], Cu[164]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd LPCVD Poly-Si</td>
<td>5.2 Piezo</td>
<td>Optical DIC (25 nm)</td>
<td>Optical DIC</td>
<td>Polymeric NF[144,148], carbon NF[165]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>10 Piezo</td>
<td>SEM image (1 nm)</td>
<td>SEM image</td>
<td>ZnO[147]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly-MUMPS</td>
<td>3.5 Thermal</td>
<td>SEM/TEM image</td>
<td>Capacitance (0.05fF = 1 nm)</td>
<td>Pd[96], carbon NT[117,166], ZnO[118,167], Ag[30], GaN[168]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUMMiT</td>
<td>6 Electrostatic</td>
<td>Optical DIC (20 nm)</td>
<td>Optical DIC</td>
<td>Polymeric NF[134]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI-MUMPs</td>
<td>10 Thermal</td>
<td>Capacitance</td>
<td>Capacitance (0.05fF = 0.25 nm)</td>
<td>Ni[108,111], Au[124]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUMMiT</td>
<td>- Thermal</td>
<td>SEM DIC (2 nm)</td>
<td>DIC</td>
<td>Pd[64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd SOI</td>
<td>100 Electrostatic</td>
<td>SEM image</td>
<td>SEM image (&lt;10 nm)</td>
<td>Co[119], Si[169]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>25 Electrostatic</td>
<td>Capacitance</td>
<td>Capacitance (1.5 nm)</td>
<td>Si[156]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI-MUMPs</td>
<td>25 Thermal</td>
<td>SEM image (6 nm)</td>
<td>SEM image</td>
<td>Si[51,150]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>5 Electrostatic</td>
<td>Capacitance</td>
<td>Capacitance (0.1 fF = 1nm)</td>
<td>C₆₀[126,170]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>20-25 Thermal</td>
<td>Optical DIC (15 nm)</td>
<td>Optical DIC</td>
<td>Pt (ultrathin film)[109]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI</td>
<td>No Electrostatic</td>
<td>SEM DIC (7.5 nm)</td>
<td>SEM DIC</td>
<td>Au[116]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOI-MUMPs</td>
<td>10 Thermal</td>
<td>SEM image (1 nm)</td>
<td>Capacitance</td>
<td>Si[171], SiC[172], Ag[67]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Displacement resolution, when available, is included after the corresponding strain measurement and/or load sensing. The tested materials are NWs by default. NT: nanotubes, NF: nanofibers.
Chapter 3.
A Microelectromechanical System for Thermomechanical Testing of Nanostructures

3.1. Introduction

1D nanostructures have been demonstrated as the building blocks of next-generation electronics and sensors. At room temperature, crystalline nanowires exhibit size dependent mechanical properties (e.g., Young’s modulus and fracture strength)[12, 29, 79, 88] and deformation mechanisms (e.g., dislocation nucleation from free surfaces)[29, 173, 174]. How about their mechanical properties and deformation mechanisms at elevated temperatures? One question of interest is brittle-to-ductile transition (BDT). Preliminary evidence showed that the BDT temperature of single crystalline silicon (SCS) reduces with sample size [175–178]. It is however unclear if SCS nanowires exhibit ductility at room temperature. Han et al. observed ductile deformation of SCS nanowires with diameter <60 nm at room temperature during in-situ tensile testing in a TEM [176]. However, Zhu et al. reported no ductility at room temperature, even for SCS nanowires of 16 nm in diameter by quantitative in-situ scanning electron microscopy (SEM) tensile testing [12]. The authors argued that electron beam irradiation in TEM could lead to the observed plastic deformation in SCS nanowires. Therefore, in-situ nanomechanical testing at varying temperatures is in timely need to further
elucidate the nanoscale BDT and other thermally-activated deformation mechanisms at the nanoscale [1].

_in-situ_ mechanical testing at high temperatures is challenging at small scale. The most straightforward way is to control ambient temperature. Zupan et al. performed tensile testing of millimeter scale samples using resistive (Joule) heating of the samples [179]. Sharpe et al. measured the fracture strength of SiC samples (a few hundred micrometers in width) in a furnace [180]. Nakao et al. studied plasticity in microscale SCS under bending on top of a hot plate [178]. Haque and Saif measured thermomechanical properties of nanoscale Al films also on top of a hot plate [181]. All above devices so far were designed for testing samples with micro-scale size.

Kang and Saif developed a novel MEMS platform for in situ uniaxial test of micro/nanoscale samples at high temperature [152], which has been introduced in previous chapter. Yet the system is quite complicated and the smallest sample was 720 nm in width and 6.5 µm in depth. Although resistive heating of the samples is relatively easy to implement, it was found to cause nonuniform temperature distribution and as a result reduction in yield and ultimate tensile strengths [182].

In this chapter, we report an integrated microelectromechanical system (MEMS) with an on-chip heater for in-situ mechanical testing of nanostructures from room to elevated temperatures. Multiphysics simulation is used to predict the temperature distribution in air and vacuum conditions. The temperature simulation in air agrees well with the measurement based on Raman spectroscopy. Mechanical testing of single crystalline silicon nanowires is carried out to demonstrate the efficacy of the MEMS stage.
3.2. MEMS tensile stage for thermomechanical testing of nanostructures

The integrated testing stages were fabricated at MEMSCAP (Durham, NC) using the Silicon-on-Insulator Multi-User MEMS Processes (SOI-MUMPs). The microfabrication process is simple and does not add any extra step compared to that for fabricating the pure mechanical testing stage. The stage is made of one layer of SCS with thickness of 10 µm. As shown in Figure 3-1, the actuator is a comb drive based on electrostatic force and the heater is based on Joule heating of the SCS structure itself (i.e., no additional metal layer).

![Figure 3-1](image)

Figure 3-1 (a) SEM image of the entire MEMS device that consists of three parts: comb drive actuator, capacitive load sensor and heater. (b) Magnified view of the heater as boxed in (a). The arrows indicate the current direction.

In order to achieve independent control of the actuation and heating, the comb drive actuator is used in our design instead of the widely used thermal actuator. Under actuation voltage \( V \), the comb drive generates electrostatic force \( F \):

\[
F = N \frac{\varepsilon_0 V^2}{d}
\]

(3-1)

where \( N \) is the number of finger pairs, \( \varepsilon_0 \) is the permittivity of vacuum or air depending on
the operating environment, \( t \) is the comb thickness, and \( d \) is the spacing between neighboring combs. A critical part of the integrated stage is the on-chip heater. To achieve identical temperature at both ends of the specimen, the entire stage is symmetric with respect to the specimen. Notably the sensor has the identical structure as the actuator. For actuation, a voltage is applied between the movable and fixed combs; for sensing, the capacitance can be measured between the movable and fixed combs. When the heater is turned on, the temperature in the shuttle arises and as a result the shuttle elongates due to thermal expansion. In this case the specimen would be compressed. Since the shuttle is very long compared to the specimen, this compression could be serious. Indeed in our initial design, a serpentine-like heater was employed (Figure 3-2) [183]. Serpentine structure is commonly used in MEMS to reduce its stiffness. As an example, to achieve 326 °C (599 K) temperature (at the heating voltage of \( \sim 7.4V \)), the gap between the two shuttles reduces 1.06 \( \mu \)m, equivalent to 53% compressive strain imposed on the specimen (the specimen length is equal to the initial gap, 2 \( \mu \)m). New designs to reduce such an undesired thermal displacement must be sought, although it appears not possible to completely eliminate it using the simple microfabrication process in the present study. In general, shielding the thermal displacement from the specimen is challenging at the micro/nano-scale.
Figure 3-2 SEM image showing the fabricated MEMS thermomechanical testing device that has a serpentine heating coil that can be resistively heated.

Here we present one design that effectively reduces the thermal displacement to 180 nm over the entire temperature range from room temperature to 599 K. The design is based on the Z-shaped thermal actuator [105], which provides an additional thermal displacement to counterbalance that due to the shuttle expansion. Note that the Z-shaped beam over the inclined beam [95] is selected due to the much lower stiffness (for the comparable dimensions) of the Z-shaped beam [105]; low stiffness of the heater is preferred as it takes less load imposed by the comb drive actuator. The key parameter of the Z-shaped design is the length of the central beam, which is easy to adjust. With increasing central beam (> 2 μm), the thermal displacement decreases [105].
Nonlinear multiphysics finite element analysis (FEA) was carried out using ANSYS 13.0 to predict temperature distribution and thermal displacement of the proposed stage both in vacuum and in air [107]. For the vacuum condition, the only heat dissipation mechanism is the heat conduction through the device itself to the anchors (substrate). For the air condition, additional heat dissipation mechanism is thermal conduction through the air to the fixed combs (connected to the substrate). Thermal convection and thermal radiation were found to be negligible in our case. The simulation is a coupled-field analysis involving electric, thermal, and mechanical fields. The electric boundary conditions are the positive and negative voltages at both ends of the heater. The thermal boundary conditions are zero temperature change at the substrate. The mechanical boundary conditions are fixed displacements at the anchors. Element type SOLID 98 was used for the stage (made of SCS) and SOLID 70 was used for the air. The former element possesses the capability of three-dimensionally thermal, electrical, and structural field simulation while the later one considers only steady-state or transient thermal analysis which could save a lot of computational resource and time. The material parameters that used in the simulation are listed in Table 3-1.
Table 3-1 Material parameters used in the simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus</td>
<td>$E$</td>
<td>170</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>$v$</td>
<td>0.28</td>
<td>–</td>
</tr>
<tr>
<td>Thermal conductivity of Si</td>
<td>$K_{Si}(T)$</td>
<td>$210658 \times T^{1.2747}$</td>
<td>W/(mK)</td>
</tr>
<tr>
<td>Thermal conductivity of air</td>
<td>$K_{air}$</td>
<td>0.026</td>
<td>W/(mK)</td>
</tr>
<tr>
<td>Free convection coefficient of air</td>
<td>$C_{air}$</td>
<td>20</td>
<td>W/(m²K)</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>$\alpha(T)$</td>
<td>$-4 \times 10^{-12}T^2 + 8 \times 10^{-9}T + 4 \times 10^{-7}$</td>
<td>K⁻¹</td>
</tr>
<tr>
<td>Resistivity</td>
<td>$\rho(T)$</td>
<td>$5.1 \times 10^{-5}[1+3 \times 10^{-3}(T-273)]$</td>
<td>Ωm</td>
</tr>
</tbody>
</table>

Figure 3-3(a) shows the temperature distribution of the testing stage in vacuum; the heating voltage (across the heater) is 4 V. Due to symmetry, only a quarter of the stage is shown. The highest temperature does not occur at the center of the heater. This is because of the presence of the support beams on the other side of the comb drive, which provides an additional route for heat dissipation. Figure 3-3(b) shows the temperatures of two points, A (where the highest temperature is) and B (center of the shuttle, where the specimen is mounted), as functions of the heating voltage. For SCS, plastic deformation for beams of 4 μm width under bending could be as low as ~680 K [178]. In the present work, the heating voltage was always kept below 8 V with the maximum temperature of 599 K at point B (and 650 K at point A). According to our careful comparison of SEM images before and after heating, no permanent deformation or damage to heating beams was observed in this temperature range. Figure 3-3(c) shows the undesired thermal displacement as a function of the heating voltage. The maximum displacement corresponds to 9% compressive strain in the
nanowires. This is the best scenario we have been able to obtain over the entire temperature range from room temperature to 599 K. By contrast, this thermal displacement in a conventional serpentine-type heater is shown in Figure 3-2, which is about 6 times of that in our present design.

Figure 3-3 (a) Simulated temperature distribution under 4 volt heating voltage in vacuum, (b) simulated temperature profile at points A and B as functions of heating voltage, (c) measured thermal displacement as a function of heating voltage, (d) displacement of comb drive actuator as a function of actuation voltage at room temperature (theoretical calculation according to Eq. (3-1))
Still the thermal displacement is undesired and should be compensated. Figure 3-3(d) plots the measured displacement of the comb drive actuator as a function of the actuation voltage, which agrees very well with the theoretical predication, via Eq. (3-1). The thermal displacement versus the heating voltage can be fitted with a polynomial equation, see Figure 3-3(c). So by comparing the fitting equation and Eq. (3-1), it is possible to compensate the undesired thermal displacement with the comb drive motion following

\[ V_A = -0.02V_H^3 - 0.23V_H^2 + 6.47V_H + 0.56 \]  

where \( V_H \) is the heating voltage of the heater and \( V_A \) is the actuation voltage of the comb drive. As an example, to achieve 599 K temperature in the specimen, 8 V heating voltage is required. Thus the comb drive should be actuated at 25 V simultaneously to eliminate the undesired thermal displacement.

Figure 3-4(a) shows the temperature distribution of the testing stage in air for the heating voltage of 4 V, while Figure 3-4(b) shows the temperatures of two points A and B as functions of the heating voltage. The air in the Figure 3-4(a) are removed intentionally in order to show a clear relationship between free comb and fixed comb. The temperature was measured using a HORIBA LabRAM HR Raman microscope in air (laser wavelength 633 nm). The laser power was kept below 0.003 mW to avoid laser-induced local heating. Each measurement took approximately 60 s. The Stokes shift was recorded and analyzed in our experiments. The Raman spectra were fit to a Voight lineshape function to determine the Stokes peak location. It is seen that with increasing actuation voltage, the Stokes peak blue-shifted. Following the calibration experiment reported previously [107], the change in the peak position can be converted to the temperature rise in the ETA, viz.,
\[ \Delta T = \frac{\Omega - \Omega_0}{-0.0242 \text{ cm}^{-1}} \]  

(3-3)

where \( \Omega_0 \) and \( \Omega \) are the measured peak positions at the laboratory temperature of 296 K and at the operating temperature, respectively. Simulated and measured temperatures at points A and B agreed very well (Figure 3-4(b)), which indicates the accuracy of the FEA simulations and verifies the predicting power of the simulation performed in vacuum (for in-situ SEM testing). The verification is important, as we are currently not capable of measuring temperature in SEM with the required spatial resolution on the order of \( \mu \text{m} \).

Figure 3-4 (a) Simulated temperature distribution under 4 volt heating voltage in air, (b) temperatures profile at points A and B as functions of heating voltage in air.

In order to check if the temperature on the nanowire is the same as that on at point B and if the temperature is uniformly distributed along the SCS nanowire, we conducted Raman-based temperature measurement and ANSYS. As shown in Figure 3-5(a), the nanowire is attached on the middle of the shuttle between actuator and force sensor. The
diameter of NW was set to be 60 nm, and the length is 2 μm. Noticed that the thermal conductivity of SCS in nano scale (~15 W/mK) [184,185] is different from that in micro and macro scale, so it should be treated as a different element type from our SCS based stage.

The inset of Figure 3-5(a) shows that the temperature is uniformly distributed along the SCS nanowire. Temperature difference between the center of the nanowire (point C) and the edge of the device (point B, the same as that in Figure 2a) is only 0.2 K while the temperature of nanowire exceeds 500 K. Figure 3-5(b) shows the Stokes-shifted Raman spectra of points C and B. The difference of temperature between two points is 2 K. The peak position is a reflection of the temperature according to Eq. (3-3). The large difference in the spectra amplitude is due to the fact that the probe areas in point C is much smaller than that in point B.

Figure 3-5 (a) Temperature contour of MEMS device and mounted nanowire. (b) Raman spectra of point B and C under 8 V heating voltage in air.
3.3. **In-situ tensile testing of SC silicon nanowire**

To demonstrate the efficacy of the integrated thermomechanical testing stage, it was used to test SC Si nanowires in-situ inside a SEM (FEI Quanta 3D FEG) to probe their BDT. The SC Si nanowires were manipulated and positioned onto the MEMS stage following the pick-place method [96]. Figure 3-6(a) and (b) show a single crystalline Si NW (with diameter of 60 nm) clamped on the testing stage before and after the thermomechanical testing, respectively. Figure 3-6(c) shows the loading-unloading behavior of the single crystalline Si NW at different temperatures. Tensile testing was initially conducted at room temperature, and then done at gradually increasing temperatures. It can be seen that the first and second loading and unloading curves, which represent temperature at room temperature and 362 K, followed identical linear paths. No plastic deformation was observed when the nanowire was fully unloaded. The Young’s modulus at room temperature was measured to be 164 GPa. However, as temperature was increased to 399 K (the third loading and unloading curve), yielding was observed with 0.5% plastic strain after the nanowire was totally unloaded. This stress-strain behavior suggested that the BDT temperature of the single crystalline Si NW (with diameter of 60 nm) lies between 362 K and 399 K, which is much lower than those of bulk single crystalline Si (>900 K) and micro-scale single crystalline Si (>600 K). The nanowire was broken at 599 K during the fourth loading curve with a failure strain of ~4.9%. The fracture surfaces, as shown in Figure 3-6(b), tilt with respect to the NW loading axis, indicating a potential possibility of shear failure, which is in contrast to the cleavage fracture
observed at room temperature [12,51]. The observed fracture surface agrees very well with that predicted by MD simulations for single crystalline Si NWs at high temperature [186].

Figure 3-6 SEM images showing a single crystalline Si NW with diameter of 60 nm on the MEMS stage (a) before and (b) after the thermomechanical testing, (c) stress-strain curve of the single crystalline Si NW under different temperatures (1st, 2nd, 3rd and 4th loading corresponding to room temperature, 362 K, 399 K and 599 K, respectively).

3.4. Summary

In summary, we report an integrated MEMS stage for thermomechanical testing of 1D nanostructures in this chapter, which could greatly enhance the instrumentation capabilities for probing the thermomechanical properties at the nanoscale. The temperature predicted by 3D multiphysics simulation in air agreed very well with that measured by Raman spectroscopy. Then the simulation was used to predict the temperature distribution in vacuum for the in-situ electron microscopy testing of nanostructures. Mechanical testing of SC Si
nanowires in SEM was carried out to investigate the BDT, demonstrating the efficacy of the integrated MEMS stage. A single crystalline Si NW of 60 nm in diameter exhibited linear elastic behavior at room temperature but plasticity and ductile failure above 399 K. Temperature effects on mechanical properties of nanostructures are interesting, but so far have been much less studied at least experimentally. The more detailed studies on thermomechanical behavior of single crystalline Si NWs will be found in next chapter.
Chapter 4.

Temperature Effect on Mechanical Properties of Silicon Nanowires

4.1. Introduction

There was not an explicit definition of material failure until the famous Griffith formula was published in the early 20th century [187], where the propagation of the sharp crack was described as “brittle fracture”. On the other hand, “ductile deformation” was for the blunted open crack. In addition, he especially pointed out that the deformation and fracture behavior for a material could be varied due to temperature [188]. Such observation brought the incipient study on brittle-to-ductile transition (BDT) of materials. Later on, Taylor defined the ductile deformation where he suggested the plastic flow was dominated by the movement of dislocation [189]. The plasticity around a crack tip of the sample in the pre-cracked experiments enhanced the resistance to brittle fracture. The competition between Griffith and Taylor processes thus became the core concept of BDT studies. The materials are treated as brittle if the crack propagation dominates the fracture behavior. On the other hand, the materials would be considered as ductile if the fracture is accompanied with dislocation activities such as motion and nucleation, and there should be a range of temperature where the BDT could occur. Although the issue rose during early 20th century, it did not receive too much attention before 1960s since the detection of dislocation activities was a challenge, which gave ambiguous conclusions on the theory of plasticity.
The initiation of studies on BDT was targeting on body-center-cubic (BCC) metals such as steels due to their importance on the construction aspect [190–193]. The transition in these ferrous materials was found to be generally gradual with the stress to fracture increasing over a wide range of temperature of about 100 K. In contrast, the transition temperature of single crystalline silicon was later found to be surprisingly sharp, occurring in an extremely narrow range of 5 K via pre-cracked fracture experiments [194]. The etch-pit and X-ray topography was the two primary techniques to detect dislocation mobility at that time [193]. In the first part of this chapter, we will briefly introduce and summary the evolution of studies of BDT on single crystalline Si.

### 4.2. Brittle-to-ductile transition of silicon

There were several reasons that silicon was treat as the model substance with a high prospective to provide a more comprehensive understanding of the fundamental of the BDT transitions. First, silicon is one of the most representative brittle materials, but shows pronounced ductility at high temperature, roughly above a fraction of 0.6 of its melting temperature \((T_m)\) of 1687 K. Second, high quality, single crystalline, and dislocation free silicon is commercially available. In addition, one can easily control dislocation density by adjusting doping level. Last but not the least, various characterization technique, such as X-ray topography, SEM and TEM can be applied to approach dislocation events due to the high crystallization of single crystalline Si specimen.
4.2.1. BDT of bulk silicon

The studies of BDT behavior of macro-scale single crystalline Si in early stage were usually carried out via fracture mechanics with controlled crack or bending experiments instead of classical uniaxial tensile testing. In the previous loading types, stress is concentrated in limited area, guaranteed a localized deflection, where is favorable for observing deformation mechanisms such as crack propagation or dislocation nucleation and multiplication.

The very initial report was demonstrated by Pearson et al [195]. They studied a series of mechanical response and fracture of <111>-oriented single crystalline Si micro-whiskers with diameter of 56 μm using three-points-bending method at various temperatures of 25 °C, 650 °C, 700 °C, and 800 °C. At room temperature, single crystalline Si micro-whisker only deformed elastically, and the maximum bending stress can be as high as 1.6 GPa. However, while the temperature increased to 650 °C, a sharp yield point was found around 1.1 GPa, and the whisker deformed plastically and finally fractured at 0.4 GPa. Both yield stress and fracture stress decreased with the continuous increasing of temperature from 650 °C to 800 °C. They ascribed this phenomenon to many dislocations locked by the impurities in the specimens were thermally enhanced propagation.

A more popular way to study BDT of SCS during early time was via fracture mechanics using a crackline-loaded profiled specimen, which is similar to the tapered-double-cantilever-beam (TDCB) structure. The most advantage of this method was that the stress would concentrate at crack-tip, and thus help to exclude the appearance of plasticity other that at the
crack-tip. This kind of experiment was first demonstrated by St. John [194]. In his study, the BDT of single crystalline Si was found to be both temperature and loading rate dependent. The single crystalline Si crackline-loaded profiled specimens with (111) crystal orientation, as shown in Figure 4-1(a), were tensile loaded to introduce mode I fracture in a wide temperature range from -196 °C to 1000 °C. The critical stress-intensity factors ($K_{IC}$) were found to be similar from -196 °C to 800 °C at a constant loading rate of 50 µm/min. However, a sharp BDT temperature was shown at 805 °C where a sudden increase in $K_{IC}$ could be found in force-displacement curve and the pure cleavage was replaced by yielding and plasticity at crack tip. Besides, the transition temperature was strongly rate dependent, decreasing from 940 °C to 700 °C while the loading rate also decreased from 500 µm/min to 5 µm/min. A crack-tip blunting mechanism for sharp transition temperature by thermally activated dislocation was proposed and dislocation activities were confirmed by X-ray topography. The activation energy obtained from the $K_{IC}$ versus temperature plot could be compared with the value in the previous report for dislocation glide in single crystalline Si (1.9 eV and 1.8 eV).
This pioneering work inspired many groups started to chase the physical fundamentals of BDT in single crystalline Si. For instance, Michot and George used the same method and sample as St. John’s work [196,197]. They applied various loads smaller than the $K_{IC}$ of crack propagation of single crystalline Si at different temperature. The growth kinetics of dislocations nucleated from crack tips with time was carefully characterized by X-ray topography. In addition to dislocation resulted crack tip blunt, they argued that dislocation shielding should be seriously considered regarding the BDT of single crystalline Si as well. While a dislocation is emitted at crack tip field and moved away from the crack tip by the applied stress, the dislocation exerts a back stress on the source. The back stress from dislocation decreases the stress around crack tip. As a result, the local stress intensity factor is actually lower than the applied stress intensity factor, which is known as dislocation shielding of the crack tip [198–200]. As the applied stress is increased, further movement of the first dislocation and emission of the second dislocation are expected. The key of shielding
is thus depended on dislocation mobility which allows initial dislocation to move sufficiently far away for consecutive dislocation emission. They found that the dislocation velocity was affected by temperatures according to the X-ray topography. However, the initiative of dislocation activities was too quickly to be captured [196]. After the first dislocation event was emitted, the plastic zone around crack tip due to dislocation activities was found to be a function of applied load and independent to the temperature. But higher temperature could reduce the time required to reach the saturation at a given load [197]. In addition, according to a preliminary dynamic experiment, they proposed there must be a threshold value of stress intensity factor where the dislocation could be nucleated, since the single crystalline Si sample is considered as nearly perfect crystal and no potential source for dislocation was existed.

Brede and Haasen also followed St. John’s work using single crystalline Si TDCB samples [201]. They further confirmed the Michot and George’s argument that the dislocation velocity played a critical role regarding the BDT of single crystalline Si by carrying out fracture experiments on Si samples with different doping level. They proposed there should be a certain value of shear stress ($\tau_c$), which had to be overcame first in order to trigger the dislocation activity. The $\tau_c$ decreased with increasing of temperature. Once the dislocations are no longer immobile, the BDT temperatures were controlled by the dislocation mobility that move outward from the crack tip instead of the dislocation process. High doping level in crystalline Si enhances the dislocation mobility resulting in a lower BDT temperature compared to St. John’s work.
Roberts and co-workers of Oxford group used a different approach to study the BDT of single crystalline Si by carrying out dynamical experiments [202–205]. Four-points-bending (FPB) experiments on rectangular SCS bars containing “thumbnail”, a small half circle pre-crack introduced by hardness indentation on the (110) surface, as shown in Figure 4-1(b). After the crack was made, the sample was heated up to 800 °C for annealing to reduce internal stresses at crack tip. They presume that there were existing dislocations in the plastic zone close to the surface under indentation, more or less. Under certain stress, the existing dislocations were moved to the crack tip, where they form sources and shield the crack. BDT is therefore mainly controlled by the dislocation velocity, which were responsible for the time it takes for the existing dislocations to reach crack front [203]. In this situation, blunting mechanism could be neglected. Furthermore, the dislocations introduced by the indentation were also ascribed as the reason of a substantially lower BDT temperature they acquired compared to St. John’s work with similar sample size and loading rate.

All of the above early researches have been summarized and can be found in a few references [206,207]. Although there were some discrepancies on interpretation of BDT of single crystalline Si, the general consensuses were concluded as follow:

1) BDT temperature is extremely sharp, occurring in a range around 5-10 K, as illustrated in Figure 4-2, and strongly strain rate dependent.

2) The strain rate dependency of BDT temperature is most likely due to the activation energy that control dislocation velocity, instead of the activation energy of nucleation.

3) Below BDT temperature, $K_{IC}$ is weak temperature dependent, showing an almost constant as the temperature increasing, drawn as black dot line in Figure 4-2.
4) In the range of BDT temperature, dislocation activities could be found via X-ray topography. The stress intensity factor at failure increases rapidly and is much larger than $K_{IC}$, as shown in red solid line in Figure 4-2. However, the failure is essentially brittle, showing crack propagation.

5) Over BDT temperature, the sample deformed fully plastically and fractured in a ductile manner. The stress intensity factors were determined by the upper yield stress, which decreased with the increase of temperature at this region, as shown in dash blue line in Figure 4-2.

6) Last but not the least, blunted and/or shielded of crack tip by dislocations are the most likely mechanisms to control BDT of single crystalline Si. Both of them were dominated by dislocation mobility, which is determined by the temperature

Figure 4-2 Stress intensity factor ($K$) versus temperature; black dot line represents brittle cleavage; red solid line represents brittle-to-ductile transition region; blue dash line represents ductile failure.
However, either blunting or shielding could not explain the sharp transition observed in experiments sufficiently. Brede assumed that there should additional shielding exist to achieve sharp transition. According to simulation results, the dislocation loops in glide system observed in experiments would enclose the crack tip, leading to a gradual transition which was a contradiction to experimental finding. In other words, there should be additional shielding process served as a threshold in the slip systems which were not considered or observed.

On the other hand, in Oxford group’s dynamic model where involved only dislocation shielding, the necessity to nucleate crack tip dislocation sources is the key to control the sharpness of BDT [206]. As mentioned above, the core of dynamic model is that the existing dislocation would move toward crack tip and form source site for further nucleation. These sources sent out avalanches of dislocations which shield the crack tip so rapidly just at a local (shielded) stress intensity factor slightly smaller than $K_{IC}$ everywhere along the crack front. If the tip sources are originally existed and the density is significant, the BDT temperature is supposed to be gradual, which could probably be the case of BCC metal samples.

Finally, different loading mode could also affect BDT temperature. A 100 K difference in BDT temperature was found between TDCB and FPB experiments with similar sample geometry. Brede claimed that FPB test would introduce an overall plasticity on specimen leading to a variation of actual loading rate. Stress distribution must be carefully characterized first before any assumptions on dislocation activities were made.
4.2.2. BDT of silicon at micro/nano scale

Silicon is one of the most technologically relevant materials in micro/nano world. Though it has been extensively used in electronics, cells and MEMS based applications and devices, yet its thermomechnical properties are not well interpreted where the high temperature and high strain were often involved. Understanding of BDT of single crystalline Si in micro/nano scale is thus not only related to the comprehension of physical phenomenon, but also regarded the reliability of industrial products.

Initial study on characterization of thermomechanical behavior of single crystalline Si in nano-scale was done by Namazu et al [23]. Top-down fabricated <110>-oriented single crystalline Si NWs with a constant thickness of 255 nm and different widths of 200, 300, 550 and 800 nm were in-situ tested inside SEM using an AFM-based three-points bending from room temperature up to 300 °C. The force-displacement response remained linearly to fracture at room temperature, but show non-linear behavior when temperature exceeded 100 °C in all of samples. The range of non-linear curve increased while the size of NW decreased and the temperature increased, as shown in Figure 4-3(a). Slip lines perpendicular to the direction of principle stress on the top of specimen due to the glide of dislocations were observed from AFM profiles just before fracture. Slip lines density also increased as the specimen size decrease and the temperature increase. An edge dislocation model was proposed to elucidate the size effect of BDT temperature, which was most likely due to an increase of activation Gibbs free energy. Kang and Saif also carried out in-situ SEM bending experiments at elevated temperature using a MEMS device with an external Joule heater to
study thermomechnical response of single crystalline Si beams with different beam width [175]. Evidences from both force-displacement curve and SEM images as shown in Figure 4-3(b) and (c) clearly indicated the onset of plasticity dependents on not only temperature but also sample size. They observed the BDT temperatures of single crystalline Si beams under bending that reduce from 375 °C to 293 °C while beam width decreased from 8.7 μm to 720 nm.

Figure 4-3 (a) Force-displacement curves in AFM bending tests for NWs with 200 nm in width at elevated temperature [23]. (b) Force-displacement curves of single crystalline silicon beam with different sample size [175]. (c) SEM images of plastic deformation of single crystalline silicon under bending.

On the other hands, Sato and co-workers carried out tensile testing via an on-chip MEMS stage to study mechanical responses and fracture mechanisms of single crystalline Si micro thin film with temperatures range from room temperature to 300 °C [178,208,209].
They followed those pioneering works to perform fracture toughness test on pre-cracked single crystalline Si thin film samples, which were designed as $100 \times 50 \times 5 \, \mu m$, as shown in Figure 4-4(a). At very beginning, they characterized $K_{IC}$ and fractography of single crystalline Si with different crystalline orientations and loading directions at room temperature and observed anisotropic behaviors of $K_{IC}$ as a result of the difference in surface energy of low index plane [208]. In addition, the fracture strength was found to be independent to the crack length, as the same as what was reported by St. John on macro-scale size single crystalline Si samples [194]. The fracture mode, however, was changed from brittle to ductile at elevated temperature condition using the same experimental setup [209]. The $K_{IC}$ remained a nearly constant value around $1.28 \, MPa\sqrt{m}$ until $60 \, ^{\circ}C$ and drastically increased between $60$ to $70 \, ^{\circ}C$ by a factor of $1.5$. After sharp increase, $K_{IC}$ continuously escalated to $2.60 \, MPa\sqrt{m}$ at $150 \, ^{\circ}C$ and then stayed in a plateau region. TEM post-mortem observed enormous dislocation activities on the fracture plane of the sample tested at $300 \, ^{\circ}C$, as shown in Figure 4-4(b), which could be barely seen in the sample tested at room temperature. Compared to early studies on BDT of bulk single crystalline Si, this report implied the role of single crystalline Si specimen size on the BDT temperature size.
Bottom-up synthesis Si nanostructures, such as Si NWs or nanoparticles (NPs) exhibit significantly enhanced mechanical behavior from their bulk counterparts. At room temperature, the mechanical properties of single crystalline Si NWs have been studied extensively via nanoindentation [210], AFM-bending [210,211,25,212], *in-situ* SEM testing [12,51,150,169] and *in-situ* TEM testing [176,213–217]. A strong size-dependence on elastic limit can be found in these literatures and the ideal strength of single crystalline Si, namely $E/10 = 16$ GPa, has been demonstrated as approachable. For instance, Zhu et al. reported that a single crystalline Si NWs with diameter under 20 nm can sustain tensile stress and strain as high as 12 GPa and 12%, respectively [12]. Stan et al. also demonstrated an ultra-high bending stress of 17 GPa in single crystalline Si NWs with diameter around 20 nm [212].

However, controversial results on either brittle or ductile failure for single crystalline Si NWs at room temperature were debated in literatures. Han et al. performed the earliest *in-situ* TEM to study tensile deformation of single crystalline Si NWs with diameter range from 15 nm to 70 nm [176]. They reported severe plastic deformation before failure at room
temperature in all tested NWs as shown in Figure 4-5(a). The plasticity was initiated by the nucleation of a high density of dislocations, followed by the formation of disordered crystalline structures, and eventually resulted in amorphous and fracture. Unfortunately, quantitative stress-strain relationship was not able to be acquired in this study. In contrast, Zhu et al. reported a pure linear elastic behavior and catastrophic failure without any appreciable plastic deformation according to stress-strain curve at room temperature for single crystalline Si NWs with similar diameter ranging from 15 nm to 60 nm, as shown in Figure 4-5(b). The discrepancy is most likely due to high energy level electron beam induced localized amorphous that triggered the dislocation activities. Later Dai et al. further characterized the effect of electron beam irradiation on Si NWs quantitatively [217]. They found that while the Si NW was exposed under high density of electron beam (3.24 A/cm²), especially high magnification imaging in local region, the elastic energy stored in the NW could be released through the bond reformation, resulting in plastic deformation and amorphous. Tang et al. [214] carried out in-situ TEM experiments on single crystalline Si NWs confirmed that while TEM image was kept in low magnification, only elastic deformation and brittle fracture could be found in the single crystalline Si NWs as small as 7 nm. However, they meanwhile demonstrated considerable plasticity in single crystalline Si NWs with the same diameter by in-situ bending experiments. Bending is the mixture of tension and compression, dividing by the neutral axis. On the tensed side, crack nucleated was observed at high bending strain (>20 %). On the compressed side, pronounced plastic deformation was driven by dislocation activities and local amorphous.
Figure 4-5 (a) A series of TEM images show severe plastic deformation of a single crystalline Si NW under tensile stress. (b) Stress-strain response of a single crystalline Si NW with diameter of 23 nm under repeated loading and unloading. Inset shows a SEM image of the broken end of the Si NW.

Gerberich and co-workers have done series of studies on mechanical responses and the nucleation of dislocations [177,218–222] of single crystalline Si by compression test on low aspect ratio nanostructures such as nanopillar and nanoparticles at room temperature. The most advantage of compressive experiments is easier to conduct, where avoiding gripping, mounting and aligning issue associated with tensile test on single NW. For instance, single crystalline Si pillars with variable size can be fabricated from commercial available silicon wafer via focus ion beam (FIB) milling technique. After placing the fabricated pillars inside a SEM chamber, a customized indenter is then conducted to provide compressive stress and record force and displacement [223].

Using this method, a direct evidence of size effect on BDT of single crystalline Si was reported by Östlund et al. [177] <100>-oriented single crystalline Si were shaped into a
slightly conical shape pillar with various diameter ranging from 230 to 940 nm with similar height of 2 µm by FIB technique [224]. In nanopillars with larger size, cracks were created and then penetrated pillars vertically by compressive stress, as shown in Figure 4-6(a). In contrast, Figure 4-6(b) shows that while the diameter of pillar was smaller than a critical value, slip lines across the cross section of pillar on {111} planes were clearly observed by SEM and the pillar therefore deformed plastically. The critical size of BDT of single crystalline Si at room temperature under compressive stress was found to be located between 310 and 400 nm. Two possible mechanisms were proposed to clarify the size effect on BDT of single crystalline Si. The first possibility is dislocation velocity. Dislocations have to nucleate from the surface and move through the pillar at a sufficient rate in order to accommodate the imposed deformation plastically. Otherwise, the pillar would fail through a brittle crack. The other one is the competition between the dislocations in glide set as the bond breakage for the same {111} planes and the dislocations in shuffle set as the breakage occurring on the {111} plane with atoms of the same indices [225,226]. The dislocations in a shuffle set are more favored to control plasticity of single crystalline Si at low temperature according to the unstable stacking fault energy calculation. The transition of dislocations from glide set to shuffle set was expected to be related to the BDT of single crystalline Si.
Later Gerberich et al. concluded a few criterion based on the compressive experiments for triggering ductile deformation in nano-scale single crystalline Si at room temperature [227]. First is the nucleation of dislocations. There is a general consensus that plastic deformation of a crystal takes place through either the interaction and multiplication of dislocation from existing sources or the nucleation of new sources from free surface. For the clear evidence in the current studies associated with nearly dislocation free single crystalline Si, dislocations must be nucleated. It is well understood that the dislocation nucleation is thermally activated, stress driven motions. At room temperature, the requirement then is that a significantly high stress must be available to nucleate a dislocation from surface, which leads to the second requirement: no initial appreciable defect. For instance, according to previous reports [209], in a nudged single crystalline Si sample, dislocations could emitted
from crack tips at $K_{IC}$ above 1.5 MPa{$\sqrt{\text{m}}$}. Considering a Si nanoparticle with diameter around 50 nm sustain a nearly theoretically strength of 10 GPa, the largest surface defect it could have and not fail is only 3 nm. This demonstrates that even a tiny defect should be avoided in order to produce enough stress for the dislocation nucleation.

Finally, like what has been revealed in bulk single crystalline Si previously, the rapid dislocation motion is necessary for continuous emitting of successive dislocation. This not only enhances the shielding mechanism but also sufficiently modifies the atomistic process to allow the activation energy to be lowered. A model then was built predicting the BDT could shift by a factor of three in absolute temperature by reducing size. The plasticity with both length scale and temperature dependence can result in a fracture toughness for SCS at room temperature up to 8 MPa{$\sqrt{\text{m}}$}.
4.2.3. Conclusion

Figure 4-7 Plot of temperature versus sample size [12,51,150,169,175,177,178,194,195, 204,23,209–211,25,212,214,220,228]. The open symbols represent a ductile deformation while the solid symbols represent only brittle failure.

Figure 4-7 summarized the available experimental results of the possible BDT temperature of silicon from literatures which have been discussed in this section and shows the temperatures as a function of size. The open symbols represent a ductile deformation while the solid symbols represent only brittle failure. A clear size dependent BDT temperature can be concluded from the plot. In additional to the size and temperature effect,
Tang et al. revealed that the loading type plays equally important role in the BDT of single crystalline Si NWs as well [214]. The [111]-oriented Si NWs suffered either tensile or bending stress showed completely different deformation mechanism. Under tension, crack was initiated from the surface and propagated very fast through the cross-section, causing the sudden failure and leaving a flat fracture surface that is perpendicular to the tension direction. Bending test, on the other hand, prompted considerable plastic deformation on Si NWs. Such phenomenon was also confirmed by Zheng et al. and Wang et al. who utilized high resolution TEM to observe bent Si NW [215,229]. While a single crystalline Si NW sustain low bending strain, the dislocation activity could only be found in the compression site in the bent NW. In contrast, at large strain (>6%), partial dislocations can be introduced from the tensile surface of the bent NW. Indeed from the summary plot of Figure 4-7 we demonstrated above, compression test possesses the largest scale of around 200 nm at room temperature where the BDT can be triggered. In contrast, only elastic response without any appreciate dislocation activity can be found in the tensile experiments at room temperature for single crystalline Si NWs even with very small diameter of 15 nm. Bending, on the other hand, a combination of tension and compression, shows intermediate scale effect between other two.

In general, bulk single crystalline Si samples are brittle and vulnerable to fracture without plastic deformation due to the extremely low mobility of dislocation in low temperature. Contrarily, they show ductile at a temperature regime higher than 0.6 $T_M$ and cumulative motion of dislocations dominates the plasticity and yield strength. With the reduction of size, the transition temperature shifts toward lower spectrum and even approaches room temperature at nano-scale. From the review above, we can thus conclude
the key features that can control the BDT temperature as follow: size, strain rate and loading type.

In addition to various approach via \textit{in-situ} experiments, molecular dynamics (MD) simulations is a powerful tool for understanding deformation mechanisms of crystalline materials in terms of atomistic aspect [230–233]. Though the ideal setting and parameters in the simulations may not practical in the real experiments, they do provide some valuable prediction and decipherment. For instance, Kang and Cai [186,234] presented MD simulations of [110]-oriented SCS NWs under a constant tensile strain rate until failure and reported a ultra-high fracture stress of 12.8 GPa. This is consistent with tensile experiments of Zhu et al. [12] and Tang et al. [214]. Moreover, according to the simulation prediction, the fracture mechanism of single crystalline NWs are dependent on not only the temperature and size, but also the crystalline direction. For the [110]-oriented Si NWs, while the diameter is less than 4 nm, ductile deformation and shear failure is dominated in full temperature spectrum. However, for the one with diameter over 4 nm, shear could only be found at high temperature. On the other hand, for the [111]-oriented Si NWs, regardless of size and temperature, showed only crack propagation. Their results indicated that the fracture behavior of Si NWs was controlled by competition between crack and dislocation nucleation from the free surface. The reason of why [111]-oriented Si NWs were more brittle than [110]-oriented ones was that the ratio of ideal tensile strength over shear strength multiplied by the corresponding Schmid factor is much smaller along [111] direction.

So far the definition of BDT of single crystalline silicon most likely relies on the monitoring of dislocation activities. The most reliable way to characterize dislocation is
through high resolution TEM imaging technique. However, *in-situ* observation dislocation evolution inside TEM has never been an easy task. As mentioned previously, high resolution TEM image possesses high electron beam energy which could easily damage crystalline structure of Si and introduce locally amorphous. Besides, to perform *in-situ* mechanical test at elevated temperature inside a TEM is still quite challenged nowadays due to the restriction of TEM chamber, which is not easy to be functionalized as SEM/FIB. As one might noticed in the summary plot of Figure 4-7, when the sizes are below 200 nm, none of those experiments were performed outside of room temperature.

Recently Gerberich and co-workers proposed a combination of experimental parameters and theoretical approach based on the fracture testing of single crystalline silicon at different size and different temperature [235,236]. They found a transition in the activation volume associated with dislocation nucleation may occur in the vicinity of about the temperature of 600 K for Si thin film with size of 1 μm which would be in the range from $1 \, b^3$ to $3 \, b^3$ ($b =$ Burger’s vector). Following their work, in the next section we introduced a new way to approach the BDT of Si NWs by the combination of *in-situ* SEM tensile testing, thermal activation model and *ex-situ* TEM observation. A relative low transition temperature we found in the crystalline Si NWs compared to experiments with micrometer scale supports the size effect of BDT temperature. Dislocation nucleation during the tensile testing is similar to what has been predicted by MD simulation.
4.3. Brittle-to-ductile transition of bi-crystalline Si NWs

4.3.1. Experimental section

Si NWs were synthesized by the CVD-VLS method on a Si wafer substrate [12]. A lacy carbon TEM grid was used to gently scratch over the substrate in order to transfer NWs onto the grid for further structural characterization and mechanical testing. Figure 4-8(a) shows an isolated Si NW attached on the TEM grid. All the Si NWs tested in this report were first characterized using high-resolution TEM and selected area electron diffraction (SAED) pattern to confirm the microstructure. As shown in Figure 4-8(b), the NW possessed <112> growth direction with a bi-crystalline structure, which consisted of two symmetric {111} planes with a twin boundary in the middle and running parallel to the NW length direction. Once the microstructure and dimension of a NW was determined, a nanomanipulator (Klocke Nanotechnik, Germany) was used to lift it off from the grid (Figure 4-8(c)) and transfer to the MEMS tensile testing stage (Figure 4-8(d)) we introduced in Chapter 3 (MEMSCAP, NC). The stage consists of a comb drive actuator, a capacitive load sensor and an on-chip heater. More detailed description of MEMS stage can also be found in reference [171]. Electron-beam-induced-deposition of platinum (EBID-Pt) was used to clamp the NW and deposit strain markers on the NW, as indicated by arrows in Figure 4-8(d). All the experiments, including manipulation and tensile testing, were carried out inside a SEM/FIB dual beam system (FEI Quanta 3D FEG) at a nominal operating pressure below $3 \times 10^{-6}$ Torr, which can eliminate potential sources to introduce contaminations or cause oxidation especially when the NW was heated up.
Figure 4-8 (a) SEM image of a Si NW attached to the lacy carbon TEM grid. The nanomanipulator was trying to approach the Si NW from the underneath to lift it off. (b) The corresponding HRTEM image and SAED pattern of the red squared area in Figure (a), showing bi-crystalline structure, which consist of two \{111\} planes with growth direction of \langle112\rangle. (c) The Si NW was lifting off from the lacy carbon grid by the nanomanipulator. (d) SEM image of the Si NW across the actuator and sensor. Two white arrows indicate the EBID-Pt strain marker.

A series of high-resolution SEM images with magnification of 35,000X were taken during the tensile test at a constant strain rate of $10^{-4}$/s to record the mechanical response. The apparent strain was measured by tracing the strain markers on the NW, which usually
provide a gauge length around 1.5 μm. The image possessed 2048 × 1887 pixels and the strain markers typically spanned 1500 pixels in length. Therefore, using a free add-on package of Matlab (File ID: 12413; The Mathworks, Inc) that offers accuracy better than 1/8 pixels, we were able to obtain the strain resolution less than 0.01%. Note that during all the processes, the acceleration voltage and current of the electron beam were kept at a low value of 5 kV and 13 pA to prevent possible damages on the NW from the high energy of the electron beam.

4.3.2. Results and discussion

Figure 4-9(a) shows the stress-strain response of a Si NW with diameter of 61 nm at room temperature. The Young’s modulus was measured to be 167 GPa, which is almost the same one as the bulk value of Si in the [112] direction (169 GPa [237]). It can be seen that the loading and unloading curves followed the same path showing a linear elastic behavior until failure. No residual plastic deformation was observed when the NW was totally unloaded and no signs of yielding can be found before the fracture occurred. The fracture stress and strain were measured as 11.52 GPa and 7.37%, respectively. These values were close to what our group has reported before [12] as well as others [51,150]. All these researchers performed in-situ tensile testing on VLS-grown Si NWs, showing consistency among the mechanical performance of these NWs.

By contrast, Figure 4-9(b) shows the stress-strain curve of a Si NW with diameter of 58 nm at elevated temperatures. Tensile testing was initially started at room temperature (295 K),
and then repeated in a few cycles of loading and unloading at gradually increasing temperatures of 362 K, 445 K and 564 K. The NW finally fractured at 564 K. The stress-strain curve indicated apparent reduction of Young’s modulus and tensile strength due to increased temperature. The Young’s modulus was measured to be 172 GPa at room temperature, and decreased to 167 GPa, 162 GPa and 156 GPa in accordance with the temperature of 362 K, 445 K and 564 K, respectively. The fracture stress and strain dropped as well with the increase of temperature, decreasing from 11.52 GPa and 7.37% at room temperature to 6.38 GPa and 4.48% at 564 K. Most importantly, a signature of yielding was observed at 564 K at the over 4% strain before the fracture. Softening of Si NWs [186] and CNTs [238] at high temperature has been predicted by MD simulation. To the best of our knowledge, this is the first time that the mechanical response at elevated temperatures of a single Si NW was quantitatively measured.
Figure 4-9 Stress-strain response of the Si NWs (a) with diameter of 60 nm under repeated loading and unloading at room temperature, (b) with diameter of 58 nm at elevated temperature.

Figure 4-10 shows the measured Young’s moduli of the tested Si NWs in this work as a function of temperature and major reported results with the size of the Si samples around millimeter to sub-micrometer scale [23,239,240]. Also drawn corresponding dashed lines are
prediction based on an empirical formula that has been used to predict the Young’s modulus at various temperature of bulk materials [241],

\[ E(T) = E_0 - BT \exp\left(\frac{-T_0}{T}\right) \]  

(4-1)

where \( E_0 \) is the Young’s modulus at 0 K, \( B \) represents the temperature coefficient of Young’s modulus and \( T_0 \) is the temperature constant obtained from experiments. For bulk silicon with size over centimeter, these parameters can be found in [242]. We correlated all the experimental data, including our work and those in references, with Eq. (4-1) and results are listed in Table 4-1. It is clear that this empirical formula for the Young’s modulus of Si demonstrates a possible size effect on temperature coefficient of Young’s modulus which increased from around 0.35 at bulk to 0.5 at nano-scales. Note that the Si samples were usually fabricated to rectangular shape so the size in Table 4-1 is expressed as cross-sectional area for comparison. The diameters of tested NWs in this work were between 55 nm to 150 nm, in order to avoid the region where size effect on the Young’s modulus would occur (< 30 nm according to [12]).

The Young’s modulus of a material is determined by the restoring force between atoms while they are forced to be apart (or close). For a general interatomic force versus interatomic distance plot, one can roughly estimate the stiffness between atoms, namely Young’s modulus, by the derivation of the force curve. High temperature environment can excite the atoms to vibrate at higher energy state, which possesses a much more gentle energy gradient than low energy state. As a result, the Young’s modulus is decreased due the ease of overall energy gradient.
The size effect on temperature coefficient of Young’s modulus could be resulted from the surface effect. It is known that atoms on the surface possess different bonding structure which leads to surface reconstruction, including bond saturation, bond contraction or elongation, and loss of bonding neighbors. This mechanism has been ascribed to the size effect on Young’s modulus of Si NWs in experimental effort and simulation report [12,243]. It is not very surprised that we found size effect on temperature coefficient of Young’s modulus at nanoscale since the temperature effect on surface binding could be different from the core counterpart. A complete analysis requires a combined experimental and modeling investigation in the future.

Table 4-1 Parameters obtained from the Eq. (4-1) and plotted in the Figure 4-10.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Size (μm²)</th>
<th>$E_0$ (GPa)</th>
<th>$B$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original [242]</td>
<td>bulk</td>
<td>173.4</td>
<td>0.035</td>
</tr>
<tr>
<td>Cho et al [239]</td>
<td>$63 \times 10^6$</td>
<td>171.7</td>
<td>0.034</td>
</tr>
<tr>
<td>Ang et al [240]</td>
<td>$10^3$</td>
<td>166</td>
<td>0.038</td>
</tr>
<tr>
<td>Namazu et al [23]</td>
<td>0.2</td>
<td>175.7</td>
<td>0.050</td>
</tr>
<tr>
<td>This work</td>
<td>0.01</td>
<td>173.9</td>
<td>0.049</td>
</tr>
</tbody>
</table>
Figure 4-10 Measured Young’s modulus of crystalline Si as a function of temperature [23,239,240].

Figure 4-12 shows the measured fracture strength as a function of the testing temperature. The fracture strength decreased significantly with the increase of temperature. Si NWs in our experiment were able to sustain an average fracture strength of 10.89 GPa at room temperature without any yielding, but dropped to 6.56 GPa when the temperature reached to 564 K. A general way to interpret the temperature effect on material strength is that high temperature can assist nucleation and increase mobility of dislocations. Here, we introduce a theoretical kinetic analysis of material strength which have been used to predict other brittle materials [244–246].
In the thermal activation theory of Eyring [247], the relationship between the nucleation rate \((\tau)\), applied stress \((\sigma)\) and temperature \((T)\) can be expressed as an Arrhenius model [246,248]:

\[
\tau = \tau_0 n_s \exp \left(\frac{-U_0 + \sigma V}{kT}\right)
\]  

(4-2)

where \(\tau_0\) is the attempt frequency, \(n_s\) is the number of sites available for the nucleation, \(k\) is the Boltzmann constant. The term of \(-U_0 + \sigma V\) is defined as the energy barrier where \(U_0\) is the activation energy, \(V\) is the activation volume. The energy barrier here represents the minimum energy for dislocation to be nucleated and is usually lowered by the applied stress and/or overcame by high temperature due to enhanced thermal motion of atoms, resulting in bond dissociations.

While the material carry a uniform stress evolving with time \((t)\), the applied stress thus can be defined as \(\sigma = \sigma(t)\). Assuming the time required for the failure of the material is \(t_r\), the probability of total failure can be expressed as a cumulative distribution function (CDF) [249,250]:

\[
F = 1 - \exp \left(\int_0^{t_r} \tau [T, \sigma(t)] \, dt\right)
\]  

(4-3)

For a brittle material possesses linear elastic relation between stress and strain, such as silicon, the stress component can be written as \(\sigma(t) = E\dot{\varepsilon}t\), where \(E\) is the Young’s modulus and \(\dot{\varepsilon}\) is the strain rate, thus the fracture stress \((\sigma_r)\) is defined as the stress in the material when the breakdown takes place:

\[
\sigma_r = E\dot{\varepsilon}t_r
\]  

(4-4)
By substituting Eq. (4-2) and (4-4) into (4-3), we should be able to obtain \([250]\):

\[
F(\dot{\varepsilon},T) = 1 - \exp \left( \frac{n_s \tau_0 kT}{VE \dot{\varepsilon}} \left[ \exp \left( \frac{V \sigma_r - U_0}{kT} \right) \right] \right)
\] (4-5)

Here we defined \(\tau_0\) is the Debye frequency \((\sim10^{13})\), and \(n_s\) is dependent on the geometry size of Si NW, roughly around \(10^4\) [245]. By substituting the fracture stress and temperature acquired from the \textit{in-situ} experiments, the activation volume involved the fracture behavior of Si NWs is obtained from the fitting of CDF and plotted in Figure 4-12 accordingly. The detailed derivation of Eq. (4-3) can be found in Appendix A.

Activation volumes are the critical and useful parameters in terms of quantitatively expressing the mechanical energy that involves in dislocation activities of materials. The activation volume of silicon thin film with micrometer scale acquired via fracture toughness testing was remained as a constant around \(1 \, b^3\) from room temperature to 600 K, and increased gradually while the temperature continuously elevated [235]. Here \(b\) is the Burgers vector for \(\frac{1}{2}<110>\) full dislocation of silicon. The above observation implies that a transition in the deformation mechanism where activation volume associated of Si thin film with micrometer scale may take place in the vicinity of about 600 K, which could be the result of brittle-to-ductile transition. Based on the thermal activation model, the activation volume of Si NWs we obtained from \textit{in-situ} tensile testing is around \(1.39 \, b^3\). When the temperature raised to 364 K, we got the very similar value of activation volume equaled to \(1.43 \, b^3\). However, when temperature kept increasing to 445 K, the activation volume started to ramp
up as well, as shown in Figure 4-12. The values we acquired are $1.75 \ b^3$ and $2.13 \ b^3$, corresponded to the tensile experiments under temperature of 445 K and 564 K, respectively.

Figure 4-11 Cumulative probability for measured fracture strength of Si NWs with temperature of (a) room temperature; (b) 362 K; (c) 445 K; (d) 564 K.
In addition to activation volume, Eq. (4-5) gave an access to activation energy of silicon which evaluated to be 2.37 eV. Compared to all the activation energy of single crystalline silicon were reported, this value is slightly greater than the highest one that has been calculated in the literature (2.2 eV [204]). Brede and Haasen reported that n-type doping could result in activation energy decrease from 1.9 to 1.6 eV during the mode I fracture experiment. Yamashita et al. also found that introducing a certain degree of hydrogen atoms in the silicon sample could increase dislocation mobility and the activation energy could dramatically drop from 2.2 eV to 1.2 eV. Considering that the bi-crystalline silicon
nanowires possess a higher crystallinity and purification compared to bulk and micro thin film sample, it is not surprised that we can acquire the highest activation energy so far.

Gerberich and co-workers have conducted the open crack experiments on single crystalline silicon thin film (thickness = 1 µm and 250 nm) and associated with literature results and suggested that the activation volume for the nucleation of dislocation is almost a constant value of $1\ b^3$ when the temperature was below 600 K [227,235,236]. The extremely low and constant value of activation volume we obtained at room temperature and 364 K showed a consistency with their report and demonstrated that an ultra-high stress concentrated on a very localized region. It seemed to be more likely a crack dominated mechanical motion rather than the nucleation of dislocation. Assuming there is the minimum activation volume for a dislocation to be nucleated in the energy barrier term $\sigma V - U_0$ and should vary with temperature based on the thermal activation theory, this means that the maximum stress we can apply on the NWs at the room temperature and 364 K cannot surpass the energy barrier for the nucleation of dislocation before the initiation of crack. In other words, this implies that below 445 K there should be a threshold energy barrier of dislocation nucleation that cannot be conquered before the fracture taking place. The BDT thus can be viewed as the competition between crack and dislocation, and whichever process has the minimum stress will dominate. The trend of increasing in activation volume also strongly suggest that a possible brittle-to-ductile transition of Si NW occurs in a temperature range between 362 K and 445 K. Considering the size effect of BDT temperature, it is not surprising we attain a relative low transition temperature on Si NWs compared to the report of Si thin films.
In order to check the legality of thermal activation model and the interpretation of activation volume, careful fractographic analysis was done through TEM postmortem imaging, as shown in Figure 4-13. The results reveal that the BDT indeed occurred at the temperature below 564 K.

For the NW fractured at room temperature and 362 K, only sharp crack could be found in the TEM image, as indicated in Figure 4-13(a). This is most likely due to the nucleation of crack from the surface of NW, probably originated from a tiny surface defect. After the nucleation, the crack line was following the \{111\} plane and cutting through the NW. It is well understood that the cracks in Si favor to forward along \{111\} planes since it possesses the lowest surface energy. Due to the symmetric of bi-crystalline structure, the crack line turned to another \{111\} plane after running into the twin boundary, left a V-shaped fracture plane behind. Similar result of crack propagation can be found in the tensile testing of single crystalline Si thin films with various loading directions at room temperature [208].

On the other hand, in addition to the crack, dislocation activities can be seen in the Si NWs which fractured at 564 K, as shown in Figure 4-13(b). A shear band consisted of \(\frac{1}{2}<110>\) full dislocation on \{002\} plane is clearly observed under high resolution TEM images. Moreover, the circled part in the vicinity of the fracture region in Figure 4-13(b) demonstrates a slightly necking. These strong evidences show that the ductile deformation was taking place before the failure of the NW.
It is worth to point out that the \{002\} plane is not the most energetically favorable site for the nucleation of dislocation. Typically, while at low temperatures (< 600 K) and large stresses, dislocations in single crystalline silicon are favored to nucleate in \{111\} shuffle set plane with $\frac{1}{2}\langle110\rangle$ full dislocation [225]. This mechanism has been ascribed to the plastic deformation of silicon nanopillars under uniaxial compression [177,251]. In addition, according to MD simulations, while a Si NW sustain a high tensile stress along $\langle110\rangle$
direction at low temperature condition, the tensile stress would also be relaxed by the nucleation of a \( \frac{1}{2}<110> \) perfect dislocation loop in the shuffle set plane [230]. A possible explanation of the uncommon dislocation activities discovered by our TEM postmortem observation is the interaction between the \(<112>\) loading direction and twin boundary, but the overall mechanism remains unknown and requires more effort. Systematic \textit{in-situ} TEM tensile testing is necessary to real-time monitor the evolution of dislocation nucleation and propagation. Besides, even the evidence of ductile deformation was found by TEM image, the nucleation of dislocation was localized and the plastic region was very limited in the stress-strain response. For the future, higher temperature environment is required in order to finish the full spectrum of BDT in Si NW.

### 4.3.3. Summary

In conclusion, we thoroughly study the thermomechanical properties of bi-crystalline Si NWs in this section. Both Young’s modulus and fracture strength of the Si NWs decrease with the increasing of the temperature. For the temperature effect on Young’s modulus, our finding is consistent with previous reports on relatively larger size, showing a consistent trend on the softening of Si at high temperature, from bulk to nano scale. For the fracture behavior, we proposed a new approach to assess the brittle-to-ductile transition of crystalline Si NWs in this report. Activation volumes of \( \frac{1}{2}<110> \) full dislocation in \(<112>\) bi-crystalline Si NWs acquired from \textit{in-situ} SEM tensile testing and thermal activation analytical model show a clear deformation mechanism transition at the temperature below 445 K. The
dislocation nucleation induced shear band and diameter reduction were confirmed by TEM postmortem imaging which strongly support that the <112> bi-crystalline Si NWs are under the transition stage between ductile deformation and brittle fracture. Further steps include conducting higher temperature and in-situ TEM tensile testing.
Chapter 5.

On the Size-Dependent Elasticity of Penta-Twinned Silver Nanowires

5.1. Introduction

Recent advance in nanotechnology has brought forth a host of nanomaterials, such as nanoparticles, nanowires, nanotubes and 2D nanomaterials that exhibit ultrahigh mechanical strength [1, 15]. Such nanomaterials not only are building blocks for a broad range of nanomaterial-enabled applications, but also provide ideal platforms for studying fundamental mechanical behaviors at the nanoscale. As an example, metallic NWs have shown promising potential for flexible/transparent electronics and stretchable electronics [11, 252]; their deformation mechanism is now known to transit from forest dislocation dynamics to dislocation nucleation from free surfaces [29, 173, 250].

A variety of metallic NWs can be synthesized now using several methods including electrochemical deposition [253] and physical vapor deposition [63, 254]. Among all the metallic NWs, penta-twinned NWs are unique in microstructure – each NW has five twin segments joined along a common quintuple line in the axial direction. In addition, synthesis of penta-twinned metallic NWs based on solution phase is relatively easy and scalable [58]. Penta-twinned metallic NWs have recently received much attention due to their excellent mechanical properties. For instance, increased Young’s modulus and yield strength with
decreasing NW diameter have been recently reported [29,30]. More recently, recoverable plasticity [67,75] and strain hardening [74] have been investigated.

However, the elasticity size effect of penta-twinned metallic NWs is still under debate. Both experimental and modeling results on the Young’s modulus of penta-twinned Ag NWs, as an example, exhibited large discrepancies. Using in-situ tensile tests in scanning or transmission electron microscopy (SEM/TEM), Zhu et al. [29] and Filleter et al. [30] reported pronounced stiffening effect, i.e., increased Young’s modulus with decreasing NW diameter. Using bending tests under atomic force microscopy (AFM), Jing et al. [31] found a similar stiffening effect to the above tensile tests. In contrast, Wu et al. [32] obtained an average Young’s modulus that is higher than the bulk value but independent of the NW diameter; Chen et al. [255] reported Young’s moduli that are higher than the bulk value but without obvious size effect, similar to the result by Alducin et al. [256] using in-situ TEM bending. In all the experiments above, the NWs were <110> oriented with diameters typically between 20 and 140 nm. However, no experiments compared the Young’s moduli of the penta-twinned Ag NW and the single-crystalline counterpart.

Atomistic simulations showed pronounced stiffening size effect but no significant effect of the penta-twinned microstructure compared to the single-crystalline counterpart [257,258]. Other atomistic simulations revealed the similar size effect, but also showed strong effect of the penta-twinned microstructure, leading to higher Young’s modulus than that of the single-crystalline NW [259,260]. The microstructure effect was attributed to the high compressive at the core of the penta-twinned NW. Similar conclusions on the size and microstructure effects were observed in other penta-twinned FCC NWs, such as Cu, Au, Ni, Pd and etc
More recently, Bizek and co-workers carried out a systematic study on the Young’s modulus of several types of FCC penta-twinned NWs using atomistic simulations and analytical modeling [263]. They found that while the size effect is atomic origin (e.g., surface stress and surface elasticity), the effect of the penta-twinned microstructure is due to compatibility constraint imposed by the microstructure and elastic anisotropy of the FCC metal.

The elasticity size effect can be generally attributed to two mechanisms [264]: surface elasticity [265–269] and bulk nonlinear elasticity (as a result of the surface stress) [270]. Under different loading modes, the elasticity size effect manifests differently for different mechanisms [88,258,265]. For instance, in the case of surface elasticity, the elasticity size effect would be stronger under bending than under tension as the surface plays a more important role under bending. More specifically, the NW Young’s modulus $E = E_c + 8 \frac{S}{D}$ and $E = E_c + 4 \frac{S}{D}$, respectively, under bending and tension, where $E_c$ is the Young’s modulus of the core and $D$ is the NW diameter [88]. Therefore, for probing the underlying mechanism of the elasticity size effect, it is valuable to obtain the Young’s modulus under different loading modes. Zhu and co-workers measured the elasticity size effect of ZnO NWs under both tension and buckling [88]. However, since the buckling force and hence the measured Young’s modulus sensitively depend on the NW diameter ($4^{th}$ power in contrast to square in the case of tension), the buckling method could lead to larger error in measuring the Young’s modulus compared to other methods such as tension and resonance [271].
This chapter reports an experimental effort to address the discrepancy about the size-dependent Young’s modulus of penta-twinned Ag NWs. Two independent experiments on the same NW, *in-situ* SEM resonance test and tensile test, were used to measure the Young’s moduli. In addition, the cross-sectional shape of the Ag NWs was measured as a function of the NW diameter, which was found to transit from pentagon to circle with decreasing NW diameter. The effect of the cross-sectional shape on the measured Young’s modulus was evaluated. This work confirmed that the Young’s modulus of penta-twinned Ag NWs increases with decreasing NW diameter, though the size effect is less pronounced compared to our previous result [29].

### 5.2. Materials and methods

Penta-twinned Ag NWs were synthesized by reducing AgNO₃ with ethylene glycol in the presence of polyvinyl pyrrolidone. More details of the NW synthesis process are provided elsewhere [58,29]. The solution of Ag NWs was diluted with deionized water and then purified by centrifugation.

*In-situ* resonance and tension tests of the same NWs were carried out inside a dual beam SEM/FIB system (FEI Quanta 3D FEG) using a two-probe setup. The first probe was glued on a piezoelectric sheet that was used to provide mechanical vibration. The second probe was installed on a nanomanipulator (Klocke Nanotechnik, Germany) for manipulating an individual NW including picking up from substrate and mounting onto a MEMS stage. After the NW was transferred from the second to the first probe and clamped using electron beam
induced deposition of platinum (EBID-Pt), the piezoelectric sheet was excited into mechanical vibration (Figure 5-1(a)). Note that the clamping condition was inspected carefully following [78] in order to obtain the Young’s modulus accurately. As soon as the frequency of AC signal was close to the resonance of NW, the vibration amplitude of NW increased sharply, as shown in Figure 5-1(b). Around the resonance frequency of the NW, SEM images of the vibrating NW were taken at a number of frequencies, from which the vibration amplitude was measured as a function of the frequency (Figure 5-3(a)). Then the resonance frequency can be determined from the amplitude-frequency plot. After the resonance test, the NW was transferred from the first probe back to the second probe (attached to the nanomanipulator) for the in-situ tensile testing, as shown in Figure 5-2 (a) and (b).

Prior to the tensile testing, the NW on the second probe as shown in Figure 5-2(b) will be further transferred to a microelectromechanical system (MEMS) stage following [96]. The MEMS stage consists of a thermal actuator, a capacitive load sensor and a gap in between where the NW will be mounted. The MEMS stage was fabricated at MEMSCAP (Durham, NC) using the Silicon-on-Insulator Multi-User MEMS Processes (SOI-MUMPs). The strain rate was nominally $10^4$ s$^{-1}$. Details of performing in-situ tensile testing using the MEMS stage can be found elsewhere [67,172].

Cross-section TEM samples were prepared by embedding Ag NWs into Gatan G1 epoxy with a φ3 Cu tube, cutting the specimen discs with a thickness of ~0.5 mm, mechanically polishing with Allied Multiprep System and finally ion milling the sample via Gatan 791 PIPS while cooling with liquid nitrogen.
Figure 5-1 (a) SEM image of a penta-twinned Ag NW with one end welded on the tip of the tungsten probe. (b) SEM image of the same penta-twinned Ag NW under resonance. (c) SEM image of the MEMS testing stage with the same penta-twinned Ag NW. Inset shows the NW across the actuator and load sensor. The two small arrows indicate the deposited strain markers. Scale bar, 500 nm.
Figure 5-2 A series of SEM images showing the process of transferring penta-twin Ag NW. (a) Use the second probe to approach the NW that attached on the first probe. (b) Detach the NW from the fixed end of the first probe.

5.3. Results and discussion

From Figure 5-3(a), the first resonance frequency of the penta-twin Ag NW was identified as 799 kHz, which was then converted to the Young’s modulus assuming a pentagonal cross section of the Ag NW. According to a simple beam theory, the $n$th mode resonance frequency of a cantilevered beam is

$$\omega_n = \frac{\beta_n^2}{L^2} \sqrt{\frac{EI}{\rho A}}$$

where $E$ is the Young’s modulus, $I$ is the moment of inertia, $L$ is the beam length, $A$ is the cross-sectional area and $\rho$ is the beam density. $\beta_0 = 1.875$, $\beta_1 = 4.694$ and $\beta_2 = 7.855$
correspond to the first three resonance modes for a cantilevered beam [78]. The Young’s modulus was calculated to be 101.8 GPa according to Eq. (5-1).

Figure 5-3 (a) The amplitude versus frequency plot of a penta-twinned Ag NW with diameter of 62 nm. (b) Stress-strain of the same penta-twinned Ag NW under tensile loading.
Figure 5-3(b) shows the stress-strain curve from the tensile test of the same penta-twin Ag NW that was characterized in the resonance test. Here again a pentagonal cross section was assumed in calculating the stress. In all our tensile tests, penta-twin Ag NWs showed clearly linear elastic behavior up to ~1.5% strain, followed with nonlinear elastic behavior and strain hardening. The Young’s modulus was extracted from the stress-strain curve as the slope of the linear elastic regime.

Figure 5-4(a) plots the measured Young’s moduli of the penta-twin Ag NWs using both the resonance and tensile tests. Note that in all cases, pentagonal cross sections were assumed. 13 tensile data points that were obtained previously using an AFM cantilever as the load sensor were included [29]. When the NW diameter is larger than ~70 nm, the Young’s modulus is approximately constant close to the bulk value (84 GPa). But when the NW diameter is smaller than ~70 nm, a strong stiffening size effect can be seen (i.e., the Young’s modulus increases with decreasing NW diameter). The size effect as shown in Figure 5-4(a) is similar to that reported by Jing et al. [31]. The stiffening trend is also in agreement with that of Filleter et al. [30] but our size effect is stronger than theirs in magnitude. A notable difference is that we used pentagonal cross section in Figure 5-4(a), but Filleter et al. used circular cross section in their work. Apparently the cross-sectional shape affects how the cross-sectional area and moment of inertia are calculated, and thus affects the Young’s modulus values obtained from the tensile and resonance tests.
Figure 5-4 (a) Apparent Young’s modulus as a function of NW diameter without any cross-sectional shape modification. (b) Modified Young’s modulus as a function of NW diameter. The measured Young’s modulus was normalized by the bulk modulus of 84 GPa. The tension data using AFM cantilever (in blue open triangle) were reported in a previous paper [29].

Cross-sectional samples of penta-twinned Ag NWs of different diameters were prepared and observed in TEM to determine their cross-sectional shapes. Figure 5-5(a) shows the cross-sectional TEM images of several penta-twinned Ag NWs of different diameters. For
relatively large diameters (larger than 100 nm or so), the cross sections generally appear to be pentagonal in shape with blunted vertices. With decreasing diameter, the blunt vertices take more percentage along the perimeter and as a result the cross section appears more like a circle. NWs typically possess well-developed surface facets with low surface energies. For FCC crystal, the surface energy increases from \{111\} to \{100\} to \{110\} planes [272]. In the case of penta-twinned NWs, the five facets correspond to \{100\} planes as a result of the unique penta-twin microstructure. On the other hand, circular surface is effective in minimizing the surface area and thus the surface energy. Therefore, the blunted vertices arise as a result of the competition of the surface faceting and surface area minimization.

However, in our calculations so far all the cross sections were assumed to be pentagonal regardless of the NW diameter. Hence it is necessary to re-evaluate the cross-sectional area as a function of the NW diameter. Figure 5-5(b) shows the cross-sectional areas measured directly from the TEM images (square dots) versus the NW diameters; the NW diameter \(d\) was defined as the largest distance between any two points on the cross section in the horizontal direction of the cross-sectional image (also the largest distance as measured in the SEM image during the mechanical testing). For the purpose of comparison, the areas of ideal pentagon and circle were included in Figure 5-5(b) too (dashed lines). As expected, the measured cross-sectional areas agree quite well with the circular area and pentagonal area, respectively, for relatively small and large NW diameters. The measured cross-sectional area can be fitted with the following function

\[
A = \frac{d - d_1}{d_2 - d_1} A_{\text{circle}} + \frac{d_2 - d}{d_2 - d_1} A_{\text{pentagon}}
\]

(5-2)
where $d_1=30$ nm and $d_2=170$ nm define the range of the diameters where the fitting was applied, $A_{\text{circle}} = \pi d^2 / 4$ and $A_{\text{pentagon}} = 5d^2 / 8\sin72^\circ$ are the areas of an ideal circle and pentagon, respectively. Eq. (5-2) fitted the measured cross-sectional areas very well.

A similar form was assumed for:

$$\frac{I}{A} = \frac{d - d_1}{d_2 - d_1} \frac{I_{\text{circle}}}{A_{\text{circle}}} + \frac{d_2 - d}{d_2 - d_1} \frac{I_{\text{pentagon}}}{A_{\text{pentagon}}}$$

(5-3)

where $I_{\text{circle}} = \pi d^4 / 64$ and $I_{\text{pentagon}} = \frac{2d^4}{192\sin^2(54^\circ)} [1 + 3\cot^2(\frac{180^\circ}{5})]$ [273] are the moments of inertia of an ideal circle and pentagon, respectively.

---

Figure 5-5 (a) Cross-sectional images of the penta-twin Ag NWs with different diameters. (b) A plot of cross-sectional area as a function of diameter.
With the fitting functions, Eq. (5-2) and (5-3), the obtained Young’s modulus can be corrected. The correction is more pronounced for the tensile test. When the cross section is changed from pentagon to circle, the Young’s moduli obtained from the tensile test and resonance test reduce as much as 19% and 8%, respectively. Figure 5-4(b) plots the corrected Young’s moduli of the penta-twinned Ag NWs using both the resonance and tensile tests. After the correction, a less pronounced stiffening size effect was obtained. When the diameter is larger than ~70 nm, a nearly constant Young’s modulus can be seen, slightly smaller than the bulk value (84 GPa); when the diameter is less than ~70 nm, the Young’s modulus increases with decreasing diameter. The size effect is in good agreement with that reported by Filleter et al. [30]. This agreement is not surprising because the circular cross section was assumed for the NWs in their work. However, our data are much more systematic compared to the only three data points in their work showing the size effect. A plot of summarizing our data and those reported in the literature is shown in Figure 5-6. The error analysis for Young’s modulus evaluation is presented in Appendix B.
Figure 5-6 Summary of the elastic modulus obtained by experiments and simulations [32,31,30,255–257,259,263]. The dashed line represents the Young’s modulus of bulk Ag.

Very similar size effects were observed in both resonance and tension tests. It appears that under resonance the size effect is slightly stronger. For example, for those NWs where both resonance and tension were performed on the same NWs, the differences between the modulus values in both resonance and tension can be seen in Figure 5-7. It is known that the loading-mode-dependent size effect is postulated to be a result of differences in NW surface and core Young’s moduli. In general, for metal NWs, the surface stress is tensile and as a result the NW core is in compression. In the case of a penta-twinned NW, five twin segments are joined along a common quintuple line with a disclination (7.35°). Such a disclination results in substantial compressive stress in the NW core and tensile stress close to the surface.
in the NW axial direction [67,263]. While this additional compressive stress leads to higher Young’s modulus in the core, the distribution of the Young’s modulus in the radial direction is rather complicated.

![Graph showing Young's modulus as a function of NW diameter for those NWs on which both resonance and tension tests were performed.](image)

Figure 5-7 Young’s modulus as a function of NW diameter for those NWs on which both resonance and tension tests were performed.

Apparently some combination of core nonlinear elasticity and surface elasticity is responsible for the observed size effect in Young’s modulus of the penta-twinned Ag NWs. In view that under resonance the size effect is slightly stronger, surface elasticity plays a slightly more important role. But it is difficult to separate the two effects. Our results agree well with the atomic simulations of <110>-oriented Ag NWs under both tension and bending, where the stiffening size effect was attributed to both core nonlinear elasticity and surface elasticity [258].
For the large NW diameters, the measured Young’s moduli are close to the bulk value for both resonance and tension. Bitzek and co-workers predicted that the Young’s modulus at relatively large diameter should be higher than the value for single-crystalline Ag in the <110> direction (84 GPa) as a result of the anisotropic elasticity and compatibility constraint imposed by the penta-twinned structure [263]. More specifically, elastic anisotropy leads to different Poisson's ratios in the directions orthogonal to the tensile axis. The constraint of constant wedge angle imposed by the penta-twinned structure effectively increases the Young’s modulus. However, in their work every twin segment was assumed to possess the same wedge angle and this angle remain constant during the tension of the NW. In reality, defects such as interfacial dislocations and stacking faults might exist near some of the twin boundaries (Figure 5-8(a)). Such defects could relax the compatibility constraint, which might account for the fact that the measured Young’s moduli at large NW diameter are close to the bulk value, smaller than the value predicted by Bitzek and co-workers. However, the exact effect of the interfacial dislocations and stacking faults on the elasticity of penta-twinned NWs is not known yet and warrants further investigation.
5.4. Conclusions

Penta-twin metallic NWs have recently received much attention due to their excellent mechanical properties. However, their elasticity size effect remains not well understood due to the large discrepancy in the reported experimental and simulation results. This chapter reports an experimental effort to address the discrepancy about the size-dependent Young’s modulus of penta-twin Ag NWs. Two independent experiments on the same NW, *in-situ* SEM resonance test and tensile test, were used to measure the Young’s moduli. The cross-sectional shape of the Ag NWs was found to transit from pentagon to circle with decreasing NW diameter, which can modify the Young’s modulus as much as 8%.
(for resonance test) and 19\% (for tensile test) for the NW diameter range used in this work. This work confirmed that the Young’s modulus of penta-twinning Ag NWs increases with decreasing NW diameter.

The penta-twinning microstructure leads to not only some very interesting and highly desirable mechanical properties such as recoverable plasticity [67] and strain hardening [74], but also complicated stress state and defect structures, which make the analysis and interpretation of their mechanical behaviors including elasticity and plasticity quite a challenge. For future work, detailed microstructure characterization, e.g., via cross-sectional TEM, should be taken into account.
Chapter 6.

Conclusion and Future Work

6.1. Conclusion

In this thesis, the mechanical response of two important 1D nanomaterials, Si NWs and Ag NWs have been briefly discussed. We especially focused on two unique phenomena which can only be found in nano-scale: low brittle-to-ductile transition temperature in Si NWs and size effect on Young’s modulus of Ag NWs. Thoroughly understanding their behaviors at reduced lengths scale is not only exploiting fundamentally physical challenges but also taking advantage to the discovery of next generational technologies and devices where the nanomaterials is employed as building blocks. Following summarizes the conclusions made through this work.

First, in Chapter 2, a brief review of in-situ mechanical characterization of 1D nanostructures using MEMS platforms is presented. Many different types of MEMS platforms have been designed, fabricated and employed for nanomechanical characterizations ranging from basic tensile testing to fatigue to thermomechanical testing and multiphysical testing. A large number of nanostructures have been characterized including carbon nanotubes, crystalline NWs, metallic glass NWs, and polymer nanofibers. MEMS platforms and related nanomechanics studies have contributed tremendously to our understanding of the nanoscale mechanical behaviors.
Secondary, a MEMS device for Multiphysics characterization of nanomaterials is designed and carefully calibrated in Chapter 3. The MEMS tensile stage consists of a comb-drive actuator, a capacitive load sensor and a local resistive heater. Multiphysics finite element analysis is conducted to optimize device structure in order to minimize undesired thermal displacement during heating, which is found can be compensated by geometry design. *In-situ* Raman spectroscopy temperature measurement confirms the prediction from finite element analysis is practical. A single crystalline Si NW with diameter around 60 nm is demonstrated showing the capability of MEMS device. A possible plastic deformation is found according to the stress-strain measurement. This prototype design will provide valuable guidelines for the future *in-situ* nanomechanical device on Multiphysics testing.

Following previous section, in Chapter 4 we thoroughly study the thermomechanical properties of single crystalline silicon where brittle-to-ductile transition play an especially important role. First, we particularly review the current literatures focused on the BDT of silicon, from macro to nano scale. Generally speaking, single crystalline Si is brittle due to the low mobility of dislocation in low temperature. However, high temperature can enhance the mobility and nucleation process of dislocation in Si, causing a transition of deformation mechanism from brittle failure to ductile deformation, roughly above a fraction of 0.6 of its melting temperature. For the clear evidence in the current studies associated with different size, the BDT temperature is decreased with the reduction of length scale. In addition, scientists also discovered that the loading condition, including type, direction and rate plays equally important role in the contribution to the BDT of single crystalline silicon. In the second part, we propose a new method to precisely investigate BDT of crystalline Si NWs by
the combination of \textit{in-situ} mechanical testing, theoretical solution and fractography. It is believed that a transition of activation volume would occur simultaneously with the BDT indicated a conversion of deformation mechanism. Based on the fracture stresses we obtained from room temperature to 564 K, together with thermal activation model, the BDT of Si NWs with diameter around 100 nm were found to be occurred at 364 K to 445 K. The fractography from TEM postmortem observation confirmed the NW underwent ductile deformation at 564 K before the fracture took place.

Finally, in Chapter 5, we study the size effect of Ag NWs. There is a general consensus on the size dependent Young’s modulus of penta-twinned Ag NWs, but the overall results is still under debate. The first possible uncertainty is from the incorrect assumption of the cross-sectional area of penta-twinned Ag NWs. The argument is whether circular or pentagonal shape should be accounted for. A series of TEM experiments thus are performed to carefully examine the cross-sectional shapes of Ag NWs and the results are recorded as a function of diameters. We find the cross-sectional shapes possess a transit from pentagon to circle with decreasing of NW diameter. A formula which can precisely evaluate the cross-sectional area of NWs is then proposed, which can modify the Young’s modulus as much as 19% for tensile experiments. The second reason caused the discrepancy on Young’s modulus measurement is due to the different loading mode. For instance, in the case of surface elasticity, the elasticity size effect would be stronger under bending than under tension as the surface plays a more important role under bending. Thus, we then validate this surface effect by using both \textit{in-situ} SEM resonance test and tensile test to measure the Young’s moduli on the same NW. All Young’s modulus acquired from resonance experiments indeed slightly
larger than one obtained from tensile experiments. In this report, we confirmed that the Young’s modulus of penta-twinced Ag NWs increases with decreasing of NW diameter, but the measured value is affected by loading mode and cross-sectional area calculation.

6.2. Future work and outlook

Our temperature controllable MEMS tensile device is restricted to be heated up to 600 K around sample testing area due to the safety issue on heat beams. However, from the results presented in this thesis, intermediate temperature is not enough for Si NWs to undergo a seriously ductile deformation. Higher temperature has to be achieved in order to accomplish a completely plastic deformation. One way is to fabricate the MEMS device using SiC as substrate [152], which can sustain higher temperature than those made of Si. Another option is to modify the device design. As one might notice that the highest temperature region in our device is on the heat beam instead of sample testing area. Taking the electro-thermal-actuator as example [107], adding additional heating source can let the highest temperature region shifted toward central shuttle of the device, and the NW accordingly. However, additional thermal displacement would be attended while the temperature distribution is changed, leaving a new challenge to be solved.

It remains a great challenge to manipulate and position individual nanostructures onto the MEMS platforms with high yield and high throughput. Novel nanorobotic manipulation or synthesis methods for preparing nanostructure specimens should be sought to overcome this bottleneck [274]. Feedback control has been successfully demonstrated to capture strain-
softening behavior [275]. But higher spatial resolution and faster response are still needed. MEMS-based platforms and related testing methods have seen rapid progress in the past decade. For the further growth of the field, it is an important step to develop standards commensurate with those at larger scales.

With the advance of nanodevices, 1D nanostructures including NWs as building blocks will undergo more and more realistic mechanical loadings. Therefore, it is of critical relevance to study other effects (e.g., time, temperature and environment) on their mechanical behaviors. For example, creep, stress relaxation and fatigue properties will be important for long-time operation and reliability of the nanodevices [276]. Strain rate, temperature and relaxation transient tests can be used to probe thermally activated mechanisms. MEMS will undoubtedly play important roles in such studies.

Due to its tiny size, a MEMS platform fits easily for in-situ SEM/TEM testing. With the recent advance in time-resolved electron microscopy [277] (e.g., dynamic transmission electron microscopy, DTEM [278]), it might become possible to capture the dynamic response of nanostructures with atomic resolution. Combination of MEMS platforms and DTEM, together with the limited volume of 1D nanostructures, could offer exciting opportunities for probing the nanoscale mechanical and structural behaviors. Beyond microscopy (e.g., SEM/TEM/AFM/ optical), it is promising to combine MEMS platforms with spectroscopy for multiphysical testing. For instance, Raman spectroscopy is commonly used to observe vibrational modes in molecules. Micro-Raman has been used to measure temperature, stress, phase transformation and etc with spatial resolution around 1 μm [279]. Photoluminescence spectroscopy can be used to measure bandgap of semiconductors.
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APPENDIX A.

Derivation of the formula for the evaluation of thermal activation process

In Chapter 4-3, the inner part of Eq. (4-3) can be dissolved as follow:

\[ \int_0^{t'} \tau[T, \sigma(t)] dt = \]
\[ \int_0^{t'} n \tau_0 \exp \left[ \frac{-U_0 + E \dot{\epsilon} t V}{kT} \right] dt = \]

\[ n \tau_0 \exp \left[ -\frac{U_0}{kT} \right] \int_0^{t'} \exp \left[ \frac{E \dot{\epsilon} t V}{kT} \right] dt = \]
\[ n \tau_0 \exp \left[ -\frac{U_0}{kT} \right] \frac{1}{E \dot{\epsilon} V} \left\{ \exp \left[ \frac{E \dot{\epsilon} t V}{kT} \right] \right\}_{t'}^{0} = \]

\[ \frac{n \tau_0 kT}{E \dot{\epsilon} V} \exp \left[ -\frac{U_0 + \sigma_j V}{kT} \right] \] (A-1)
APPENDIX B.

Error analysis of Young’s modulus

It is of important relevance to address the influence of potential sources of experimental error in the calculation of Young’s modulus prior to evaluating the size effect. In this work, we considered two major sources of error – NW diameter and NW length (only in the resonance test). Other sources of errors such as measurement of strain and load are negligible.

High magnification SEM image was used to measure the NW diameter, with a resolution of nm. Though the error was quite small, it could lead to a relatively large error in calculating the cross-sectional area of NWs, especially for the thinner one. Figure A-1(a) shows the error of the cross-sectional area as a function of NW diameter as a result of nm error in NW diameter. For a NW with diameter of 34 nm, the thinnest one in this work, the error in NW diameter can result in an error in the Young’s modulus as large as 6.0%, in both resonance and tensile tests.

The second error source lies in the measurement of the NW length due to the imaging resolution and uncertainty in determining the exact center of the clamp, which is relevant in the resonance test. In our case, the maximum error in measurement of the NW length is estimated to be 50 nm, contributing to an error in Young’s modulus no more than 3%, according to the Eq. (5-1) in the main text of the manuscript.

Figure A-1(b) shows the experimental data of Young’s modulus as a function of NW diameters, after taking into account the transition of the cross-sectional shape. The cumulative errors as discussed above are reflected in the error bar and the grey dashed line.
represents the elastic modulus of bulk silver in the <110> direction. It is apparent that the observed size effect in the Young’s modulus is not due to the experimental errors.

![Figure A-1](image_url)

Figure A-1 (a) Potential error on measuring and computing cross-sectional area of NWs as a function of diameter. (b) Modified Young’s modulus with error bar as a function of NW diameters.
APPENDIX C.

Anisotropic Young’s modulus of silver

In the Chapter 5, the Young’s modulus obtained via the resonance test was assumed isotropic. However, silver is an anisotropic crystalline material whose Young’s modulus dependents on the crystalline orientation. In order to quantify the effect of anisotropic elasticity, finite element analysis was carried out using ABAQUS to compare the difference between isotropic and anisotropic cases. The size of the NW was set to be 80 nm in diameter and 5 μm in length, which is typical for the NWs used in this work. For the isotropic case, the Young’s modulus of bulk silver in <110> orientation (84 GPa) was used. The anisotropic Young’s modulus can be obtained from stiffness matrix of silver, where $C_{11} = 124.3$ GPa, $C_{12} = 93.9$ GPa and $C_{44} = 46.4$ GPa. The penta-twinned Ag NWs are grown in the <110> direction and the five surface facets are along {100} planes. Thus, the Young’s modulus of <110> direction was set for the axial direction and <100> for the radial direction using a cylinder coordinate system. The resonance frequency was calculated to be 1111.6 kHz. By contrast, in the isotropic simulation, the Young’s modulus of [110] direction was set for the axial direction as well as the radial direction. The resonance frequency was calculated to be 1113.5 kHz, which is 0.2% smaller than the value for the anisotropic case.

According to Euler-Bernoulli equation, the anisotropic elasticity effect is negligible for a cantilevered NW vibrated at resonance frequency based on the certain circumstances listed below. First, the length to diameter ratio (aspect ratio) of samples should be at least over 10. Second, the resonance amplitude has to be maintained below a certain fraction of the total
length of the NW (\(< L/10\)). In our work, we carefully chose the NWs with aspect ratio of over 50 in the vibration experiments and the excitation voltage in our vibration experiments was set to 0.5 volts, which resulted in a low but distinguishable vibration amplitude at resonance.