2011

Molecular dynamics simulation studies of surface-stress effects in metallic nanostructures

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MOLECULAR DYNAMICS SIMULATION STUDIES OF SURFACE-STRESS EFFECTS IN METALLIC NANOSTRUCTURES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical Engineering

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May, 2011
ACKNOWLEDGEMENTS

I would like to take this opportunity to express my sincere thanks to all the people who directly or indirectly have been instrumental to my success throughout study here at Louisiana State University.

First and foremost I would like to express my deep gratitude to Dr. Dorel Moldovan, my major professor, for the invaluable guidance and inspiration ideas extended through my study. His constant supervision, helpful discussions, patience and insistence on learning deserve a special mention. Many thanks to the committee members for giving their valuable time to serve in the examination committee and evaluate my dissertation.

Tremendous support and encouragement from my wife and my parents who have made it possible for me to reach this stage. Their love and blessings have always been with me. Without their help, I wouldn’t have been here.

Last but not the least, I would like to thank all my colleagues in the Materials Simulations Laboratory and all my friends whose support was very valuable during my study at LSU.
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ABSTRACT

Using molecular dynamics (MD) simulations we investigate the surface-stress-induced structural transformations and pseudoelastic behavior in palladium (Pd) crystalline nanowires. For a $<100>$ initial crystal orientation our studies indicate that the surface stress can cause Pd nanowires to spontaneously undergo structural changes with characteristics that are determined by the wire cross-sectional area. Specifically, when the cross-sectional area is below $2.18 \text{ nm} \times 2.18 \text{ nm}$ the wire changes spontaneously its crystal structure from the initial fcc structure to a body-centered tetragonal (bct) structure. In wires of larger cross-sectional area (i.e., $2.57 \text{ nm} \times 2.57 \text{ nm}$) the structural transformation is achieved via a spontaneous lattice reorientation leading to an fcc wire with $<110>$ orientation and $\{111\}$ side surfaces. In both cases, under tensile loading and unloading Pd nanowires transform reversibly between the corresponding transformed structures and the original $<100>$ structure exhibiting pseudoelastic behaviors characterized by comparable, fully recoverable, strains of up to 50%. Moreover, the temperature-dependence of the two pseudoelastic behaviors enables the shape memory effects in Pd nanowires in both cases.

In the nanofilm case, our MD simulation results show that if the film is only a few nanometers thick the spontaneous reorientation of the (001) top layer leads to rolling-up of the initially planar free standing, (001)/(111) bilayer into a tubular or coiled structure. The driving force for this process is given by the existence of an initial mismatch strain between the two nanometer thick layers of different textures. Our detailed analysis of the reorientation process indicate that the bilayer self-rolling is determined by both energetic and kinetic processes characterizing the spontaneous structural reorientation of the top
(001) textured layer to the (111) orientation of the substrate layer. Specifically, the analysis of the simulation results indicate that reorientation of the (001) top layer proceeds via a mechanism characterized by nucleation from multiple sites, propagation and growth of the new (111) oriented domains embedded in the original (001) oriented layer. While individually the newly formed (111) domains grow free of defects a region containing a surface dislocation like linear defect forms at the boundary where two such domains meet. The equilibrium of the newly formed bilayer structure containing the surface dislocations is attained by multiple localized bendings of the bilayer structure about the direction coinciding with the dislocations line (the [110] direction). The spacing (density) of the nucleation is a function of temperature and influence the radius of curvature of the resulting structure.
CHAPTER 1

INTRODUCTION

Nanotechnology, which has attracted intense research activities in the past several decades, is an interdisciplinary research area cutting across the disciplines of engineering, chemistry, material science, and physical/biological sciences. It has became a branch of science and engineering dealing with the synthesis and fabrication of new structural materials, functional devices, and machines ranging in size from 1 nm to 100 nm. Research in nanotechnology involves three basic topics: nanomaterial synthesis, physical properties characterization, devices design and assembly. There are in general two conceptually distinct methodologies of fabrication of small objects: the so-called top-down and bottom-up approaches.

In the top-down approach, small features are patterned in bulk materials by a combination of lithography, etching, and deposition to form functional devices and corresponding integrated systems. The top-down approach has been exceedingly successful in many venues with microelectronics being perhaps the best example today. While developments continue to push the resolution limits of the top-down approach, these improvements in resolution are associated with a near-exponential increase in cost associated with each new level of manufacturing facility. These economic limitations and other scientific challenges with the top-down approach, such as making nanostructures with near-atomic resolution and incorporating materials with distinct chemical and functional properties, have motivated efforts worldwide to search for new strategies to meet today and future demands for nanoscale structures [1, 2].

The bottom-up approach, in which functional structures are assembled from well-defined chemically and/or physically synthesized nanoscale building blocks, much like the way nature
uses proteins and other macromolecules to construct complex biological systems, represents a powerful alternative approach to conventional top-down methods [3]. The bottom-up approach has the potential to go far beyond the limits and functionality of top-down technology by defining key nanometer-scale metrics through synthesis and subsequent assembly and not by lithography. Moreover, it is highly likely that the bottom-up approach will enable entirely new device concepts and functional systems and thereby create technologies that we have not yet imagined. For example, it is possible to combine chemically distinct nanoscale building blocks that could not be integrated together in top-down processing and thus obtain unique function and/or combinations of function in an integrated nanosystem.

Some of the most active areas of research in nanotechnology are the synthesis and property characterization of nanomaterials including carbon nanotubes, nanowires, quantum dots, and nanoparticles. During the past two decades, nanomaterials have become an exciting and rapidly expanding research area and much of this excitement has arisen from the discovering of new physical phenomena, increased functionality, and high integration density of nanostructured components. Metallic and semiconducting nanowires have shown great promise as building blocks in future nanoscale structures due to their novel mechanical, electrical and optical properties [4–8].

As shown in Figure 1.1 (a), nanowires have been suggested to be used in solar cells, which are devices that convert energy of light into electrical energy. The introduction of nanowires to solar cells increases the rate of charge (electrons) collection and thus improves the energy conversion efficiency of solar cells. Figure 1.1(b) and (c) illustrate the usage of nanowires as key components in nanosensors [7, 10] and nanophotonics [8, 11]. Photonics is the science of generating, collecting and detecting photons. The small size of nanowires offers the opportunity
Figure 1.1 Examples of potential applications of nanowires: a) solar cells, b) nanosensors and c) nanophotonics (bottom). Pictures are taken from [9].

of manipulation and utilization of optical energy in integrated photonic nanodevices for communication and sensing. For example, it has been demonstrated that metal nanowires are
suitable for low-loss optical wave guiding and surface plasmons resonators, which might enable improved spatial resolution in plasmon-based photonic circuitry. Due to the small mass and high stiffness nanowires have very high natural frequencies, therefore when biomolecules, such as viruses or proteins, attach to a nanowire its mass will change dramatically and so will the frequency. Thus the nanowires can be used as key component in high resolution nanosensors in biodetection and in medicine.

In the past few years, significant progresses have been made in experimental, theoretical, and computational study of nanowires structures and properties. Despite these advances the application of nanowires requires fundamental understanding of their structural characteristics and thermo-mechanical properties, which are critical for their fabrication, assembling, and functioning. The nanowires have many attractive properties and in the present research we focused on their size-dependent structural stability and mechanical properties. The interest in the mechanical properties arises from the following two facts: (1) nanowires exhibit superior mechanical properties compared to the corresponding bulk material, including high stiffness, large yield/fracture stress and strain, which are enabled by free surfaces at nanoscale, and (2) the physical properties of nanowires are intricately coupled, i.e. electromechanical [12–14] and optomechanical [15–18]. Therefore, advances in understanding the mechanical properties, structural stability and deformation mechanisms of nanowires can greatly impact our ability to design highly multifunctional NEMS devices.

1.1 The Concepts of Surface Energy and Surface Stress

When compared with traditional bulk materials the attractive properties of nanowires arise mainly due to their spatial dimensions, which play important roles in determining their
often superior physical properties. At the nanoscale the number of atoms on a specimen surfaces is comparable to the number of bulk atoms. This, leads to substantial influences of surface atoms on material properties, known as surface effects. For example, the ratio of the surface area to volume is about 0.6 nm$^{-1}$ for a cubic box with the edge length of 10 nm. This ratio is only 0.006 nm$^{-1}$ for a cubic box with the edge length of 1000 nm. As the system size increases further, the ratio becomes even smaller leading to a negligible contribution of surface atoms to the overall properties of nanowires.

Figure 1.2 Schematic representation illustrating spontaneous self-contraction of a $<100>/\{100\}$ FCC palladium nanowire due to the presence of a compressive surface stress. The elastic contraction is about 6%. The top figure depicts a newly-formed wire prior to elastic contraction while the bottom figure shows the resulting wire after self-contraction.

As shown in Figure 1.2 a newly-formed nanowire, created by “cutting” it from the corresponding bulk material, contracts spontaneously in the axial direction while expanding in the lateral directions. The cross sectional edge length of this wire is about 2.5 nm and no externally applied force was present during this contraction. Although the self-contraction effect is negligible at macroscopic scale, this plays a major role at nanoscale. This is because the surface stress, which is the driving force for contraction, can be very large when at least one of
the spatial dimensions is in the nanoscale range. In addition to the surface stress differences in structural characteristics, and dislocation nucleation and propagation mechanisms confer novel mechanical properties to nanostructured materials, many of which are distinct from those of the corresponding bulk materials; these include Young’s modulus, yield stress, fracture strain, and resonance properties [19–21].

A fundamental understanding of the surface properties, such as surface energy and surface stress, can be traced back to the thermodynamic studies of surfaces formulated by Gibbs [22]. According to Gibbs definition, surface energy, \( \gamma \), is generally considered as the reversible work per unit area needed to create a new surface. The work, \( dW \), required to create a new surface \( dA \) is given by

\[
dW = \gamma dA.
\]  

In the case of elastically stretched solids, another quantity, named surface stress, is commonly used. Surface stress is a symmetric second rank tensor, denoted as \( f_{ij} \). It is defined as the work per unit area to elastically stretch a pre-existing solid surface and can be related to surface energy as [23-25]

\[
f_{ij} = \frac{1}{A} \frac{\partial (\gamma A)}{\partial \varepsilon_{ij}} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial \varepsilon_{ij}},
\]  

where \( \varepsilon_{ij} \) is the elastic strain of area \( A \) and \( \delta_{ij} \) is the Kronecker delta symbol. Surface stress and surface energy have the same units, representing the force per unit length. The relationship between surface stress and surface energy can be better understood by using the representation depicted in figure 1.3 giving two equivalent reversible paths of an elastically stretched solid. In figure 1.3, \( \gamma \) is the surface energy, \( A \) is the surface area, and \( \varepsilon \) is the elastic surface strain, \( \varepsilon \).
$w_2, W_1$ and $W_2$ are the energies associated with the corresponding deformation process. From figure 1.3, it can be found that $w_2-w_1$ equals to $W_2-W_1$, which are expressed as:

$$w_2 - w_1 = 2\int A f_{ij} d\varepsilon_{ij} ,$$  \hspace{1cm} (3)

$$W_2 - W_1 = 2\gamma (\varepsilon_{ij}) A (\varepsilon_{ij}) - 2\gamma_0 A_0 = 2\int d(\gamma A) .$$  \hspace{1cm} (4)

Thus,

$$Af_{ij} d\varepsilon_{ij} = d(\gamma A) = \gamma A \delta_{ij} d\varepsilon_{ij} + Ad\gamma ,$$  \hspace{1cm} (5)

from which the equation (2) is derived.

Figure 1.3 Schematic representation of two reversible paths that one can use to cut a stretched and un-stretched solid. The diagram illustrates the relationship between surface free energy and surface stress. The figure is taken from [23].

The origin of the surface stresses can be understood intuitively from the atomic scale perspective by considering the different local bonding environment of surface atoms and bulk atoms. Figure 1.4 displays a schematic atomistic representation of a two-dimensional system. The atom A is taken to illustrate a surface atom and atom B to represent a bulk atom. It can be
seen from this two-dimensional representation that the atom B has six nearest neighbors whereas atom A has only four. Moreover the nearest neighbors are distributed symmetrical around (bulk) atom B and asymmetrically around the (surface) atom A. Thus, atoms at free surfaces, such as the atom A, are in a higher energy state due to the distinct bonding environment. These surface atoms can be subjected to local rearrangements that maximizes the atomic density at surfaces, lowers material surface energy, and may cause self-contraction as mentioned previously. The rearrangement process can be treated as a result of surface effect induced by surface stress.

Figure 1.4 Schematic atomistic representation of a two-dimensional system illustrating the difference in bonding environment between surface atoms (e.g. atom A) and bulk atoms (e.g. atom B).

1.2 The Effect of Free Surfaces on the Properties of Nanostructures

The surface effects have great influences on the overall material mechanical properties of nano-structured systems [19, 26]. Due to the different bonding environment of surface and bulk atoms, the elastic properties of surfaces differ from those of an idealized bulk material [21, 26]. The differences between surface and bulk elastic properties are magnified by the increase of the
surface to volume ratio, which is achieved by decreasing the characteristic dimensions of the system. Specifically, at the nanoscale the surface elasticity becomes very important. For example, mechanical resonance of a suspended silicon wire exhibits strong dependence on the wire surface to volume ratio; that is, the resonance frequency increases as the wire size becomes smaller. The size-dependence of the resonance frequency can be used to improve the sensitivity of nanowire-based sensors [27]. The surface elasticity and the size dependence of materials mechanical properties including elastic modulus [32, 34], yield stress [36], material ductile to brittle transition [37, 38], and crystal nanoindentation [39] have been observed and studied by many researchers [19, 20, 28–39].

The size dependence of material systems mechanical properties can be understood from the work of Mullins et al. [40]. According to their study, the surface stress is caused not only by the atoms located on free surfaces but also by the atoms located on layers near the free surfaces. Therefore one can expect that in a given material the rearrangement of atoms will extend several atomic layers below free surfaces. Molecular dynamics (MD) simulations have indeed revealed that for Al, Ni, and their alloys oscillatory surface relaxation decays exponentially into the bulk [41]. These results show that the free surface induced lattice distortion extends only about three atomic layers into the bulk [26, 42]. Consequently one can conclude that in bulk specimens volume quantities dominate material properties over surface quantities and surface effects are negligible under most conditions.

The influence of free surfaces on the size dependence properties are easier to understand when using energy balance arguments. The total energy of a system, $E_T$, comes from two contributions: surface energy $E_S$ and bulk energy $E_B$, and can be written as $E_T = E_S + E_B$. With the decrease of the structure size, the number of atoms in the bulk is decreasing more
rapidly compared to the number of surface atoms, indicating an increase of the area to volume ratio. Therefore, the weight or the importance of $E_S$ as compared to the total energy $E_T$ is increasing with the decrease of the specimen size. As specimen size reaches nanoscale dimensions (such as in the case of nanowires or nanofilms) the influence of free surfaces on material properties becomes substantial, leading to the rearrangement of interior atoms [43, 44]. Thus, material properties become size-dependent and can be dramatically different from those characterizing bulk materials.

In FCC metal nanowires surface stresses play an important role in determining their properties. For example, driven purely by surface stresses, a $<100>/<100>$ metal nanowire can reorient into a $<110>$ wire with $\{111\}$ side surfaces if the cross sectional area of the wire is smaller than a critical value [45]. During the structural reorientation, due to tensile surface stresses on the side surfaces of the metal nanowires the wire contracts in the longitudinal direction at a strain level of about 30%. During the reorientation process, the nanowire surface atoms maximize their bonding density by rearrangement leading to the conversion of the original surfaces to $\{111\}$ lower energy surfaces. For example, in the simulation of structural reorientation [46] the surface energy of gold on $\{111\}$ layers is 1.283 Jm$^{-2}$, and on $\{100\}$ layers is 1.627 Jm$^{-2}$. In gold this amounts for about 21% surface energy reduction as result of the structural reorientation. At the newly-formed configuration, atoms are arranged at current equilibrium positions and the stresses, including the tensile surface stresses and intrinsic compressive stresses, balance each other. In the FCC metal nanowires, surface effects are substantial and responsible for various interesting phenomena, such as asymmetric yield strain [47], tetragonal phase transformation [48, 49] and surface reorientations [45, 50, 51].
The importance of free surfaces on the deformation behavior and mechanical properties of metallic nanowires can be observed mainly from the two aspects: (1) it acts as the defect nucleation sites due to the high energy of surface atoms; (2) tensile surface stresses existing on free surfaces induces substantial compressive intrinsic stresses inside the nanowires; in turn this is responsible for asymmetry yield strain and stress, enhanced elastic properties, and many other interesting nanoscale behavior. Diao et al. [52] provided a set of equations that allows evaluation of the intrinsic compressive stress along the wire length direction due to the existence of a surface stress. According to Diao et al. derivation, the stress state in the interior of the nanowire is given approximately by:

\[
\begin{bmatrix}
\sigma & 0 & 0 \\
0 & \frac{1}{2}\sigma & 0 \\
0 & 0 & \frac{1}{2}\sigma \\
\end{bmatrix},
\]

(6)

where,

\[
\sigma = -\frac{4fl}{A},
\]

(7)

and \(f\) is the surface stress (of the order of 1 J/m\(^2\) for metals), \(l\) is the width of the nanowire, and \(A = l^2\) is the cross-sectional area (see Figure 1.5).

According to Equation (7), the magnitude of intrinsic stresses is correlated to the magnitude of surface stresses and the thickness of the nanowire. The intrinsic stress induced by surface stress is negligible at macroscopic scale (i.e. micron or millimeter size) and can be on the order of MPa or even GPa as the wire thickness shrinks into nanometer range. The variation of the magnitude of intrinsic stress as a function of wire thickness is illustrated in Figure 1.5.
1.3 Objectives and Outline of the Research Project

The objectives of this research project was to study the effect of free surfaces on the mechanical behavior and thermal stability of fcc metallic nanowires and nanofilms, including structural reorientation, phase transformation, shape memory behavior, and film self-bending phenomena. As indicated previously, the surface stresses play a very important role on nanowires properties, including the self-contraction, which can be substantial as the nanowire cross section reduces to a few nanometers. In this study we use molecular dynamics (MD) simulations to predict the mechanical properties of metal nanowires and nanofilms and to analyze the nanostructures characteristics on their structural and geometrical stability.

The dissertation material is organized as follows: In Chapter 2 we present a brief literature review of the mechanical properties of nanowires, nanofilms, and related novel
phenomena such as surface-stress-induced structural reorientation and shape memory effect in nanowires. A brief description of structural defects present in single crystals including dislocations and stacking faults will also be introduced. In Chapter 3 we give a brief description of the molecular dynamics simulation methodology and of the embedded atom method (EAM) parameterization of the inter-atomic interactions in metals. In Chapter 4, we present our research results of the study of surface-stress-induced crystalline lattice reorientation and pseudoleastic effects in palladium nanowires. In addition, we describe our simulation methodology based on the top-down “fabrication” process and describe and characterize in detail the deformation mechanism in Pd nanowires. The shape memory effect (SME) that is present in nanowires is investigated by employing the loading and unloading of nanowires under a quasistatic conditions at various temperatures. The focus in Chapter 5 is on understanding the details characterizing a novel phase transformation phenomenon in palladium nanowires and on a corresponding shape memory effect. In Chapter 6, we present our MD simulation results that document the potential of a new methodology for generating metallic (in our case aluminum) nanotubes, nanobelts, and nanocoiles by spontaneous self-rolling of initially planar free-standing bi-layer films that are prepared by stacking two nanometer-thin sheets with different crystalline orientations. The spontaneous self-rolling of the bilayer structure proceeds via crystalline structure reorientation driven by the intrinsic interfacial strain. In Chapter 7 we give the Summary and Conclusions as well as a brief overview of the future work.

1.4 References


CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

As the scale of a material is reduced to just a few interatomic distances across at least one of the three spatial dimensions both the structure and properties can be quite different from those of bulk materials. When two spatial dimensions of the systems are in the nanometer range (i.e. nanowire structures) the structural characteristics and stability are strongly influenced by both surface energy and surface stress. Metal nanowires are of great technological importance due to their potential applications in miniaturized electrical, optical, thermal and mechanical systems.

2.1 Size-dependence of Nanowire Structures

For a large class of bulk metallic materials the FCC crystalline structure represents the lowest energy, highest atomic-packing, crystal structure. In wires of large diameters (e.g. of the order of a few microns or millimeters) most of the atoms are located inside the material. As the wire diameter decreases in the nanometer range the fraction of surface atoms increases driving the wire into new states. Several novel structures have been identified in metallic nanowires including: multishell helical gold nanowires, “weird” aluminum and lead nanowires, and body-centered tetragonal (BCT) gold nanowires.

Gold nanowires have been synthesized down to the lowest diameter possible; the gold single-atom chains [2-4]. In practice these single-atom chains are usually formed between a scanning tunneling microscope (STM) tip and a gold substrate by driving the tip into the substrate and then retracting it in a controlled manner. This new structures are not in the lowest energy state and can only exist in the presence of an external tensile loading. At low
temperatures, these wires can be as long as 5 atoms and remain stable for less than a few seconds. The nanowires are stable in the absence of an external loading only if their diameter exceeds a critical value. Both experiments and atomistic simulations have predicted that existence of nanowires of the smallest dimensions in the form of helical spiral strands and they have been identified in Au [5], Pb, and Al [6]. Usually, the critical lateral size for such structures is of the order of 2 to 3 lattice constants. At this size, more atoms are located on surfaces than in the core (or “bulk”) [6]. As the wire size increases, helical and cylindrical multi-shell structures occur more often in metallic nanowires such as Cu [7, 8], Au [5, 9-11], and Al [6]. The critical size range for such structures is between 0.6 nm and 2.2 nm for Au nanowires [5]. When the wire size increases further, to a point where there are significantly more internal (bulk) atoms than surface atoms, FCC crystalline structures become dominant for metallic nanowires [12-14].

2.2 Mechanical Properties of Nanowires

From a mechanical viewpoint, metal nanowires are of great interest because they can sustain extremely large stresses and strains, and because their electrical, thermal and optical properties are coupled to the mechanical deformations. For example, it has been demonstrated that the yield strength of metallic nanowires increases with the decrease of wire cross sectional area, and the yield strength can be around 100 times larger than that of the corresponding bulk material [15]. Aside from the superior mechanical properties, coupled physics, including electrical-mechanical and optical-mechanical properties, has also been demonstrated by various researchers [16, 17]. The coupled electrical-mechanical property has been proposed to be utilized in future nano-electro-mechanical-systems (NEMS), where an external electric field is capable of inducing bending moment on freestanding nanowires. The deterioration of the nanowire optical properties has been correlated to its mechanical properties. The connection is rooted in
the formation of cracks in nanowires, which simultaneously degrade the optical and mechanical properties of nanowires [16]. Besides the properties mentioned above, metal nanowires have exhibited many other exotic properties such as tensile loading induced atom-thick chaining [18] and strain-rate induced amorphization [19].

The research work on the mechanical properties of nanowires thus far has mainly relied on atomistic simulations rather than on experiments. Due to the small cross sectional area of the nanowires, the experimental requirements in handling, positioning, and gripping them accurately are difficult to achieve, which leads to significant scatter in reported experimental mechanical properties [15, 20–23] and thus impedes on the reliability and repeatability of nanoscale experiments. On the other hand, due to the high accuracy, feasibility, and reasonable computational cost, atomistic simulations are well poisoned as proven tools for studying the mechanical properties of nanowires.

Using molecular dynamics simulations, two observations have been made by Mehrez et al. [18]: first, gold nanowires have exhibited necking down to a single atom chain under tensile loading before breaking into two pieces; and second, the conductance of nanowires is closely related to the morphology at the yield neck of nanowires. In their work on gold nanowires Mehrez et al, have shown that the conductance curves exhibits a staircase-like variation with loading steps. This behavior was linked to the nucleation and interaction of defects in nanowires under tensile loading. A similar phenomenon has been observed in experiments in atomic chains, showing the dependence of conductance on the wire structural variations [24-26]. To understand the tensile loading induced atom chaining phenomenon, much effort has been devoted to analyzing its formation mechanism and stability through both experiments and atomistic simulations [27–34]. It has been demonstrated that this single atom chaining phenomenon
appears more frequently in nanowires with <111> and <100> orientations than in <110> oriented wires [34], and that the <110> wires are prone to form stable nanobridges [33].

One interesting phenomenon observed is that nanowires exhibit a crystalline to amorphous structural change under extremely high loading rates, around $10^{10}$ s$^{-1}$ [19]. MD simulation studies have shown that the crystalline structures of Ni and NiCu nanowires transform homogeneously into amorphous states and that there are no twins or dislocations in the subsequent loading process. Accordingly, amorphous nanowires exhibit fundamentally different stress-strain curves compared to crystalline materials and show extremely high yield strength due to the absence of the typical crystalline defects, such as twins or dislocations. Similar strain rate induced amorphizations phenomena in Ni nanowires have been observed by Branicio et al. [35].

One of the main focuses in atomistic simulations of metallic nanowires is on the understanding of fundamentals of deformation mechanisms. Using a tight-binding potential (SMA-TB) based on a second-moment approximation, Kang et al. [36] simulated a <100> copper nanowire under tensile loading conditions. In their work, they showed that the first yield point appears at a strain of $\varepsilon = 13.3\%$, and the subsequent deformation alternates between quasi-elastic and yielding stages. The first yield is due to an abrupt slip on \{111\} planes, while alternating elastic and yielding stages correspond to energy storing and atomic structure disordering period, respectively. This alternation process in stress-strain curves has also been observed in MD simulations by Mehrez et al. [18]. In addition, Kang et al. have revealed that the deformation of <100> copper nanowires is mainly attributed to two distinct slip mechanisms: the glide of a dislocation on \{111\} planes and the homogeneous slip of one plane over another. The crossover of the two slip events is responsible for a reduction of nanowire diameter, thus leading to necking. Discussions on metal nanowires under other mechanical loading forms, such as compression, torsion and shear, have been studied by researchers as well [36-38].
One of discoveries concerning metal nanowires is that their mechanical properties are closely related to loading rates and cross-sectional sizes [29, 39–41]. Loading rate dependence is expressed with the magnitude of yield stresses and yield strains, which are distinct under different loading conditions. It is believed that metal nanowires exhibit largest strength under two conditions: one is with quasistatic loading and another one is with the loading rates above $10^{10}\text{s}^{-1}$ [29]. The high strength, which appeared in quasistatic loading, is due to the fact that atoms can relax to their equilibrium positions after each loading increment, while the latter case is related to loading rate induced amorphization [19, 29]. Of the present accessible loading rates, $10^7 - 10^9\text{s}^{-1}$, it is noticed that yield stresses and yield strains increase with the increase of loading rates, although the difference in magnitude is strong. The increase in the magnitude of yield strain indicates a strain rate hardening mechanism in nanowires. The dependence in yield stress is believed to be associated with phonon drag or dynamic wave effect [40], which inhibits the dislocation initiation or occurrence of slip in metal nanowires. The cases with even lower loading rates, below $10^6\text{s}^{-1}$, are not readily available yet due to the limitations of current of computational power.

The dependence of the deformation behavior and mechanical properties on the cross sectional size has been documented by various researchers as well. For example, it has been found that if the metallic nanowires preserve their crystalline structure during the deformation, crystalline slip is the main deformation mechanism for wires with small cross sections and cross slip is responsible for the plastic deformation of wires with relative larger cross sectional areas [40, 42]. This phenomenon can be understood by noticing that in wires with larger cross sectional areas there is an enhanced opportunity for dislocation motion which in the end leads to a decrease in both yield strain [29] and yield stress [15, 40, 43]. Besides the magnitude of the cross sectional area, the axial orientation does have an important influence on wire mechanical
deformation mechanism and properties. Although most research studies on nanowires so far have been concentrated on <100> wires [19, 27, 29, 32, 35, 36, 40, 44], deformation behavior of nanowires is of different crystallographic orientations have been considered as well [34, 46]. These studies have indicated for example that <110> wires can form long stable nanobridges under tensile loading, while <100> and <111> wires cannot [31, 33, 45].

Recently, an novel feature has been revealed in metallic nanowires indicating that phase transformations and structural reorientations can occur spontaneously provided the cross-sectional area of the nanowire is below a critical value [6, 25, 50, 53, 86]. For example, gold nanowires can undergo a phase transformation from face-centered cubic (FCC) to body-centered tetragonal (BCT) when the diameter of the wire is below about 2 nm [6, 25, 53]. This phase transformation process is driven primarily by the surface stresses and allowing at the same time a reduction of the wire surface energy. This phenomenon is an intrinsic nanoscale phenomenon and does not occur in wires of macroscopic diameters because surface effects are size dependent and are substantial only at such small scale. The same surface stress can also lead to other structural transformation mechanisms such as crystalline structure reorientation, in which a <100> wire can spontaneously reorient into a <110> nanowire with {111} side surfaces. Atomistic simulations have been performed to study this phenomenon by various research groups [48, 49, 46, 47, 50-52]. The existence of both the phase transformation and structural reorientation phenomena have been confirmed recently by density functional theory calculations [53].

Of further interest are the phenomena of shape memory and pseudoelastic behavior which have been observed in various pure metal nanowires [49–52]. The pseudoelastic behavior has also been observed in NiAl nanowires; process that has been proven to be mediated by a martensitic-like phase transformation [54]. The ability to exhibit shape memory effect indicates
that metal nanowires may fill a critical need as self-healing materials in the next-generation of nanodevices; a role similar to that played by the shape memory alloys (SMAs) in today’s applications. However, due to the novelty of nanowires, more fundamental research work needs to be carried out to understand their governing mechanisms and then to better utilize these shape memory effect characteristics in the future.

Recently, Park et al. [46] revealed that the mechanical deformation mechanism of metallic nanowires depend not only on the wire axial orientation but also on the side surface facets. For example, a $<100>/\{100\}$ nanowire exhibits twins in the post-yield period under compression, resulting in $\{111\}$ side surfaces; while a $<100>/\{110\}$ wire under compression exhibits distributed stacking faults along the wire axial direction. Both of these wires have the same axial orientations and size but different side surfaces orientations. The specific crystalline orientations of the wire surfaces impact on deformation mechanism is another example of nanoscale phenomena. To gain a better understanding of the influence from side surfaces facets, fundamental research work has been performed to characterize the coupled effects of geometry and side surface orientation on the deformation behavior and mechanical properties of metal nanowires [42, 55, 56].

2.3 Surface-Stress-Induced Phenomena in Nanofilms

Similar to nanowires, films of nanometer scale thickness (systems in which one dimension is in the nanometer range) exhibit novel properties. It is now well established that the surfaces of semiconductors and some metals undergo surface reconstruction. Many (001) oriented surface of fcc metals on a substrate reconstruct to a contracted, quasihexagonal, closed packed layers [57,58]. The driving force for the reconstruction is the reduction of the surface energy enough to compensate for the ensuing mismatch strain between the
reconstructed and unreconstructed layers. Nevertheless, surface reconstruction on a substrate in fcc metals is by no means spontaneous and favored. Surface reconstruction phenomena can be controlled by changing the temperature or the stress. In some cases, external stress must be applied to overcome the substrate resistance to produce reconstruction [57]. Reconstruction can also be induced by increasing temperature [58].

For free standing or suspended metallic films, surface stress should become increasingly comparable to the remaining bulk force as the film thickness decreases. This in turn can lead crystal structure reorientation of the entire film. In their experimental work on gold (001) oriented free standing nanofilms Kondo [59] et al., have shown that local thinning by irradiation with an electron beam, leads to spontaneous filmwide crystalline reconstruction. Namely when the irradiated region becomes very thin, about 2nm, the film spontaneously transforms into the (111) orientation. The critical thickness for this transition was determined by electron holography to be about 2nm. Therefore in order to remain stable a gold (001) oriented film must be at least eight layers thick. The spontaneous structural reorientation of gold thin films was also investigated using molecular dynamics simulations by Hasmy and Medina [60]. Their simulations showed that, indeed, the (001) to (111) structural reorientation occurs even at very low temperature results that are in good agreement with experimental investigations. Further simulation studies on Pt, Al, Ag, and Ni suggested that in suspended films the structural transition is generic to other metal nanofilms. Understanding the forces and the mechanisms leading to structural changes in nanofilms may be great relevance for the future developments in nanoscale science and technology.

Exploiting the unique surface properties of a large class of materials, recently new methodologies were proposed [61] to form nanotubes from thin solid films. Two methodologies of rolling-up thin films into nanotubes have received a great deal of attention lately and they are
referred to as the ‘general’ and the ‘specialized’ method. Both rely on the release of pre-strained thin films of the given material from a substrate by a selective etching process. The general method, shown schematically in figure 2.1a, includes the following steps: i) an etchant-sensitive material is deposited on a substrate ii) on top of this sacrificial layer it is deposited a thin film iii) after selective etching of the sacrificial layer, the thin top layer is wrapped up and folded back onto the sample surface, where it can bond to itself. At the position where the layer bends, a nanotube has formed. The specialized method shown in figure 2.1b differs from the general one in the layer sequence. Basically, the layer sequence consists of an etchant-sensitive material, followed by a bilayer of two different materials (material 1 and 2). Material 1 has a larger lattice constant than material 2. Once the bilayer is released by selective etching, each material tends to acquire its inherent lattice constant. The bilayer bends upwards, finally forming a nanotube after one complete revolution.

Figure 2.1 Schematic representation of two methodologies (generalized and the specialized) used for forming solid-state nanotubes [61].

Experimental work in this area have shown that the two methods described above allow fabrication, with an unprecedented level of control, of a variety of nanostructures such as:
nanotubes, nanorings, nanodrills and nanocoils, using combinations of different materials, etchants, and substrates [62]. All these different classes of nanostructures are formed by the same mechanism, namely, the tendency of strained bilayer films to bend (or to fold). One outstanding advantage of this nanofabrication technique is its versatility. Not only can a variety of nanomechanical architectural design be made, but they can also be made with different materials, including semiconductor, metals and insulators, as well as combination of these materials. An interesting analyses based on experimental data show that there exits fundamental geometric and physical conditions controlling the formation of nanotubes (nanorings) versus nanocoils. For an elastically isotropic film, the critical geometric condition for nanocoil formation is that the film width must be smaller than $2\pi R$, where $R$ is the characteristic bending radius of the given bilayer film. For an anisotropic film, nanocoil formation depends critically on the alignment of the most compliant direction of the film with respect to the film geometry (i.e., its long edge).

The self-bending mechanism of semiconductor heterostructures has been investigated by direct atomistic simulations [73] and continuum theories [62]. The driving force for nanofilms self-bending comes from various sources such as: elastic misfit strain between the constituents of the bilayer nanostructures, the asymmetry in the surface stress caused by molecular adsorption or as result of surface reconstruction. In a recent atomistic simulation study Zang et al. [63] have demonstrated that ultrathin Si and Ge nanofilms of certain thicknesses may self-bend even in the absence of an external stress, under their own intrinsic surface stress imbalance.

2.4 Basic Overview of Dislocations, Stacking Faults and Twins

The mechanical properties of FCC metals are determined to a large extent by the lattice defects that are present or are nucleated during deformation process. These defects include
dislocations, stacking defaults, and twin boundaries. In this section, a brief overview of these three types of crystalline defects will be given.

A dislocation is a line defect, whose magnitude and moving direction are characterized by its Burgers vector. Depending on the relative orientation of the Burgers vector with respect to the dislocation line there are two types of dislocations present in FCC metals. When the dislocation line is parallel with the Burgers vector, the dislocation is called screw dislocation. When the Burgers vector and dislocation line are perpendicular the dislocation is called edge dislocation. The commonly observed dislocations in crystals have curved shapes and have mixed screw-edge character. Figure 2.2 presents a schematic representation of an edge dislocation in a two-dimensional close-packed plane. Although the edge dislocation, represented in this figure as the atomic position where the half extra plane ends, is easy to represent and visualize in three-dimensions this task becomes more complicated.

Based on the understanding of dislocation motion and interactions one can rationalize: (1) why the stress required to plastically deform a crystal is much less than the theoretical shear strength of a perfect crystal and (2) why the materials harden as result of plastic deformation. In general in a FCC crystalline structure a full dislocation has a high energy and can be lowered if
the dislocation splits into two partial dislocations. Namely in an FCC metal a full \( \frac{1}{2} [110] \) dislocation can be decomposed into two partial dislocations, a \( \frac{1}{6} [121] \) and a \( \frac{1}{6} [21\bar{1}] \). Once the partials are created, they may move away from each other due to their mutual interactions and/or the presence of external stresses. As the partial dislocations move away from each other they remain connected through a planar defect called stacking fault (see Figure 2.3). In FCC crystals, the \{111\} plane is the close-packed plane, and thus it is the dislocation glide plane and the stacking fault plane. The normal stacking sequence of a perfect FCC crystal along \(<111>\) directions is ABCABCABCABC, while with a stacking fault, the stacking sequence is modified to ABCABABCABC, missing a ’C’ layer between the two layers marked in red in the sequence containing a stacking fault. Twin boundaries (or twins) correspond to a mirror reflection in the \{111\} layer in FCC crystal. For a twin, the previous stacking sequence becomes to ABCAB\(\overline{C}\)BACBA, where the middle C layer with a bar is the twin boundary.

![Diagram of dislocation splitting](image)

Figure 2.3 An illustration on the formation of stacking fault from partial dislocations a \( \frac{1}{6} [121] \) and a \( \frac{1}{6} [21\bar{1}] \), which in turn formed from a full dislocations a \( \frac{1}{2} [110] \). This figure is taken from [64].

Due to the higher energy of full dislocations compared with partials, the initiation and development of plastic deformation mediated by full dislocations requires more work compared
to those mediated by partials that lead to the formation of both stacking faults and twins. In FCC crystals, the twinning energy is around one half of the stacking fault energy [65]. Thus the material that shows plastic deformation with twins has a lower yield stress.

2.5 Shape Memory Effect and Pseudoelasticity

Until recently shape memory effect (SME) and pseudoelastic behavior were usually considered only when referring to bulk materials and were observed in certain metallic alloys, liquid crystal elastomers, and piezoelectric ceramics [66]. In our research on single crystalline FCC palladium nanowires a novel pseudoelastic behavior and shape memory effect is reported and investigated. The novel pseudoelastic behavior arises from the presence of reversible lattice reorientation process present in these systems. As elaborated in the following chapters this phenomena is mediated by two distinct mechanisms: twin boundary propagation and phase transformation. The pseudoelastic behavior mediated by phase transformation mechanism is similar to, but still different than, the martensitic transformation which is responsible for the shape memory behavior in most bulk shape memory alloys (SMAs). The fundamentals of SME in bulk SMAs can help understanding the novel SME in nanowires; mainly because both behaviors share many common characteristics such as: the presence of large reversible strains, the temperature dependence of the process, and the diffusionless, short-range atomic rearrangement, mediated phase transformation.

SME and pseudoelastic behavior refer to the phenomenon according to which a specimen after being plastically deformed recovers its original configuration after mechanical unloading combined with heating [66]. These unique properties are observed in bulk SMAs such as NiTi, Cu-Zn-Al, and Cu-Al-Ni. They have been used in a wide variety of applications such as
transducers, sensors, and actuators. SMAs have also been regarded as smart materials mainly because they can function as sensors and actuators simultaneously [67, 68]. Until recently, the shape memory effect and its underlying pseudoelasticity were considered unique to SMAs, liquid crystal elastomers, and piezoelectric ceramics [66]. Recent research has shown however that pseudoelasticity may also be found at the nanoscale, in gold nanowires [69] and carbon nanotubes. For example, Yakobson et al. [70] and Falvo et al. [71] observed in experiments and atomistic simulations that carbon nanotubes can completely recover from severe deformations at strains of up to 15% without presenting any residual defects. Bilalbegovic [72] reported that Au nanowires can recover their initial lengths and radii after very large compressive strains. However, in most of these materials irreversible defects are nucleated under even small compressive strains, in contrast to the defect-free processes seen in carbon nanotubes. Landman et al. [69] observed reversible changes in structural and electromechanical properties of gold nanowires under tensile loading and unloading. Although the aforementioned reversibility in the deformation of nanowires provides some evidence of pseudoelastic behavior, so far, no systematic research has been done on the SME and pseudoelastic behavior of nanowires regarding the controlling mechanisms, constitutive modeling, and the thermomechanical conditions under which the behavior exists.

2.6 References


CHAPTER 3

MOLECULAR DYNAMICS SIMULATION METHODOLOGY

There are many practical difficulties in experimental studies of the structure, properties, and kinetic behavior of nanostructured systems. Although today’s cutting-edge high-resolution transmission electron microscope (HRTEM) can resolve individual atoms, obtaining three-dimensional structures of complex nanostructures is still a daunting task and these are often inferred from analysis of many two-dimensional images through tedious trial-and-error methods. Moreover, it is extremely difficult (if at all possible) to experimentally monitor the real-time evolution of nanostructured systems during their structural and conformational changes driven by internal or external forces. Therefore molecular dynamics (MD) simulation methodologies are well positioned in this respect as in these simulation methods the nanostructures evolution can be easily captured and analyzed by tracking the movement of all atoms comprising the system. By employing the MD simulation methodology one can predict the structure, stability, and the dynamic behavior of nanostructured systems before they are actually fabricated experimentally. Moreover, by providing mechanistic insights on the physical processes controlling the behavior of the system the MD simulations can yield useful information for interpreting experimental results and help the design effort of new experimental investigations.

In our research projects we use MD simulations to characterize the structure, time evolution, and mechanical behavior of metallic nanowires, nanofilms, and nanotubes. The parallel MD code called HELL2dv (developed in the Interfacial Materials Group lead by Dr. Dieter Wolf from The Materials Science Division at Argonne National Laboratory) was used to
carry out the computations. Embedded atom method (EAM) interatomic potentials were used to
describe the interatomic interactions in the two metallic systems, Pd [1] and Al [2, 3], used in our
studies. The graphics package Visual Molecular Dynamics (VMD) was used to visualize the
simulation results [4]. The computations were carried out on two high performance parallel
computing clusters, ERIC and TEZPUR, from The Louisiana Optical Network Institute (LONI)
and The Center for Computation & Technology (CCT) at Louisiana State University. Some of
the large simulations were run on LONI’s supercomputer Queen Bee.

3.1 Overview

Molecular Dynamics (MD) is a computer simulation technique where the time evolution
of a set of interacting atoms is followed by integrating their equation of motion. It basically
consists in integrating Newton’s second law for each atom present in the system by discretization
of time. One should be aware that the Newton’s second law is not suitable to characterize the
motion of atoms involving coupled behavior of electrons and nuclei, whose motion obeys more
complex quantum mechanical laws, and whose behavior can be inferred by solving Schrödinger
equation. The foundation for using Newton’s second law to track the motion of the atoms
without explicit reference to the electrons is provided by the Born-Oppenheimer approximation,
according to which nuclei, which are much heavier than electrons, move on a time scale that is
two orders of magnitude larger than that characterizing the motion of the electrons. Thus it is
reasonable to neglect the details of the electrons movement and limit on tracking the motion of
the nuclei; motion that obeys Newton’s second law [5].

Based on the Newton’s 2nd law, the motion of the atom \( \alpha \) is determined by the force
acting on the atom
where the index $i$ in the expression of the force $F_i^\alpha$ denotes $i^{th}$ direction, $m_\alpha$ is the mass of the particle $\alpha$, and $\dot{x}_i^\alpha$ is the $i^{th}$ component of the particle $\alpha$ acceleration. For a complex system, the equations of motion are derived using the Hamiltonian dynamics formalism. The formalism is based on the system Hamiltonian which represents the total energy of the simulation system written in terms of the generalized coordinates and the corresponding momenta. For an isolated system the total energy is constant and the Hamiltonian, $H$, can be written as

$$H = \sum_{\alpha=1}^{N_k} \frac{p_k^\alpha p_k^\alpha}{2m_\alpha} + U(x_1^N, x_j^N, x_i^N)$$

where, $p_k^\alpha$ denotes the momentum of particle $\alpha$ in the $k^{th}$ direction; $U$ is the potential energy of the system and is a function of positions of all particles comprising the system; $x_i^N$ denotes the set of all $i^{th}$ components of the positions of all of the particles, $N$ is the total number of particles. The forces can be derived from the Hamiltonian by using the expression $F_i = -\frac{\partial H}{\partial x_i}$.

In general, it is difficult to obtain an analytic, closed form, solution for the atoms trajectories. Therefore in simulations the equations of motion are solved numerically using a time discretization finite difference methodology. One commonly used finite difference method in molecular dynamics is the Verlet method [6]. The Verlet algorithm is developed starting from a Taylor series expansion of the position at times $t + \delta t$ and $t - \delta t$,

$$x_i^\alpha(t + \delta t) = x_i^\alpha(t) + \dot{x}_i^\alpha(t)\delta t + \frac{1}{2} \ddot{x}(t)_i^\alpha \delta t^2 + \frac{1}{6} \frac{d^3x_i^\alpha(t)}{dt^3} \delta t^3 + O(\delta t^4)$$

$$x_i^\alpha(t - \delta t) = x_i^\alpha(t) - \dot{x}_i^\alpha(t)\delta t + \frac{1}{2} \ddot{x}(t)_i^\alpha \delta t^2 - \frac{1}{6} \frac{d^3x_i^\alpha(t)}{dt^3} \delta t^3 + O(\delta t^4)$$
By adding the equation (3) and (4) we obtain:

$$x_i^\alpha(t + \delta t) = 2x_i^\alpha(t) - x_i^\alpha(t - \delta t) + \ddot{x}_i^\alpha(t)\delta t^2 + O(\delta t^4)$$

(5)

According to equation (5), the expression for the position has 4th order accuracy in the integration time step $\delta t$. Combining equation (1) and (5) gives

$$x_i^\alpha(t + \delta t) = 2x_i^\alpha(t) - x_i^\alpha(t - \delta t) + \frac{F_i^\alpha}{m_i} \delta t^2 + O(\delta t^4)$$

(6)

Based on the Verlet algorithm one can predict the positions of an atom at time $t + \delta t$ using the atom current position and the position at a previous time step. This algorithm has the virtues of high stability and high order accuracy and performs the iterative position calculation without using the velocities. However, velocities are necessary to calculate kinetic energy and temperature. A first order central difference method is used to estimate the velocities

$$\dot{x}_i^\alpha(t) = \frac{x_i^\alpha(t + \delta t) - x_i^\alpha(t - \delta t)}{2\delta t}$$

(7)

Here, the velocity in the Verlet algorithm has 2nd order accuracy and thus the accuracy of Verlet algorithm is $O(\delta t^2)$

Often, another variant of the Verlet algorithm is used, the so called velocity Verlet method, which incorporate the velocities explicitly into the integration scheme. According to the velocity Verlet algorithm:

$$x_i^\alpha(t + \delta t) = x_i^\alpha(t) + \dot{x}_i^\alpha(t)\delta t + \frac{1}{2}\ddot{x}(t)^\alpha\delta t^2 + O(\delta t^3)$$

(8)

$$\dot{x}_i^\alpha(t + \delta t) = \dot{x}_i^\alpha(t) + \frac{1}{2} [\dddot{x}(t)^\alpha + \ddot{x}(t + \delta t)^\alpha] \delta t$$

(9)
and the new velocity is calculated based on the force at the current position and the force at the new position. Compared with Verlet algorithm the accuracy of velocity is improved and it is of the order of $O(\delta t^3)$.

Integrating the equations of motion in an MD simulation requires specification of an appropriate integration time step $\delta t$. The time step, $\delta t$, should be small enough to capture the detailed motion of the atoms and it should be large enough to allow simulations that follow the system over large times. Typically $\delta t$ is chosen to be about $1/50$ of the vibration period of the atoms around their local minima.

To start a simulation, it is necessary to specify a set of initial positions and velocities for all atoms in the system. For metallic systems, the initial positions are defined on a lattice that the specific material crystallizes in, while the initial velocities are assigned according to the Boltzmann distribution at the given simulation temperature.

3.2 Description of the Interatomic Interactions in Metals: The Embedded Atom Method (EAM) Potentials

The validity and accuracy of MD simulation results are primarily determined by the accuracy and efficiency of the interatomic forces used. The accuracy of the interatomic forces in simulations is determined by the selection of the underlying interatomic potential. Among the various parameterizations of the interatomic interactions, those based on the first principles (ab initio) are the most accurate. According to these methodologies interatomic forces are calculated directly from the underlying electronic structures of all atoms present in the system. Although there are certain advantages in using this methodology, this method is computational very expensive and the computation cost scales as $O(N^3)$, where N is the number of atoms in the simulation system. Thus, the simulations based on ab initio MD methodology are restricted to
very small systems. Pair potential interaction models, including Lennard-Jones potential and Morse potential, are computationally much more efficient.

The expression for the Lennard-Jones interatomic interaction potential is given by

\[
\phi(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right),
\]

where \(\varepsilon\) is the depth of the potential well, \(\sigma\) is the distance at which the inter-particle potential is zero, and \(r\) is the distance between the two particles.

There are however serious issues with using pairwise potentials to describe the interactions in metals since they fail to capture the essential physics of metallic bonding, such as surface effects and local bond order. It is also not adequate to model situations where strong localized bonds may form (as in covalent systems).

To keep a balance between having the correct physical description of the interactions, high accuracy, and computational efficiency, many semi-empirical potentials have been proposed. The computation of the interatomic forces based on the semi-empirical potentials is efficient and the cost is of the same order of magnitude as that for pair potentials, \(O(N)\), where \(N\) is the number of atoms in the simulation system. These semi-empirical potentials are generally derived by fitting specific functional forms containing adjustable parameters such that the simulation data matches specific experimental data or data derived from first principles \textit{ab initio} calculations.

Of the various semi-empirical potentials, the embedded atom method (EAM) potential is one of the most common used in modeling FCC metals. The parameters of EAM potential are generally obtained by fitting cohesive energy, equilibrium lattice constant, cubic elastic constants, unrelaxed vacancy formation energy, and bond length and bond strength of the
diatomic molecule. Since first introduced by Daw et al. [9], the ability and viability of EAM in modeling metals have been analyzed and tested by various researchers [1, 9, 10]. We should mention that the classical EAM method is not suitable for describing systems in which there are covalent bonds present [10], such as silicon, germanium or carbon (in diamond or graphite structures). This is because the EAM description can not account for the angular dependence of the interatomic interactions. In cases in which angular dependence is important, such as the case of the body centered cubic (BCC) structures, modified embedded atom methods (MEAM) have been proposed [11].

For a system of N atoms, the total energy $U$ in the EAM framework can be written as

$$U = \sum_{i}^{N} \left( F_{i}(\overline{\rho}_{i}) + \frac{1}{2} \sum_{j \neq i}^{N} \phi_{ij}(R_{ij}) \right),$$

(11)

where the summation extends over the total number of atoms N in the system. $\phi_{ij}$ is the pairwise interaction term which is related to the interatomic distance $R_{ij}$ of atom $i$ and $j$. $\phi_{ij}$, the pairwise interaction term, corresponding to the electrostatic interaction between atom $i$ and $j$; while $F_{i}$, the embedding term, describes the quantum effects and is a function of the local electron density. This embedding term can be considered as the energy to embed an atom into an electron gas with a density $\rho_{i}$, which comes from the contributions of neighboring atoms. The embedding term, which includes the contribution of electron density is key to EAM and provides a many-body contribution to the energy. $\rho_{i}$, the electron density term, can be written as

$$\overline{\rho}_{i} = \sum_{j}^{N} \rho(R_{ij}),$$

(12)

where $\rho_{i}$ depends only on the distance between two atoms. For a system of atoms in equilibrium state, the force that comes from embedding term together with the force derived from pairwise
interaction term are balanced. A simple way to understand the many-body effect of the embedding term, \( F_i(\langle \rho_i \rangle) \), is to look at the variation of bonds strength with the number of bonds per atom. In EAM framework, as an atom makes more bonds each bond strength becomes lower. Namely making a new bond decreases the average energy per bond although it increases the total bonding energy. This is consistent with the traditional chemical bonding, which can not be captured in pair potential. Thus the \( F_i(\langle \rho_i \rangle) \) has a positive curvature (\( \partial^2 F / \partial^2 \rho > 0 \)).

In this project, EAM interatomic potentials are chosen for Pd [1] and Al [2, 3]. Additional details regarding the numerical expression (given is the so-called potential file) for EAM potential for Pd are given in Appendix 1.

### 3.3 Dealing with the Boundary Conditions

When performing MD simulations one is faced with the question of what should be done with the boundaries of the simulated system? One possibility is to do nothing special; that is, the system simply terminates, and atoms near the boundary would have less number of neighbors than atoms inside. In other words, the simulated system would be surrounded by free surfaces. Unless we really want to simulate a cluster of atoms, this situation is not realistic. No matter how large is the simulated system, its number of atoms \( N \) would be negligible compared with the number of atoms contained in a macroscopic piece of matter (of the order of \( 10^{23} \)), and the ratio between the number of surface atoms and the total number of atoms would be much larger than in reality, causing surface effects to be much more important than what they should. Consider 1000 atoms arranged in a 10 *10 *10 cube. Nearly half the atoms are on the outer faces, and these will have a large effect on the measured properties. Even for \( 10^6 \) atoms, the surface atoms amount to 6% of the total, which is still nontrivial.
A solution to this problem is to use periodic boundary conditions (PBC). When using PBC, particles are enclosed in a box and the images of this box are replicated to infinity by rigid translation in all the three Cartesian directions, completely filling the space. In other words, if one of our particles is located at position \( r \) in the main simulation box, we assume that this particle really represents an infinite set of particles located at positions \( r + la + mb + nc \), where \( l, m, n \) are integer numbers and \( a, b, c \) are box sizes along the three spatial directions. Although all these image particles move together in the same way, only one is represented and has its coordinates tracked in the computer program.

The key point is that now each particle \( i \) in the box should be thought as interacting not only with other particles \( j \) in the box, but also with their images in nearby boxes. That is, interactions can go through box boundaries. In fact, one can easily see that (a) we have virtually eliminated surface effects from our system, and (b) the position of the box boundaries has no effect (that is, a translation of the box with respect to the particles leaves the forces unchanged). In the course of the simulation, if an atom leaves the main simulation box through one facet, it re-enters the main simulation box through the opposite facet. Of course, it is important to bear in mind and to account for the imposed artifacts due to the periodicity when considering properties which are influenced by long-range correlations. Special attention must be paid to the case where the interaction potential is long ranged like for example in charged and dipolar systems.

### 3.4 Controlling the Temperature and Pressure in the Simulated System

Statistical mechanics provides a link between the macroscopic properties of matter (like temperature, pressure, etc.) and the microscopic properties (like positions, velocities, individual kinetic and potential energies) of atoms and molecules that the system is made of. These
macroscopic properties reflect the time average behavior of the atoms at equilibrium. Next we give a brief description of the basic technical terms pertinent to the MD simulation methodology.

Prior to starting an MD simulation one is faced with the task of initializing the atomic positions and velocities for all atoms comprising the simulated system. In the case of crystalline solids like metals the starting positions will be defined by the crystal symmetry and the positions of atoms within the unit cell of the crystal. The unit cell is then repeated periodically in space to fill up the desired simulation box that has the characteristic dimensions of the system to be investigated. The initial velocities are assigned according to a Boltzmann distribution at a certain temperature. This is achieved numerically by using Gaussian distributed random numbers that are multiplied by the mean square velocity which in turn is given by $\sqrt{2k_BT/m}$ in each of the three directions. By generating the initial structure and assigning initial velocities to each atom both the initial temperature and the total energy of the system are predefined. The total energy of the system is given by

$$E_{tot} = KE_{tot} + PE_{tot},$$  \hspace{1cm} (13)

where $KE_{tot}$ is the total kinetic energy of the system and is given by

$$KE_{tot} = \sum_{i=1}^{N} \frac{1}{2}m(v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2).$$  \hspace{1cm} (14)

$PE_{tot}$ is the total potential energy of the system and it is expressed as a sum of the potential energies of all atoms in the systems. Knowing the total kinetic energy at a moment in time one can use this relation to define an instantaneous temperature, $T(t)$, at time $t$:

$$T(t) = \sum_{i=1}^{N} \frac{1}{k_BT}m(v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2).$$  \hspace{1cm} (15)
where $k_B$ is the Boltzmann constant, $m$ is the mass of an atom and $N$ is the total number of atoms in the system. In addition to temperature, the pressure also needs to calculated and often controlled during a typical MD simulation. There are several different (but equivalent) ways to calculate the average pressure in a classical N-body system. The most common methodology is based on the virial equation for the pressure. For pairwise additive interactions, one can write [12]

$$p = n k_B T + \frac{1}{3V} \left( \sum_{i<j} f(r_{ij}) \cdot r_{ij} \right),$$

where $f(r_{ij})$ is the force between particles $i$ and $j$ at distance $r_{ij}$, $n$ is particle density, $T$ the temperature and $V$ the volume of the system.

There are many methods that have been developed to control and maintain the temperature and pressure constant [12-14]. Commonly used methods are based on the so called Berendsen thermostats and barostats [14]. According to Berendsen thermostat the temperature is controlled by scaling the velocities of all atoms at each time step such that $\vec{v}_i \rightarrow \lambda \vec{v}_i$ and the scaling factor, $\lambda$, is given by

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T} \left( \frac{T_0}{T} - 1 \right)}$$

where, $\Delta t$ is the integration time step, $\tau_T$ is the time constant for temperature control and has to be greater than $100 \Delta t$, $T_0$ is the desired temperature and $T$ is the current temperature. The Berendsen pressure control is implemented in a similar way by changing at each time step the volume of the simulation box and rescaling all atom positions. Accordingly, the simulation box size $L_i \rightarrow \mu L_i$ and atoms positions $\vec{r}_i \rightarrow \mu \vec{r}_i$, and the scaling factor, $\mu$, is given by
\[ \mu = 1 - \frac{\kappa_T \Delta t}{3 \tau_p} (p_0 - p) \quad (18) \]

where, \( \Delta t \) is the integration time step, \( \kappa_T \) is the isothermal compressibility of the system, \( \tau_p \) is a time constant for pressure control, \( p_0 \) is the desired pressure and \( p \) is the current pressure. There are advantages of using these methods as they ensure steady and stable evolution of the system to equilibrium. The drawbacks are that the statistical ensemble they generate is not known.

**3.5 Time and Size limitations**

Molecular dynamics evolves a finite-sized molecular configuration forward in time, in a step-by-step fashion. There are limits on the typical time scales and length scales (system size) that can be investigated and one should account for them when planning and preparing a simulation study or analyzing the simulation results. Typical MD simulations can be performed on systems containing thousands or, perhaps, millions of atoms and for simulation times ranging from a few picoseconds to hundreds of nanoseconds. While these numbers are certainly respectable, it may happen to run into conditions where time and/or size limitations become important.

A simulation is reliable from the point of view of its duration when the simulation time is much longer than the relaxation time of the quantities we are interested in. However, different properties have different relaxation times. In particular, systems tend to become slow and sluggish in the proximity of phase transitions, and it is not uncommon to find cases where the relaxation time of a physical property is orders of magnitude larger than times achievable by simulation.

A limited system size can also constitute a problem. In this case one has to compare the size of the MD cell with the correlation lengths of the spatial correlation functions of interest.
Again, correlation lengths may increase or even diverge in proximity of phase transitions, and the results are no longer reliable when they become comparable with the box length.

3.4 References


CHAPTR 4

SPONTANEOS STRUCTURAL
REORIENTATION AND QUASI-ELASTIC
EFFECTS IN PALLADIUM NANOWIRES

As the scale of a material is reduced to just a few interatomic distances across at least one of the three spatial dimensions the structure and properties can be quite different from those of bulk materials. Many (001) oriented surfaces in FCC metals reconstruct to denser quasi-hexagonal packed layers [1]. The reconstruction is driven by the reduction of the surface energy which should be large enough to compensate for the corresponding mismatch strain between the original and the reconstructed atomic layers. In thin films the rearrangement of the surface atoms such that to minimize the surface energy can drive structural changes well beyond the surface layers throughout the bulk of the entire film [2]. The reorientation of FCC (100) gold films into (111) films, when the film thickness is less than eight atomic layers, has been observed experimentally [3]. Recent molecular dynamics simulation studies have demonstrated that such crystalline reorientations in thin films are generic and representative for a larger class of FCC metals [4].

When two spatial dimensions of the systems are in the nanometer range the structural characteristics and stability of are strongly influenced by both surface energy and surface stress. Several novel structures have been identified in metallic nanowires including: multishell helical gold nanowires [5,6] “weird” aluminum and lead nanowires [7], and body-centered tetragonal (BCT) gold nanowires [8,9]. In the presence of external stresses these single-crystalline metal nanowires can undergo large pseudoelastic deformations of up to 50%, well beyond the recoverable strains of 5-8% typical for most bulk shape memory alloys. Recent atomistic
simulation studies have identified two distinct mechanisms that mediate the pseudoelastic behavior in metal FCC nanowires. In certain metals when the cross sectional area is below 4nm\(^2\) the surface stress can be large enough to cause a phase transformation that drives the system from the initial FCC structure into a BCT structure [8, 10, 11]. For nanowires with larger cross sectional areas the pseudoelastic behavior is the result of spontaneous and reversible crystal reorientation; that is it was found that FCC wires with initial <100> orientations can reorient spontaneously under the effect of surface stress into <110> orientations [12-14].

In this chapter we present the results of our investigations of the crystallographic reorientation and deformation processes in palladium nanowires using molecular dynamics simulation. Our studies indicate that <100> Pd nanowires can reorient spontaneously to energetically more favorable <110> orientations provided the wire cross-sectional area is below 2.57 nm \(\times\) 2.57 nm and the temperature is above a critical value \(T_c = 300\text{K}\). Upon tensile loading of the reoriented <110> wire the initial <100> orientation is reached via a novel stress-strain behavior that is drastically different from those corresponding to bulk metals. The lattice reorientation driven by the externally applied tensile stress is mediated by the propagation of twin boundary separating the initial <110> phase from the new <100> phase. Because its reversibility upon unloading the twin-boundary-mediated lattice reorientation process is the main ingredient to the pseudoelastic behavior of the Pd nanowires.

In our investigations the wires structures were generated by simulating a top-down fabrication process. Specifically, nanowires with <100> axis and \{100\} surfaces (named <100>/\{100\} wire structure or configuration) were created by cutting them from bulk single-crystalline samples that were previously allowed to undergo relaxation consistent with the simulated temperature. Since the surface energy constitutes a significant portion of the total free energy, metal nanowires tend to assume surfaces in specific orientation to lower the total surface
energy. Structural reconstruction or reorientation may occur in the wires fabricated via top-down approach if the initial configurations do not have the preferred orientation. Structural changes present a challenge for controlling the morphologies and dimensions of nanowires during the fabrication process and can be the source of various important processes that determine many attractive properties of the nanowires. In order to obtain nanowires with desired properties, morphologies and dimensions, it is important to understand the mechanism and structural changes in the top-down fabrication process.

### 4.1 Top-down Fabrication Process and Simulation Methodology

![Diagram](image)

Figure 4.1 The initial structure of a 2.57 nm × 2.57 nm Pd nanowire fabricated through simulated top-down method. (a) The lateral view of the nanowire; (b) Atomic arrangement of the nanowire in cross-sectional view.

The wires used in this study were created by simulating a top-down process similar to the fabrication process described by Kondo and Takayanagi [5]. Specifically, the nanowires are created by “slicing” square columns of atoms from single crystal crystal bulk Palladium (Pd) along the [100], [010] and [001] directions by subsequent computational relaxation following the slicing. The initial single crystalline Pd [100] nanowires have a square cross section and surface orientation of [100], [010], and [001]. The original cross sectional area and length of the wire
were 2.57 nm × 2.57 nm and 31.2 nm respectively. Then the wires were relaxed to corresponding minimum energy states at various simulation temperatures. Free boundary conditions were used in all directions during the following simulation. The initial configuration of Pd nanowire is illustrated in Figure 4.1.

4.2 Structural Reorientation during Relaxation

Figure 4.2 Five snapshots depicting the dynamic progression of spontaneous crystalline reorientation at 300K in a Palladium nanowire of 2.57 nm × 2.57 nm cross sectional area. Snapshots of the nanowire after 3.8ps, 9.6ps, 15.3ps, 19.1ps and 25.8 ps, respectively, are shown here.

As result of the reorientation process, the nanowire exhibits an axial contraction accompanied by a corresponding lateral expansion. Using free boundary conditions in all directions, as documented previously [12] the reorientation process occurs through the propagation of coherent twin boundaries that are nucleated at the two ends. Figure 4.2 shows the
dynamic progression of structural reorientation in the Pd nanowire. During the first 3.8 ps the wire contracts elastically. After the elastic contraction the lattice reorientation nucleates at the ends and propagates towards the center of the nanowire. After the reorientation was completed, we verified the stability of the new nanowire by a simulated annealing process. The temperature was raised slowly from 300K to 600K, held at 600K for more than 50ps and then gradually lowered to 300K. The wire in the reoriented configuration retains its structure during the annealing process. The complete structural reorientation yields an axial strain of approximately -29% and an increase in cross-sectional area of approximately 13%. Wires with cross-sections large than 2.57 nm $\times$ 2.57 nm do not undergo such a spontaneous structural reorientation at 300K without external stimuli.

Figure 4.3 Cross section representation of: (a) the initial Pd fcc <100> nanowire with square cross section and (b) the fcc <110> nanowire after relaxation (rhombic). All atoms from two lattice planes of ABAB stacking sequence are shown in both representations.

Although maintaining the FCC crystalline structure, the reconstructed wire has clearly different morphology than that of the initial un-reconstructed wire. Specifically, the initially <100> oriented nanowires (with <100> axis and all around {100} surfaces with square lattices) reorient to assume <110> axis, {111} lateral surfaces, and {110} cross-sections. The new side surfaces have the symmetry of perfect hexagonal {111} crystalline planes.
Figure 4.3 shows the cross sections of the initial <100> oriented wire and the new <110> wire after reorientation. Because both the initial and new wire can be represented as a repeat in an ABAB stacking sequence in the length direction only two adjacent lattice planes are shown here. The new reoriented wire has rhombic cross section with all four {111} orientated surfaces. The atoms located at the corners are slightly distorted from their FCC lattice positions. By checking the ABAB stacking sequence in the wire length direction and the size of the projected unit cells on the A and B lattice planes of the new wire, we found that that new wire has indeed FCC structure with the same lattice parameter as the original FCC structure.

The structures of the fully reconstructed wires reported above are in good agreement with those of the laboratory fabricated wires including Cu, Au, and Pt nanowires, e.g., the Cu wires fabricated by vacuum vapor deposition [15] and by a complex surfactant-assisted hydrothermal reduction process [16], and Au wires fabricated by cutting Au nanofilms using electron beam eradiation [5]. Similar to defect free simulated wire structures, The laboratory obtained nanowires have defect free FCC crystal structures and are similar to those of the simulated wires with <110> axes and {111} surfaces, indicating that <110> is the preferred growth orientation and {111} planes are preferred lateral surfaces.

4.3 Mechanical Behavior

4.3.1 Quasistatic Loading and Unloading

So far, the strain rates that can be considered in MD simulations (at or above $10^7$/s) are much higher than what can be obtained in controlled experimental investigations. These artificially high strain rates are, to a degree, warranted by the limited speed of computers available. The total simulation time that can be reached in many simulations is of the order of
100 nanoseconds, partly limited by the time step size needed to resolve the high frequency thermal vibrations of the atoms in MD calculations which is of the order of 1 femtosecond (1 fs = \(10^{-15} s\)). To achieve significant deformation within such a short time, high strain rates are needed. It should be noted that this is purely a computational necessity and is not part of any realistic physical deformation process. Therefore, special algorithms are needed to allow physically interpretable results to be obtained using available computer resources and to avoid the artificially high rates of deformation.

Figure 4.4 Schematic of displacement controlled quasistatic loading method for a nanowire. After all atoms are displaced with a designed strain, the two ends of the nanowire are fixed during the relaxation process.

To this end, we use a displacement-controlled quasistatic loading and unloading scheme introduced by Gall et al. [9]. In this method, the nanowires are relaxed to reach equilibrium states between loading steps. Hence, the deformation proceeds through a series of equilibrium states, which essentially corresponds to a quasistatic deformation process. Specifically, during each loading step, all atoms are displaced from their position according to a prescribed uniform strain increment of \(\Delta \varepsilon = 0.125\%\) in the length direction, as shown in Figure 4.4. The proportional scaling of atomic coordinates in the axial direction is carried out on all atoms comprising the wire, regardless of whether or not an atom is part of structural defect. The wires are then equilibrated at constant temperature for 15 picoseconds (ps) to obtain a macroscopic equilibrium
configuration at the prescribed strain. During this equilibration stage the wires have their ends kept at fixed locations. This relaxation process allows structural changes to occur, if the conditions so dictate. This process usually takes less than 12 ps and the average stress over the last 3 ps of the relaxation period at each load step is taken as the stress in the wire at the current strain. Unloading is implemented in the same manner, with a negative strain increment of $\Delta \varepsilon = -0.125\%$. The results from the quasistatic loading and unloading method are compared with those from dynamic and static simulations. It is found that as long as the maximum atom displacement is less than $0.2a$ (where $a$ is the lattice constant), this quasistatic method does not artificially affect deformation mechanisms.

Figure 4.5 The stress-strain curve of a Pd nanowire during loading (blue) and unloading (red) at 300K. The linear portion of curve, between points B and C, is corresponding to the sample elongation caused by the steady advance of the lattice reorientation from the ends toward the center of the nanowire.
Figure 4.5 shows the stress-strain curve for Pd nanowire with lateral dimensions 2.57 nm × 2.57 nm during loading and unloading at 300K. The curve indicates that indeed the Pd nanowire is very ductile with fracture strains of approximately 55%. Along the loading part of the stress-strain curve one can identify the following stages:

i.) Between points O and A the <110>{111} wire undergoes elastic straining with an elastic strain about 6%.

ii.) Point A corresponds to the nucleation of two twin boundaries at the ends of the wire. Their subsequent motion marks the beginning of the lattice reorientation; process which is also associated with a sudden drop of the applied stress from 6.2 GPa to about 2.0 GPa.

iii.) Between points B and C the linear portion of the curve corresponds to the sample elongation caused by the steady advance of the lattice reorientation from the ends toward the center of the nanowire. At point C the entire wire has achieved the <100>{111} configuration. What should be mention here is that a slow strain hardening is also found in this portion of the curve.

iv.) The portion between C and D corresponds to the linear stretching of the new <100>{111} wire.

v.) Further loading beyond point D causes the wire to neck and ultimately to fracture at point E.

The stress-strain curves generated indicate that Pd nanowire show indeed a unique ductile behavior with a fracture strain above 50%. One can quantify the overall straining by using the following equation: the total strain = elastic strain of the <110> wire + strain due to lattice reorientation + elastic strain of the <100> wire = 5.1% + 41.4% + 6.0% = 52.5%.
4.3.2 Deformation Mechanism

Figure 4.6. Cross sectional representation at three location along a Pd nanowire during $<110>/\{111\}$ to $<100>/\{100\}$ reorientation process. The snapshot corresponds to 20% straining during tensile loading of the initial $<110>$ oriented wire.

The lattice reorientation is achieved through the propagation in steps of twin boundaries (corresponding to the point B to C on the stress-strain curve depicted in Figure 4.5). The twin boundaries are formed through the nucleation at the edge of the wires and propagation across the $\{111\}$ planes of Shockley partial dislocations. As the twin boundary moves along the wire axis
(see the process depicted in Figure 4.6), the wire is progressively transformed into the <100> orientation.

Figure 4.6 shows three cross section representations of the wire structure at three different locations along the wire depicting details of the structural changes that develop during reorientation process. The top, 1-1, cross section shows the square lattice in the <100> reoriented domain with <100>/\{100\} configuration. The rhombic cross section, 3-3, at the bottom shows the ordering in the domain having the original <110>/\{111\} configuration. The middle, 2-2, cross section is from the transition region containing both <100>/\{100\} and <110>/\{111\} configurations. This figure clearly shows a view of Pd nanowire while the twin boundary is in the middle of the transforming wire. The twin boundary separates the new formed <100>/\{100\} region from the untransformed <110>/\{111\} region during the loading process.

![Figure 4.7 Twin boundary propagation through dislocation nucleation, glide and annihilation: (a) a side view of details of \{111\} twin boundary, cut along the diagonal of \{110\} plane and (b) a perpendicular view of the same \{111\} twin boundary and gliding partial dislocation.](image)
The reorientation is completed through the propagation of a \{111\} twin boundary, which involves repetitive nucleation, gliding, and annihilation of Shockley partial dislocations. The mobile twin boundary is formed by mismatch defects between \(\langle 100\rangle/\{100\}\) lattice and \(\langle 110\rangle/\{111\}\) lattice, as shown in Figure 4.7. Specifically, the partial dislocation is nucleated from one edge, glides across the wire on the \{111\} plane adjacent to the twin plane, and finally annihilates at the other edge. This process repeats itself and at each cycle the twin boundary propagates by an inter-planar distance between two neighboring \{111\} planes. As the twin boundary sweeps through its length, the wire is progressively transformed into the new \(\langle 001\rangle\) orientation.

### 4.4 Pseudoelasticity and Shape Memory Effect

The stress-strain curve in Figure 4.5 shows the pseudoelastic behavior uploading, unloading of Pd nanowire. Clearly, the responses are drastically different from those of the corresponding bulk metals. Specifically, the nanowire seems highly ductile with the fracture strains of approximately 52%. In comparison, the fracture strains of most bulk FCC metals are usually less than 15%. The unique structural reorientation process (from point B to C in Figure 4.5) is the key to the pseudoelastic behavior of the wire. As explained in the previous section, the structural reorientation progresses with the propagation of twin boundary.

#### 4.4.1 Large Strain Related with Pseudoelasticity

The larger strain associated with the structural reorientation can be quantified with a simple crystallographic analysis. The analysis shows that the strain corresponding to the
reorientation is 41.4% for a complete process. Figure 4.8 compares the same atomic plane which is cut along the cross-sectional diagonal of wire, shown in (b) and (c) respectively.

Figure 4.8 Reversible structural reorientation upon loading and unloading in Pd nanowires; (a) a schematic of the wire configurations before and after structural reorientation, (b) the atomic plan cut along the diagonal of wire highlighted in blue, (c) the same atomic plane after reorientation highlighted in red.

Apparently, the structural reorientation manifests as 90° rotation of the rectangular unit cell in the \{110\} atomic plan shown in figure. The length and width of the rectangular unit cell in
both cases are, respectively, $a$ and $\frac{\sqrt{2}}{2}a$, where $a$ is the lattice constant of the Pd wire. Hence, we calculate the axial strain associated reorientation process by

$$\varepsilon_{<110>\rightarrow<100>} = (a - \frac{\sqrt{2}}{2}a) / \frac{\sqrt{2}}{2}a = 0.414$$

On the other hand, if we consider the opposite reorientation for, $<100>/\{100\}$ wire $<110>/\{111\}$ wire with $<100>$ configuration as reference state. Then the strain is given by

$$\varepsilon_{<100>\rightarrow<110>} = (\frac{\sqrt{2}}{2}a - a) / a = 0.293$$

This strain associated with structural reorientation is consistent with result from the stress-strain curve in figure 4.5. From the above analysis, we can see that the strain related with reorientation is attribute of the FCC crystal structure and is independent of lattice parameter $a$.

4.4.2 Shape Memory Effect

Our simulations indicate that when the temperature is maintained above a critical value $T_c = 300K$, the load driven $<100>$ reoriented wire undergoes a spontaneous transformation to the original $<110>$ wire configuration provided the two ends of the wire are released. The unloading curve (generated during the quasistatic unloading) is shown in figure 4.5 (highlight in red). The driving force for the spontaneous reorientation can be viewed as coming from the surface stress which induces a compressive stress in the interior of the wire. This stress is given by

$$\sigma = -4f l / A$$

where $f$ is the surface stress of the $\{100\}$ plane in $<100>/\{100\}$ configuration, $l$ is the wire length and $A (=l^2)$ is the corresponding cross-sectional area. Obviously, the magnitude of this stress increases as the wire size decreases and can be very high when the wire size is at the nanoscale, as shown in figure 1.5. Note that $\sigma$ is only of the order of a few Pascals in bulk.
materials (a negligible value), providing an explanation for why a similar behavior is not seen in bulk metals.

The loading and unloading paths shown in figure 4.5 form a hysteresis loop which is typical for shape memory materials. Thus we found that the shape memory effect (SME) exists in the Pd nanowires. The reversible structural reorientation endows the Pd nanowire with the ability for pseudoelastic strain up to 52%, which is much higher than the typical 5-8% recoverable strain for the most shape memory alloys (SMA).

![Diagram of shape memory and pseudoelasticity in FCC metal nanowires.](image)

Figure 4.9: Schematic of shape memory and pseudoelasticity in FCC metal nanowires. Tc is the critical temperature for an initially <100> nanowire to reorient to a <110> nanowire with {111} side surfaces for a given wire cross sectional length [13].

Similar to the behavior of normal bulk SMAs, the pseudoelastic behavior of Pd wires reported here is strongly temperature-dependent. Specifically, the reverse lattice reorientation from <001> to <110> occurs only above a size-dependent critical temperature Tc. If unloading takes place at temperatures below Tc, the reverse lattice reorientation does not occur and the wire
retains the <100>/<100> configuration. When subsequently heated above Tc, the unloaded <100>/<100> wire spontaneously returns to its original <110>/<111> configuration through the reverse lattice reorientation. This is a novel SME driven by surface stress and the high surface-to-volume ratios of the nanowire. It is a one-way SME that has the <110>/<111> wire configuration as the parent state, as illustrated in figure 4.9.

Our simulations show that the critical temperature Tc for Pd nanowire with 2.57 nm × 2.57 cross sectional area is around 300K. The value of Tc is obtained by gradually heating a <001>/<001> wire until lattice reorientation occurs. The heating starts at 0 K and the temperature is increased by 10 K in each heating step. At each temperature, the wire is relaxed for about 20 ps.

What causes the <100>/<100> wire to spontaneously revert back to its original <110>/<111> configuration upon unloading, since both states have the same FCC crystalline structure and, perhaps, the same “stability”? The answer lies in the surfaces and the extremely high surface-to-volume ratios of nanowires which can significantly affect structural stability. Specifically, {111} surfaces in FCC metals have the lowest energy among all surfaces. This difference in surface energy causes the <110>/<111> configuration to have a lower energy and to be more stable compared with the <100>/<100> configuration.

If the <110>/<111> state always has a lower energy than the corresponding <100>/<100> state regardless of size, why does the reverse reorientation only occur above Tc? The answer has to do with the energetic barrier and driving force for the process. To initiate the reorientation, partial dislocations nucleate and propagate to accommodate mobile twin boundaries. These defects are of higher energies and thus constitute an energy barrier for the reorientation, which is
closely related to unstable stacking fault energy. Thermal energy can provide the necessary energy for overcoming the barrier.

4.5 Chapter Summary

We have used MD simulations to study the structural stability and mechanical properties of Pd nanowires. For a <100> initial crystal orientation and wire cross-sectional area below 2.57 nm × 2.57 nm, our studies indicate that the surface stress can cause Pd nanowire to undergo spontaneous structural reorientation leading to a FCC structures with <110> orientation, with cross section cross-sectional shape changing from square to rhombic and the wire length decreasing approximately 29.3%. Under tensile loading and unloading Pd nanowires transform reversibly between the two crystallographic orientations exhibiting pseudoelastic behavior characterized by fully recoverable strains of up to 52.5%. The temperature-dependence of the pseudoelastic behavior enables the shape memory effect in Pd nanowires.

4.6 References


CHAPTER 5

SPONTANEOUS PHASE TRANSFORMATION IN PALLADIUM NANOWIRES

In Chapter 4, we studied the structural reorientation and shape memory effect in the Pd nanowire when the size of wire is below a certain characteristic value. In this chapter, we investigate structural stability and mechanical response of even thinner Pd nanowires. Specifically, we investigate the fundamentals of surface-stress-induced phase transformation and pseudoelastic deformation processes in palladium nanowires using molecular dynamics (MD) simulation. Our MD simulations indicate the existence of a novel surface-stress-induced phase transformation and pseudoelastic behavior in these systems. For a <100> initial crystal orientation and wire cross-sectional area below \(2.18 \text{ nm} \times 2.18 \text{ nm}\), our studies indicate that the surface stress can cause palladium nanowires to undergo a spontaneous phase transformation from face-centered cubic (FCC) structure to a body-centered tetragonal (BCT) structure. Under tensile loading and unloading Pd nanowires transform reversibly between the two crystalline structures exhibiting pseudoelastic behavior characterized by fully recoverable strains of up to 50%. The temperature-dependence of the pseudoelastic behavior enables the shape memory effect in Pd nanowires.

5.1 Introduction

With the miniaturization of electrical, optical, thermal and mechanical systems, the feature size of relevant materials will be reduced down to several or tens nanometers. These nanometer-scale materials have a very large surface-to-volume ratio as compared to bulk
materials. As the scale of this material is reduced to just a few interatomic distances across at least one of the three spatial dimensions both the structure and properties can be quite different from those of bulk materials. In thin films the rearrangement of the surface atoms, such that to minimize the surface energy, can drive structural changes well beyond the surface layers throughout the bulk of the entire film [1]. Recent molecular dynamics simulation studies have demonstrated that such crystalline reorientations in thin films are generic and representative for a larger class of FCC metals [2]. The reconstruction is driven by the reduction of the surface energy which should be large enough to compensate for the corresponding mismatch strain between the original and the reconstructed atomic layers. Nanowires are technological important nanoscale structural elements which have been the focus of intense research over the last years [3]. Recent experimental and atomistic simulation studies have demonstrated that the structures and properties of metallic nanowires can be quite different and unique [4-7] when compared with the bulk properties. For example, a novel surface stress driven phase transformation from FCC to BCT was found in single crystalline gold nanowires when the cross section dimensions of wire are smaller than about 2.0 nm [8-10]. More recently, the pseudoelastic deformation and shape memory effect were observed in FCC metallic nanowires [11-15]. This shape memory and pseudoelasticity operates via a reversible reorientation between a <100> orientation with square cross section and <110> orientation with rhombic cross section through twin propagation and annihilation. The reorientation was driven by surface stress of the nanowires and it is energetic favorable because of the energy difference of {100} and {111} side surface.

Here, in this chapter, we present the research findings from our MD simulations of the surface-stress-induced phase transformation and pseudoelastic deformation processes in palladium nanowires. The MD simulations were performed using the embedded-atom method (EAM) potential for Pd [16]. Single crystalline Pd [100] nanowires with a square cross section
and surface orientation of [100], [010], and [001] were created with initial atomic positions corresponding to the bulk fcc Pd crystal. The original cross sectional areas of the two wires investigated were $1.78 \text{ nm} \times 1.78 \text{ nm}$ and $2.18 \text{ nm} \times 2.18 \text{ nm}$ respectively. Both wires considered were 31.2 nm in length. Free boundary conditions were used in all directions.

5.2 Phase Transformation in the Pd Nanowires

Figure 5.1 Six snapshots depicting the time evolution of a Pd nanowire during the spontaneous, surface-stress-driven, FCC to BCT phase transformation at 100K. Snapshots of the $1.78 \text{ nm} \times 1.78 \text{ nm}$ Pd nanowire at 1, 7, 11, 15, 20, 30 ps respectively are shown here. The BCT phase nucleates at the two ends and propagates toward the center of wire.

At 100K the MD simulations show that the FCC, initially <100> oriented, Pd nanowire undergoes a spontaneous phase transformation to a BCT crystalline structure. As result of the crystal structure change the nanowire exhibits an axial contraction accompanied by a corresponding lateral expansion. Figure 5.1 shows the dynamic progression of the phase
transformation in the Pd nanowire. Six snapshots are shown in the figure, during the first 3.0 ps
the wire relaxes elastically and contracts longitudinally by about 6%. After the elastic contraction
a new BCT crystalline phase nucleates at the ends and propagates with a speed of approximately
538 m/s toward the center of the nanowire. The FCC to BCT phase transformation is completed
in about 30ps and leads to a further wire longitudinal contraction of about 31%. A similar FCC to
BCT phase transformation was previously observed in MD simulations of Au nanowires by Diao
et al [8].

Crystallographic analysis of the FCC to BCT phase transformation is documented further
in Figures 5.2 which depicts wire cross-sections viewed from the x, y, and z directions for both
the initial FCC and the newly transformed BCT nanowire. Only two adjacent lattice planes of the
ABAB stacking sequence are shown in each selected view. Atoms in different crystalline planes
are shown in different colors. Due to the tensile surface-stress components and in the presence of
phase transformation the nanowire contracts in the longitudinal x direction and expands in the
lateral y and z directions. Using the average positions of the atoms located inside the wire and
neglecting those located at the ends we obtained the lattice parameters, \( a = 4.884/\sqrt{2} = 3.454 \text{ Å} \),
and \( c = 2.724 \text{ Å} \) of the Pd wire of BCT crystal structure. We should notice that the lattice
parameter of the original FCC, Pd wire is 3.95 Å.

The driving force for the FCC to BCT phase transformation in nanowires is the
compressive stress in the interior of the wire induced by the tensile surface stress. The magnitude
of the induced longitudinal compressive stress, estimated based on a continuum model, is
approximately given by \( \sigma = -4f/l/A \), where \( f \) is the surface stress component on the
\{100\}wire surfaces in the initial fcc <100>/<100> configuration, \( l \) is the width of the nanowire
and \( A \) is the cross section area [10]. Given that the surface stress is of the same order of
magnitude as the surface energy, i.e. $f = 1\text{J/m}^2$, the magnitude of the induced compressive stress increases significantly with the decrease of wire diameter and can reach GPa values in nanowires. Consequently the internal stress alone can drive crystallographic phase transformations and/or structural reorientations that can lead to lower energy states when the wire diameters are below certain critical values in the nanometer range. To understand the role a

Figure 5.2 The unrelaxed and relaxed configurations of wire and the cross sections of FCC and BCT nanowires, observed from x, y and z directions respectively, atoms in two adjacent crystalline planes are shown in different colors.
wire diameter on the structural stability of Pd nanowires we have extended our MD simulations to nanowires of various cross-sectional areas. Wires of both larger and smaller diameters were investigated. Our MD simulations of FCC, initially \(<100>\) oriented, Pd nanowires of \(2.57 \text{ nm} \times 2.57 \text{ nm}\) cross-sectional areas did not show the FCC to BCT phase transformation at 100K. Instead, the wire maintained the FCC crystal structure and experienced a lattice reorientation transformation from the \(<100>\) axis orientation and \(\{100\}\) side surfaces [the so called \(<100>/{\{100}\}\) nanowire] to the \(<110>\) axis orientation and \(\{111\}\) side surfaces \([<110>/{\{111}\}\text{ nanowire}]\). Similar lattice reorientations were also observed in Au, Cu and Ni nanowires [12,13].

5.3 Mechanical Behavior

After the completion of the spontaneous FCC to BCT phase transformation in the \(1.78 \text{ nm} \times 1.78 \text{ nm}\) nanowire, the BCT wire was loaded in the longitudinal direction to investigate the pseudoelastic behavior. Both tensile loading and unloading studies were conducted under simulated quasistatic conditions. Namely, in each load step the coordinates of all atoms were modified according to a prescribed uniform strain increment of 0.125\% in the length direction. To allow the wire to reach local microscopic equilibration, after each straining step the wire was relaxed for 15ps at 100K holding the wire ends at fixed positions consistent with the newly prescribed wire length. The relaxation process usually takes less than 10ps and the stress evaluated and averaged over the subsequent 5ps was taken as actual stress in the wire at the corresponding strain state. The unloading process followed a similar protocol with a strain decrement of -0.125\% at each unloading step. Figure 5.3 shows the dynamic progression of the BCT wire under tensile loading at 100K. Upon loading the wire transforms back to the original FCC crystal structure via a phase change mechanism mediated by short range atomic rearrangements that nucleate at the ends and propagate toward the center of the wire.
Figure 5.3 The dynamic progression of the phase transformation of nanowire under loading at 100K, snap shots of nanowire at strain of 0.125%, 6.6%, 15.4%, 36.8% and 44.1% are shown respectively.

Figure 5.4 shows the stress-strain curve of the BCT/FCC wires during loading and unloading at 100K. The curves indicate that the Pd wire is very ductile with fracture strains of approximately 50%. Along the loading part of the stress-strain curve one can identify the following stages:

i) During the stage delimited by points O and A on the loading curve the wire maintains its BCT crystalline structure while undergoing elastic straining.

ii) When the tensile stress reaches 7.5 GPa, corresponding to point A on the curve, the nucleation of the FCC phase starts at the ends of the wire. The subsequent motion of the newly nucleated FCC regions marks the beginning of the BCT to FCC phase transformation; process which is also associated with a sudden drop of the applied stress from 7.5GPa to approximately 3.5 GPa.
iii) Between points B and C the linear portion of the curve corresponds to wire elongation caused by the steady advance of the BCT to FCC phase change from the ends toward the center of the wire. At point C the entire wire has been converted to the FCC structure.

iv) The portion between C and D corresponds to the elastic linear stretching of the new FCC wire.

v) Further loading beyond point D at a stress level exceeding 8.2 GPa, causes the FCC wire to neck and ultimately to fracture at point E.
One can quantify the overall straining by using the following equation: the total strain = elastic strain of the BCT wire + plastic strain due to BCT to FCC phase change + elastic strain of the FCC wire = 5.6% + 38.5% + 6.1% = 50.2%.

5.4 Pseudoelasticity and Shape Memory Effect

The 1.78 nm × 1.78 nm fcc wire transforms spontaneously back to the 2.196 nm × 2.196 nm BCT configuration via phase change mediated by short range atomic rearrangement processes in reverse to what is described above when the temperature is above a certain value. The reversible FCC to BCT phase transformation results from a cooperative and collective motion of atoms over distances smaller than a lattice parameter in the absence of any diffusive processes. The absence of diffusion renders the FCC to BCT phase transformation almost instantaneous. These characteristics are similar to those present in traditional shape memory alloys (SMA) that commonly involve austenite to martensite phase transformation. The curve depicted in red in figure 5.4 traces the stress-strain relationship during the controlled simulated quasistatic unloading of the FCC wire. Similar to the behavior of traditional bulk shape memory alloys, the reversible phase change in Pd nanowire has temperature dependence. The spontaneous FCC to BCT phase change in both 1.78 nm × 1.78 nm and 2.18 nm × 2.18 nm wires happens only when the temperature is above a critical value Tc. If the temperature is below Tc, the FCC wire configuration is stable. However, when heated above Tc, the wire spontaneously transform to BCT structures. Our MD simulations indicate that the critical temperature Tc, for the Pd nanowire investigated is around 22.5K.

Since the crystal lattice of BCT phase has lower symmetry than that of parent FCC phase, several variants of BCT phase can be expected to be formed from the same parent FCC phase
which will affect the value of inelastic strain due to this phase transformation. Diao et al [8] reported that two BCT phases with different lattice parameters were observed driven by surface stress using MD simulation in gold nanowires. However, we did not observe any variants of BCT phase in this work.

5.4.1 Similarities and Differences in Structural Reorientation and Phase Transformation Processes

Figure 5.5 comparison of stress-strain curve for 1.78 nm × 1.78 nm (a) and 2.57 nm × 2.57 nm (b) nanowire under quasistatic loading and unloading.

The pseudoelastic strain associated with the BCT to FCC phase transformation can be evaluated simply by using the lattice parameters for the BCT and FCC structures as follows: 

\[ \varepsilon_{\text{BCT} \rightarrow \text{FCC}} = \frac{(c_{\text{BCT}} - a_{\text{FCC}})}{c_{\text{BCT}}} \approx 44.8\% \]. This strain is indeed consistent with our MD simulation results obtained from the stress-strain curve upon quasistatic loading. There are two observations that are worth making here: i) the pseudoelastic strain associated with the <110>/<{111}> to <100>/<{100}> lattice reorientation process (see Chapter 4) is an attribute of the FCC crystal structure and it is independent of the actual lattice parameter; therefore it is the same for all FCC materials, ii) the pseudoelastic strain associated with the FCC to BCT phase transformation is
function on the lattice parameters of the corresponding FCC and BCT structures and it therefore varies across the family of the FCC metals.

Figure 5.5 shows side by side the strain-stress curves obtained during loading and unloading of two wires of different cross sectional showing pseudoelastic behavior mediated by the two mechanisms: BCT to FCC lattice reorientation and crystal structure reorientation. Comparison of the two stress-strain curves (Figure 5.5), quantifying the two pseudoelastic behaviors, indicate that there are both similarities and differences between the two systems. Namely, although both transformations can achieve similar levels of strains they differ qualitatively and quantitatively in the plateau regions. While the loading stress-strain curve for the lattice reorientation-controlled pseudoelastic behavior exhibits a small strain hardening over the range of strains delimited by the begin and the end stage of the reorientation process, see Figure 5.5 (b), no such phenomena is observed on the corresponding portion of the stress-strain curve for the FCC to BCT phase transformation-controlled pseudoelastic behavior, see Figure 5.5 (a). Moreover, although in both mechanisms the deformations are fully recovered when the stress is reduced to zero, there are major differences between the two stress-strain curves during the unloading stage. While for the FCC to BCT phase transformation-controlled pseudoelastic behavior the loading and the unloading stress-strain curves follow almost the same path (Figure 5.5 (a)) for the lattice reorientation-controlled pseudoelastic behavior the loading and unloading paths form a well defined hysteresis loop (Figure 5.5 (b)). The differences between the stress-strain curves depicted in figures 5.5 are due to the major differences between the mechanisms mediating the two pseudoelastic behaviors. Both strain hardening and hysteresis loop are the products of repetitive nucleation, gliding, and annihilation of Shockley partial dislocations; processes that are intricate components of the lattice reorientation mechanism.
Figure 5.6 Stress-strain response during quasistatic loading of both 1.78 nm × 1.78 nm and 2.18 nm × 2.18 nm Pd wires (the dotted lines indicated the plateau stresses during the BCT to FCC phase transformation).

The magnitude of the induced longitudinal compressive stress, estimated based on a continuum model, is approximately given by $\sigma = -4fl/A$, where $f$ is the surface stress component on the {100} wire surfaces in the initial fcc <100>/<100> configuration, $l$ is the width of the wire, and $A$ is the cross section area [9]. Figure 5.6 shows the stress-strain curves for both 1.78 nm × 1.78 nm and 2.18 nm × 2.18 nm wires during quasistatic loading at 100K. The stress plateaus delimited by the beginning and the end of the reversible BCT to FCC phase transformation.
transformation (i.e., the region of the stress-strain curve between 0.05 and 0.45 strain values) are approximately 3.50 GPa and 2.82 GPa respectively. The ratio of these two stress values 3.50/2.82=1.24 is approximately equal to the inverse ratio 2.18/1.78 = 1.22, of the corresponding nanowires widths.

5.5 Chapter Summary

In summary, we have shown that the surface stress can cause palladium nanowires to undergo spontaneous phase transformation from FCC to BCT structure when the initial wires cross-sectional areas are below 2.18 nm × 2.18 nm. Moreover, under tensile loading and unloading Pd nanowires transform reversibly between the two crystalline structures exhibiting a novel pseudoelastic behavior characterized by fully recoverable strains of up to 50%. The temperature-dependence of this pseudoelastic behavior enables the shape memory effect in Pd nanowires. These novel properties can greatly impact nanowires usage in a large class of nanodevices including sensors, actuators and transducers.

5.6 References


CHAPTER 6

SPONTANEOUS SELF-ROLLING OF Al (100)/(111) BILAYER NANOFIMS INTO NANOTUBES AND NANOCOILS

6.1 Introduction

Nanostructure design and control have attracted a great deal of attention in recent years. Various nanostructures have been successfully fabricated in bulk or grown on surfaces by self-assembly processes [1, 2]. However, given the complexity and the limited level of control associated with these processes there is a strong need for the development of alternative nanofabrication techniques with a higher degree of control over both sizes and geometries of the nanostructures and which are applicable to a wider class of materials. Recently, Prinz et al.[3, 4] introduced a self-rolling procedure for fabrication of tubes (with radii varying from a few nanometers to several microns) starting from strained semiconductor double layer heterostructures freed from their substrate by a selective etching procedure. Subsequently, this technique was extended to a wide range of materials by appropriately choosing the deposition methodology, the selective etchant, and ensuring the existence of a certain elastic straining in the nanotube material grown on the chosen substrate [5, 6]. The self-bending mechanism of semiconductor heterostructures has been investigated by direct atomistic simulations [7] and continuum theories [8]. The driving force for nanofilms self-bending comes from various sources such as: elastic misfit strain between the constituents of the bilayer nanostructures, the asymmetry in the surface stress caused by molecular adsorption or as result of surface
reconstruction. In a recent atomistic simulation study Zang et al. [9] have demonstrated that ultrathin Si and Ge nanofilms of certain thicknesses may self-bend even in the absence of an external stress, under their own intrinsic surface stress imbalance.

It is well established that when at least one of the spatial dimensions of systems are in the nanometer range (i.e., nanofilms or nanowires), the structural characteristics and stability are strongly influenced by both surface energy and surface stress [10]. In many metallic FCC films when the film thickness is reduced to just a few atomic layers, the (001) oriented films spontaneously transform into the (111) orientation [11]. Recent molecular dynamics simulation studies have demonstrated that (001) to (111) crystalline reorientations in nanometer thin films are generic and representative for a larger class of FCC metals and occur at relatively low temperatures even in the presence of fixed (001) oriented borders that constrain changes in the nanometer thin region [12].

In this chapter we present our MD simulation results which document that in FCC metals the (001) to (111) crystal structure reorientation also occurs when the nanometer thick (001) film rests on a (111) oriented substrate. Moreover, if the (111) film is only a few nanometers thick the spontaneous reorientation of the (001) top layer leads to rolling-up of the initially planar free standing, (001)/(111) bilayer into a tubular or coiled structure. The driving force for this process is given by the existence of an initial mismatch strain between the two nanometer thick layers of different textures. Our detailed analysis of the reorientation process indicate that the bilayer self-rolling is determined by both energetic and kinetic processes characterizing the spontaneous structural reorientation of the top (001) textured layer to the (111) orientation of the substrate layer. Specifically, the analysis of the simulation results indicate that reorientation of the (001) top layer proceeds via a mechanism characterized by nucleation from multiple sites, propagation, and growth of the new (111) oriented domains embedded in the original (001) oriented layer.
While individually the newly formed (111) domains grow free of defects a region containing a surface dislocation like linear defect forms at the boundary where two such domains meet. The equilibrium of the newly formed bilayer structure containing the surface dislocations is attained by multiple localized bendings of the bilayer structure about the direction coinciding with the dislocations line (the [110] direction). The spacing (density) of the nucleation is a function of temperature and influence the radius of curvature of the resulting structure.

6.2 Initial Structure and Simulation Methodology

The MD simulations were performed using the embedded-atom method (EAM) potential for Al [13]. Two single crystalline Al nanofilms were created computationally by “slicing” the rectangular slabs of atoms from single-crystalline bulk Al perpendicular to the [101], [110], and [001] directions to generate the (001) surface oriented film and to the [101], [112], and [111] directions respectively, to generate the (111) oriented film. The films were cut from the bulk single crystal that was previously allowed to undergo relaxation consistent with the simulated temperature. The initial (001)/(111) bilayer structures were generated by pairing the two films along the common, in-plane, [101] direction (see Figures 6.1). To investigate the roles of bilayers geometrical characteristics and the relative orientation of the bilayer edges with respect to the [101] direction we carried out MD simulations of Al bilayer structures of various film thicknesses, surface areas, and slab orientations. As explained in the text and indicated schematically in Figures 6.1(a) and 6.1(b), when the common [101] direction in the initial structure is chosen parallel to one of the edges of the rectangular-shaped bilayer the film rolls-up into a tubular structure whereas when this direction is tilted with respect to the orientation of the shortest edge of the bilayer a coiled structure is obtained. The in-plane dimensions of the
rectangular bilayer structures investigated were 16.2 nm x 32.4 nm and 4.2 nm x 60 nm respectively (the narrow films were chosen to obtain coiled structures). The thickness of the initial (001)/(111) bilayer structure was varied by changing the number of atomic layers in the (001) and (111) oriented slabs comprising the initial structure. Specifically, structures with 2x2, 3x3, 4x4, 5x5, and 6x6 atomic layers were investigated. Free boundary conditions were used in all directions.

Figure 6.1 Representation of the (100)/(111) Al bilayer nanofilm showing the process of spontaneous self-rolling of the initial planar film into: (a) a nanotube when the initial orientation of the common [110] in-plane direction (the rolling direction) is parallel to the edge of the bilayer slab or (b) a nanocoil when the rolling direction makes an angle with the orientation of the bilayer slab edge. Each of the two rectangular films comprising the initial bilayer structure consists of two atomic layers having the (100) respectively (111) surface orientation. The lattice orientations of the two slabs comprising the bilayer of figure (a) are indicated explicitly. The self-rolling process occurs spontaneously and it is completed in a few hundreds picoseconds provided the temperature is larger a critical value, which for 2x2 atomic layers thick slab is 30K.
6.3 Simulation Results

We present first the simulation results of the systems in which the common $[\bar{T}10]$ direction in the initial (001)/(111) bilayer structure is chosen parallel to the short edge of the rectangular-shaped bilayer; initial configuration that leads to rolling-up of the bilayer structure into a tubular structure.

Figure 6.2 Representation of the very early stage of the (001) to (111) reorientation process of the (001) top layer of the bilayer (001)/(111) rectangular slab. (a) Depiction of the nucleation of (111) oriented regions in the (001) oriented top layer. (b) Depiction of the early stage of film bending.

As indicated in figure 6.2 the surface reconstruction of the (100) oriented top layer in the $2 \times 2$ (001)/(111) bilayer structure is indeed initiated at very low temperature, about 30-50K. Moreover, we can see that the nucleation of the (111) phase starts at various sites along the edge, of the initially (100) oriented top layer, that is parallel to the $[110]$ direction and propagate along the perpendicular $[\bar{T}10]$ direction (the direction which the same for the (111) oriented the substrate layer). Close inspection of the reconstructed top layer indicate that the newly formed (111) domains grow free of defects. However at the boundary where two such domains meet a region containing a surface dislocation-like linear defect forms. The equilibrium of the newly formed bilayer structure containing the surface dislocations is attained by multiple localized...
bendings of the bilayer structure about the direction coinciding with the dislocations line (the [110] direction). The spacing (density) of the nucleation is a function of temperature and influence the radius of curvature of the resulting structure. When the entire top (100) oriented film transforms into a denser (111) film the bilayer structure folds up into a nanotube, occasionally exhibiting some overlap at two ends.

Figure 6.3 The spontaneous formed nanotubes from the (001)/(111) bilayer structures with (a) 2x2 and (b) 3x3 respectively initial bilayer thicknesses.

When the thickness of initial bilayer structure is increased from 2 x 2 (001)/(111) layered structure to a 3 x 3 (001)/(111) layered structure, the critical temperature at which the (001) to (111) reorientation starts increases from 30K to 90K. Figures 6.3 (a) and (b) shows the spontaneous self rolled up nanotubes; the corresponding geometrical characteristics are also indicated.

The cross section analysis of the formed tubes indicates that the radii of the tubes are not uniform. Instead, we found that the cross section of tube consists of several line segments as shown schematically in figure 6.4. Each line segment, of length $L_i$, is straight and starts and ends
at transition regions called bending regions. The bending angles between two segments meeting at the same defective region take values between $15^\circ$ and $55^\circ$ and are function of the length of both segments delimiting the corresponding angle.

![Diagram](image)

Figure 6.4 Cross sectional representation of a self rolled metallic nanotube from an initial planar (001)/(111) bilayer film structure. (a) The illustration of segmented circumference of the nanotube. (b) Depiction of the characteristic structure of a typical defective region that mediates the bending of the initial planar bilayer structure.

The values of bending angles $\theta_i$ and the length of the line segments $L_i$ are actually closely relate to the average radius of the formed nanotube. We calculated the bending angles and the length of each line segment form the relative arrangement of atoms in the formed tubes, shown in histograms (see Figure 6.5 and 6.6). From Figures 6.5 and 6.6 we infer that both the bending angles and segments lengths are distributed non-uniformly along the circumference of the nanotubes. Moreover, one can see that the larger the value of the bending angle the larger the average length of the two adjacent segments (see Figure 6.7). This result is consistent with misfit strain induced bending mechanism of bilayer film, namely, the larger length of line segment, the more shrinkage of from (100) thin film, thus leading to the larger bending angle.
Figure 6.5 Histograms showing the bending angles and length of line segments characterizing the cross sectional conformation of nanotube obtained from spontaneous self assembly from a 2 x 2 (001)/(111) bilayer structure.

Figure 6.6 Histograms showing the bending angles and length of line segments characterizing the cross sectional conformation of nanotube obtained from spontaneous self assembly from a 3 x 3 (001)/(111) bilayer structure.

Using a similar approach to that outlined previously we estimated the radii of the formed metallic nanotubes. For an initial 2 x 2 (001)/(111) bilayer the radius of tube is about 5.48 nm when the simulation temperature is just above the critical temperature for spontaneous bilayer bending, Tc=50 K. When the initial structure is 3 x 3 (001)/(111) bilayer film the radius of the tube formed is about 6.63 nm at the increased simulation temperature of 100K which just above
the new critical temperature, $T_c=90$K, for spontaneous bilayer bending. Our simulations indicate that increase of the thickness of the initial bilayer structure leads to an increase of the critical temperature for spontaneous bilayer self-rolling. We found this critical temperature to be about 350K for an 4 $\times$ 4 (001)/(111) bilayer structure.

Figure 6.7 Representation of length segment versus average bending angle characterizing the cross sectional conformation of nanotube obtained from spontaneous self assembly from a 3 $\times$ 3 (001)/(111) bilayer structure.

The dependence of the radius of self rolled-up nanotube on initial bilayer thickness is represented in figure 6.8. Interestingly Figure 6.8 show that the radius of the tube increases from 5.5 nm to 62 nm when the thickness of the bilayer structure is increased from about 0.9nm (for the 2 $\times$ 2 bilayer) to 2.8 nm (4 $\times$ 4 bilayer). We should mention that the values of tube radii shown in figure 6.8 are obtained from simulations of the bilayer structures at different temperatures; i.e., larger than the corresponding critical temperatures for various initial bilayer thicknesses.
We also analyzed the effect of temperature on the radius of formed nanotubes. Figure 6.9 shows the radius of self-rolled-up nanotubes as a function of simulation temperature for the

![Figure 6.8 Radii of self-rolled-up nanotubes as function of the thickness, h, of the initial (001)/(111) bilayer structure.](image)

![Figure 6.9 Radii of self-rolled-up nanotubes as function temperature for an initial 2x 2 (001)/(111) bilayer structure.](image)
initial 2x2 (001)/(111) bilayer structure. We can see from this figure that the radius of tube decreases as the increasing of simulation temperature. At the critical temperature about 50K, the radius of the rolled-up tube is around 5.5nm, however, when the temperature is increased to 150K, the radius of the formed tube decreases to about 3.8nm. One can rationalize the temperature dependence of the nanotube formed by inferring the mechanism of self-rolling of the initial bilayer structure. Specifically, as indicated previously the larger the temperature the higher the density of the initial nucleation centers for the (001) to (111) reorientations (see Figure 6.2) this in turns leads to a larger number of straight segments the rolled-up structure is composed of. The larger number of segments translates into smaller diameters of the final structures.

Figure 6.10 The spontaneous formed nanocoils from the (001)/(111) bilayer structures with (a) 2x2 and (b) 3x3 respectively initial bilayer thicknesses.

We extend the previously developed nanotube formation technique to fabrication for more complex three dimensional objects using a merely geometric approach. The essence of the
approach is the following. Obviously, the geometry of the initial plane area determines the sites at which the rolling process is initiated and terminated; this predetermines the rolling directions suitable for rolling more complicated objects. If the edges of the rectangular (100)/(111) bilayer initial structure are tilted with respect to with the [\(\overline{1}10\)] common bending direction the bilayer film strip will roll up into a nanocoil structure (see Figure 6.10). By changing the tilt angle one can form a series of nano-helical structures with different chiralities.

In this study we have demonstrated a new technique for fabricating pure metallic nanotubes by self-rolling process from the initial bi-layer thin film with different textures on the top and bottom respectively. Both the thickness and simulation temperature affect the radius of self-rolled up nanotubes. Based on the simulation results we proposed a defect mediated bending mechanism. This new technique also allows us to form more complicated three dimensional nanostructures such as nanocoils. The fabrication of a variety of nanostructures through the fabrication technique may offer novel device opportunities.

6.4 Chapter Summary

We report molecular dynamics simulation studies presenting a method for forming metallic nanotubes and nanocoils via spontaneous self rolling-up of initially planar free standing (001)/(111) bilayer nanofilms. Our detailed analysis of the reorientation process indicate that the bilayer self-rolling is determined by both energetic and kinetic processes characterizing the spontaneous structural reorientation of the top (001) textured layer to the (111) orientation of the substrate layer. Specifically, the analysis of the simulation results indicate that reorientation of the (001) top layer proceeds via a mechanism characterized by nucleation from multiple sites, propagation and growth of the new (111) oriented domains embedded in the original (001) oriented layer. While individually the newly formed (111) domains grow free of defects a region
containing a surface dislocation like linear defect forms at the boundary where two such domains meet. The equilibrium of the newly formed bilayer structure containing the surface dislocations is attained by multiple localized bendings of the bilayer structure about the direction coinciding with the dislocations line (the [110] direction). The spacing (density) of the nucleation is a function of temperature and influence the radius of curvature of the resulting structure. The radii of the resulting structures are determined by bilayers thickness and temperature. Thus, we demonstrate the feasibility of a new design methodology for nanofabrication of metallic nanotubes and nanocoils.

6.5 References


APPENDIX: NUMERICAL VERSION OF EMBEDDED ATOM METHOD POTENTIAL FOR PD

The following is part of the numerical version of embedded atom method potential for Pd (so-called potential file) used in molecular dynamics simulations. The first four lines of the file define some parameters used in simulation. These parameters include lattice parameter, mass of atom, cut-off radius and type of atom etc. The main body of potential file shows the value of the embedding term $F_i(\bar{\rho}_i)$ and the electron density term $\rho_i$ up to second derivative.

```
  0   1   0   9   1   1
4.509018036072117D-05  2.200963972906085D-04  0.1000000000000000
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VITA

Jijun Lao was born in Ningbo, Zhejiang, China in December 1978. He earned his bachelor’s and master’s degrees in materials science from Shanghai Jiaotong University, Shanghai, China, in 2001 respectively 2004. After spending one year in industry working as a process engineer in a semiconductor manufacturing company in Shanghai, he joined, in January 2005, the doctoral program in the Department of Mechanical Engineering at Louisiana State University.

His professional publication include:


At the May 2011 commencement, he will receive the degree of Doctor of Philosophy.