Chapter 1

Introduction

A new field, called *Nanotechnology*, was developed very recently in science and technology. Nanotechnology is the creation of new materials and devices at the molecular level-phenomena associated with atomic and molecular interactions strongly influence macroscopic materials properties; with significantly improved mechanical, optical, chemical, electrical, etc. characterizations. The main idea behind nanotechnology is to control and/or engineer the structure and physical/chemical or biological properties of materials on the nanometer-(atomic-) scale. Nanotechnology is much attracting attention and is expected to have a profound impact on our economy and to have the most promising potential for future technology development, including the mechanics of *Nanoelectronic*, *Nanobiology*, *Nanomaterial*, *Nanomechanical* and *Nanotribology* etc. In the schematic picture in Fig.1-1 the classifications in nanotechnology field is shown.

The ongoing miniaturization of electronic and mechanical devices has led to an interest in the generation of nanometer-sized structures on surfaces. With the scaledown in dimensions of very large scale integration devices to the nanometer region, a concurrent interest has developed in the possible use of proximal probes as

tools for the fabrication of electronic devices on nanometer-scale. New measurements tools are required in the rapidly burgeoning field of nanotechnology; therefore, the viability of *Scanning Probe Microscopes* (SPMs) techniques as tool for the fabrication of nanometer-scale structures on surfaces are beginning to make possible the long-standing goal of nanometer-scale mechanical and electronic devices. The focus will be primarily on the mechanisms that determines the precision and limitations of nanofabrication technology with an emphasis on those techniques in use for the fabrication of nanostructures. Nevertheless, this technology has severe limitations in terms of throughput and reproducibility during fabrication. To meet these challenges in nanodevices development and manufacturing not only new novelty in engineering are needed, but the thorough understanding of responsible for the characterizations and the nanostructures fabricated of materials is required.

Recently, there has been increasing interest in nanometer-object-based devices including *Single-electron Transistor* (SET), quantum dot/wire systems etc. These devices are notable for a number of unique features and capabilities such as charge carrier spectrum quantization, amplification and transformation of very weak signals, low dimensionality and extremely low energy consumption, which makes them the objects of choice for elements of further-generation ICs and electronic devices. To ensure stability of performance at room temperature, such devices have to be around 10nm in size. This problem has been solved successfully in the growth of vertical structures by using *Molecular Beam Epitaxy* and *Metal-Organic Chemical-Vapor Deposition* methods, currently in widely use. Nevertheless, fabrication of horizontal structures in the planar technology involves many difficulties related to such low dimensionality.

Progress in semiconductor nanofabrication technology has generated tremendous interest in physics, electronic, chemistry and their interdisciplinary fields. In particular, *Atomic Force Microscope* (AFM) is a powerful experimental technique for

nanofabrication because it can operate on insulating as well as conductive surfaces and has proven to be successful in imaging surfaces at an atomic level. Examples of AFM nanofabrication include that *Tip-induced Local Surface Reaction* [1-2], *Dip-pen Nanolithography* [3-4] and *Nanografting* [5-6]. Among them, local oxidation or field-induced oxidation of metallic, semiconductors and organic surfaces by AFM has established itself as a robust, reliable and versatile lithographic method for the fabrication of nanostructures and nanodevices [7-11]. In scanning probe-based oxidation, a water meniscus provides both the chemical species (oxyanions) and the spatial confinement for the anodic oxidation of a nanometer-scale region of sample surface [12]. The process is rather general because many different materials and/or surfaces have been patterned, such as semiconductors [3, 7, 12], metals [8, 13-14], dielectrics [15] and polymers [9] etc. Furthermore, local oxidation can be scaled up by using stamps with multiple nanometer-scale protrusions [16].

A more attractive feature of AFM, however, in my opinion, is high-precision probe positioning, which enables the imaging of a surface structure, selection of a desired area and activation of a probe at a specified point, to be accomplished all in one experiment. In this way it is possible to make contacts to individual quantum dots or nanoislands, or to further develop locally a planar structure on various sample surfaces by means of AFM techniques. For optimal AFM anodic oxidation processing of nanodevices, it is essential to understand the mechanisms and kinetics of the process so that the diagnostics can be reliably controlled.

Taking into account that studying of the mechanical characteristics of materials on the nanoscale has been motivated by increasing need for small-scale materials featuring, miniaturization of engineering electronic components and, furthering development of nanostructured materials, thin films technology and surface science.

Herein, information about mechanical characterizations on the nanoscale is needed. In the design of micro/nanodevices, mechanical characterizations are essential since most mechanical characterizations are known to exhibit a dependence on sample size [17]. Knowledge of the mechanical properties such as elastic modulus, strain and adhesion is critical to successful development of new films and nanoscale assemblies. Such information is also needed to assess integrity or reliability in applications from micro/nanoelectronics to biotechnology. The demand for nanomechanical information is fuelled by the fact that applications often involve multiple materials integrated in the micro- or nanoscale (e.g., composites).

Nanomechanical behaviors of materials have gained considerable attentions because of the ever-shrinking dimensions of thin film materials in nanoelectronics, data storage and electromechanical sensors/actuators and, also the advancements in bulk nanostructured materials. Mechanical properties of materials are influenced by their length-scales. Recent developments in science and engineering have advanced the capability to fabricate and control structures on the scale of micro/nanometers. This presents a whole new spectrum of opportunities to build micro/nanoscale structures and devices and, brings problems of material behaviors on the micro/nanoscale into the domain of engineering. A precisely property of the mechanical characterizations of these micro/nanostructures is required to use them as structural/functional elements in the micro/nanodevices. Mechanical and structural aspects are of critical importance in determining the long-term stability of such small structures. Presently, many potential applications for micro/nanoscale structures are not really practical because their mechanical characterizations have not been explored completely [17-18]. The extremely small dimensions of micro/nanostructures impose a tremendous challenge for experimental study of their mechanical properties and reliability. An accurate approach for measuring the mechanical properties of

nanostructures is direct *NANOINDENTATION*. This *Nanoindenter/AFM* combination provides the “eyes”, “hands” and “tools” for imaging, characterizing, manipulating and machining the structures, fulfilling the dream of manufacturing on the nanometer-scale. *Nanoindentation* is now routinely used as a means of measurement of the mechanical properties of thin films and small volumes of materials [19-20]. The technique is useful to establish a connection between the atomic-scale processes during the indentation and the measurable mechanical properties. The usual mechanical properties that are evaluated during nanoindentation are the hardness and Young’s modulus of the materials. These are obtained from an analysis of the dynamics relationships between the applied indentation load and the penetration depth. An advantage of the technique is that it can be used to image and locate the material and then *in-situ* indents the material with the same indenter tip. The method has many potential applications for examining nanomechanical properties of (ultra)small areas and thin films. The probe size can be controlled by adjusting the load applied to the indenter, and very low-load ranges have become available so that formation of cracks during the tests can be avoided.

Better understanding of the mechanics associated with the contact of small volume becomes increasingly important from both scientific and technological viewpoints. SPM and related microscopes have been demonstrated as tools for fabricating nanostructures — a top-down approach to nanotechnology. To overcome the present limitations in nanofabrication and the future problems with working nanomachines, it is essential to understand the underlying atomistic phenomena associated with material modification at the nanometer-scale. The whole theoretical analysis methodology is illustrated in Fig.1-2. Materials properties are affected by structures with a variety of length-scales, from 10^{-10} to 10^{-2} meters and undergo dynamic

processes with a range of time scales from 10^{-15} to 10^{7} seconds. Clearly, computer simulations cannot fully describe such systems. They can, however, probe a range of length and time scales inaccessible to experiments. Computer simulations are an important bridge between theoretical and experimental investigations. In order to be tractable, theoretical models are simplified by resorting to limiting assumptions. These assumptions often eliminate details from the model necessary for the theory to be compared in a meaningful fashion with experimental data. Experimental studies also suffer from intrinsic limitations, including technological limitations as well as more fundamental limitations. It is often difficult or impossible to measure a single quantity or set of quantities that can be compared to a theoretical model. Computer simulations, while suffering from limitations of their own, can often bridge this gap.

Computer simulations are interesting for several reasons. First of all, they could be considered as a necessary complement of experiments. For example, in the microscopy experiments, it is sometimes difficult to interpret directly the images. Second, computer simulations allow us to explore easily a large range of system configurations, even for usually or extreme conditions. For example, properties of matter under very high pressures or high temperatures, what occur inside notable objects, can only be investigated with modeling. Finally, another advantage of simulations is prediction. Fast and cheap calculations could be carried out to test ideas about materials or processes, before building an expensive experiment.

At the macroscopic level, we know that the solid properties are well described by a continuum description and classical mechanics, if we exclude specific phenomena where quantum properties manifest themselves at this scale. Finite element techniques are widely used for performing such calculations. At the other extreme, the atomic level, a continuum description of the matter is inadequate and, each atom must be considered as a definite entity, in the so-called atomistic approach. Also, quantum

mechanics should be considered and simulations should be done with first principles methods for example, allowing a very accurate description of the matter properties. Nevertheless, only nanoscopic systems with less than about thousand atoms can be currently considered, even using the most powerful supercomputers, because of the tremendous difficulty to solve the Schrödinger equation for large systems. Obviously, there is a need for an intermediate description between the classical continuum and the quantum atomistic approaches, able to deal with systems whose characteristic dimensions are up to few tens of nanometers (i.e. about 10^6 atoms). This class of techniques exists and is commonly called “classical potential” or “atomistic” methods. They combine a classical mechanics approach with an atomistic description of the system. These methods cannot model explicit quantum properties. Nevertheless, the quantum contributions responsible for the atomic cohesion are implicitly included in the interatomic potentials. Thus, typical applications in materials science focus on the atomic structures of specific systems: extended (dislocations) or localized (vacancies) defects, surfaces, interfaces and etc. This approach allows the description of the atomic properties in a large number of physical problems, as well as a very good scalability of the needed computational power with the system size.

The use of simulation methods such as *Molecular Dynamics* (MD) simulations with good quality interatomic potentials can be helpful in analyzing data and extracting reliable information. MD simulations, by virtue of their high temporal and spatial resolutions, offer a novel approach to gain insights into the understanding of atomistic processes and mechanisms. Recently, a remarkable enhancement in computational capability and high-performance computation techniques has enabled researchers to employ computer simulations to investigate the nanoindentation processes and gain significant insights into atomistic behaviors of metals [21-22], ceramics [23] and semiconductors [24-25]. Herein, in this dissertation, we investigate the deformation of

III-V semiconductor (GaAs) during nanoindentation with the aid of MD simulations using a rigid tip, based on a local deformed diagnostic, to identify and characterize the plastic deformation during nanoindentation processes. The advantage of the MD simulations is that provides possible theoretical evidence of the transition from elastic to plastic behavior in the experiments and enables us to better understand the mechanisms involved in such small area during the nanoindentation process. Clearly MD simulations and experimental details can be mutually beneficial.

§ Aim of this present study

First part of this dissertation

Nanotechnologies have attracted the attention of many research groups. One of the most important targets of nanotechnology research is the construction of nanosized electronic devices. To achieve this goal, advances in nanometer-scale manipulation of semiconductor surfaces is essential. It is difficult is to modify semiconductor surfaces on a nanometer-scale by optical or electron beam lithography but *Scanning Probe Lithography* (SPL) is considered to be a promising tool for solving this difficulty.

AFM tip-induced local oxidation is a promising tool for the fabrication of nanometer-scale structures and devices. Nevertheless, little information is available on the chemical, structural and mechanical properties of the grown oxides. In the first part of this thesis, we report on the AFM nanooxidation mechanisms of *p*-GaAs(100) surface and, nanofabrication of oxide dots, wires and bumps pattern on the GaAs surface. To understand the factors that control the spatial resolution, we investigated the effects and mechanisms of the anodization voltages, the anodization times and the relative humidity on the fabricated patterns. As well, the electrical properties of a GaAs surface modified by an AFM have been measured.

Second part of this dissertation

Nanoindentation tests have been widely used to measure the mechanical properties of materials. The load-displacement curves obtained by *Depth-sensing Indentation* (DSI) are the characteristics of materials. Accurate determination of mechanical properties from the load-displacement curve demands a full comprehension of the indentation

behavior of the material, such as, how the load-displacement curve is related to the mechanical properties of materials, and how the deformation behavior is influenced by the variation of the mechanical properties.

Basic recognizing of the material characterizations requires knowledge on a microscopic level of the underlying energetic and interaction mechanism. In most situations, this knowledge is not accessible by experimental tools and the problem is too complex to be treated by analytical theories. In these situations, which include the majority of material systems and phenomena, the use of computer-based methods is unavoidable. Growth in computer power is allowing systems of increasing complexity to be investigated and, refinements in interatomic potentials are leading to greater precision in the calculations. In this study, we use *Molecular Dynamics Simulations* to model the indentation-induced plastic deformation processes of GaAs (zincblende structure) on the nanometer-scale. At the origin was the intention to recognize how these semiconductors reflected in thermodynamic, structural and dynamic properties of such semiconductor. The availability of the microscopic information (atomic positions and velocities) makes possible the direct calculation of these properties.

The motivation here is to identify deformation mechanisms. In this regard Berkovich indentation used in this study has been favored since; in this case, the stress field is more uniformly distributed under the indenter and, hence analysis is more straightforward. We report the results of nanoindentation measurements on *Si*, *Ge*, *GaAs*, *GaSb*, *InP* and *GaN*-based semiconductors. In addition, MD simulations are used to investigate the dislocations nucleation and mechanical deformation mechanisms due to nanoindentation of these semiconductors in details.

§ Outline

Chapter 2 describes the nanometer-scale oxide patterns were fabricated on GaAs surface by means of AFM tip-induced anodic oxidation technique and, further investigated the mechanisms of growth kinetic and determined how the parameters affect the growth of the oxides. Finally, using this technique and measured its electrical property successfully.

In **Chapter 3** describes the mechanical deformation behaviors with the aid of both nanoindentation technique and MD simulations. Moreover, *Atomic Force Microscope* (AFM), *micro-Raman spectroscopy* and *Transmission Electron Microscopy* (TEM) are used to display the indentation-induced deformation behaviors. The underlying principle for the nanomechanical properties of semiconductor materials by using SPM systems is described in **Appendix A**. In **Appendix B** we introduce the MD methodology that is used to describe the plastically deformed behavior during nanoindentation processes, including the basic hypothesis, the physical model, the potential function, boundary conditions, and numerical methods. In **Appendix C** we also introduce the dislocation theory which supports the mechanisms of indentation-induced mechanical deformation on the nanometer-scale.

Summary and future works of the results are given in **Chapter 4** and **Chapter 5**.

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Figures Captions

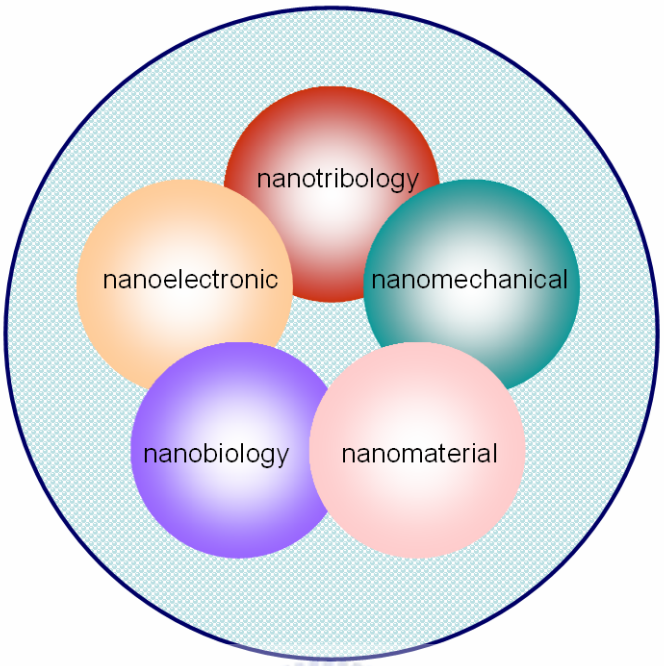

Figure 1-1. The classifications in nanotechnology field.

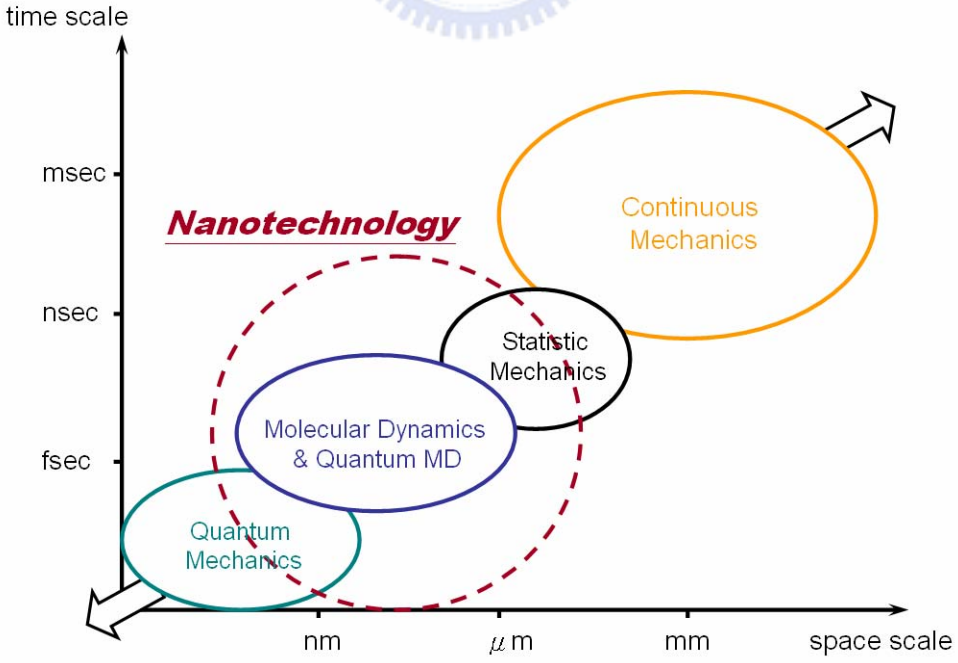

Figure 1-2. The terminology of relevant length scales together with referring physical methodologies.