半導體材料之介觀物理特性研究

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摘　要

掃描式探針微影技術在奈米科學領域佔了決定性的角色。它可以在原子等級上操控奈米粒子與物質特性的探測。因此，本論文藉此新穎的技術來研究半導體之物理機制與特性。

(I) 奈米氧化

近年來在基礎研究與奈米元件的應用領域上，利用掃描式探針氧化技術來製作奈米圖案已佔有決定性的角色。本研究中，利用原子力顯微鏡之局部場致電化學反應，以不同的環境濕度、氧化電壓、氧化時間與探針的掃描速率在 P 型砷化鎵(p-GaAs)表面上製作出不同形狀的奈米結構。實驗結果指出，氧化物深寬比之值取決於電場及離子擴散現象。從成長運動學上分析，氧化物的極高初始成長速率會隨著電場強度的減弱而快速地減慢，而氧化物高度($\frac{dh}{dt} \propto \exp(-\frac{h}{l_c})$)之成長速率會呈現指數關係劇降；當氧化物停止

成長時，所對應的電場強度是 $2–3\times10^{7}$V/cm。歐傑電子能譜顯示了砷化鎵表面因局部場致電化學反應所產生的氧化物訊號。當濕度高達 80%時，氧化物會因離子擴散現象而有雙層的結構。此外，微奈米結構的機械性質(如：材料硬度值的量測)對微奈米機電之元件應用就顯得格外的重要。於此，以原子力顯微術為基礎的奈米壓痕技術，則運用來估算氧化結構的奈米硬度值。另一方面，電性機制則遵循 Fowler-Nordheim (FN)之電流穿隧模型。

(II) 奈米壓痕

半導體材料之機械特性與變形機制，對於薄膜長晶是相當重要的。這部分主要是利用奈米壓痕器(Nanoindenter)與分子動力學模擬(Molecular Dynamics Simulations)，在矽(Si)、鍺(Ge)、砷化鎵(GaAs)、氮化鎵(GaN)、銻化鎵(GaSb)與磷化銦(InP)來研究材料因壓痕所導致的變形機制。

奈米壓痕技術在研究材料與薄膜表面的塑性變形領域上提供了一個很重要的應用。因此，結合奈米壓痕(nanoindentation)、原子力顯微鏡(AFM)、掃瞄式電子顯微鏡(SEM)、微拉曼光譜(micro-Raman)、集中離子束(FIB)與穿透式電子顯微鏡(TEM)來詳細研究半導體材料因壓痕所引起的局部相變化機制。對四族的矽與鍺而言，在壓痕曲線的卸載部分會有”pop-out”與”elbow”的現象產生，把這樣的現象歸於壓力釋放後所導致的相變化機制。而三五族的砷化鎵、氮化鎵、銻化鎵與磷化銦, 則在負載的部分會有”pop-in”的現象，而此現象則代表錯位

成核的機制。此外，由奈米壓痕所導致的相變化機制會存在於矽與鍺的高壓亞穩態相變結構中。相反的，對三五族的材料而言，在奈米壓痕的過程中則無相變化的產生。

分子動力學(Molecular Dynamics)理論是基於原子內的勢能，來精確的建構半導體材料的性質特性。在奈米壓痕的模擬過程中，Berkovich 探針與基板材料是以 Tersoff 勢能所建構而成的，其中探針是保持剛體性質。為了減少電腦計算時間，則採用 Gear 五階預測修正法來計算原子的位置與速度。從模擬所得到的力位移曲線中，可以估算材料的機械特性(硬度與楊氏模數)。此部分將以實驗所觀察到的現象與分子動力學所模擬的結果，來做定性與定量上的分析。

關鍵字

奈米氧化、奈米壓痕、分子動力學、原子力顯微鏡、微拉曼光譜、集中離子束、穿透式電子顯微鏡、掃瞄式電子顯微鏡、歐傑電子能譜儀、矽、鍺、砷化鎵、氮化鎵、銻化鎵與磷化銦。

Mesophysical Characteristics of Semiconductors

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Abstract

Scanning Probe Microscopes (SPMs) have great impact on the development of nanoscience. It has attracted attention as potential new tools for nanomechanics because of their demonstrated ability to manipulate nanoparticles and explore the properties of matters on atomic level. The purpose of this dissertation is to investigate the physical mechanisms of semiconductors by means of SPM systems, as following:

(I) *Nanofabrication*

Nanopattering using *Atomic Force Microscope* (AFM) has become an important area of research, both for fundamental research and for future nanodevice applications. In this study, AFM tip-induced local anodic oxidation on *p*-GaAs(100) surface is presented in an ambient way and, is viewed as a promising lithography approach for patterning surfaces at nanometer-scale due to its very precise control of

the feature size. Nanostructures are fabricated at various relative humidities, applied voltages, anodization times and scan rate of the tip. Results indicate that the higher aspect ratio of oxide increases because of enhanced electric field or ionic diffusion. An exponential decay relation of the growth rate with the grown oxide thickness $(\frac{dh}{dt} \propto \exp(-\frac{h}{l_c}))$ can be found from the kinetic data. It can be seen that the high initial oxidation rates (~300nm/s at 10V) decrease rapidly with decreasing electric field strength E, and that the oxide practically ceases to grow any further for an electric field strength of the order of $2\text{–}3\times10^{7}$V/cm.

Auger electron spectroscopy (AES) experiments confirm the modified structures takes the formation of anodized *p*-GaAs(100) surface. Also, the contribution of ionic diffusion increases about 80% at a higher relative humidity. In addition, it has become necessary to measure the hardness of materials such as with micro/nanoscale structures for micro/nano-electromechanical applications. New techniques are needed to measure at very shallow depth. Mechanical and structural aspects are of critical importance in integrating nanoscale building blocks into functional micro/nanodevices, thereby, AFM-based nanoindentation technique was carried out on anodized structures for determining their nanohardness values. The electrical characterizations of AFM tip-induced nanooxidation process show that the *Fowler-Nordheim* (FN) *tunneling* current model.

(II) *Nanoindentation-induced Physical Characterizations of Semiconductors*

Mechanical characterizations and deformation mechanisms of semiconductors are therefore of the significant technological importance, with contact-induced damage, cracking and epilayer delamination being of particular interest. The part of this thesis is to investigate the nanomechanical properties and elastic-plastic behavior of single crystals *Silicon* (Si), *Germanium* (Ge), *Gallium Arsenide* (GaAs), *Gallium Nitride* (GaN), *Gallium Antimonide* (GaSb) and *Indium Phosphide* (InP) by using the *Nanoindenter* and *Molecular Dynamics* (MD) simulations.

The nanoindentation technique has proved to be of great importance in this field of research as it allows investigation of the plastic response of surfaces and thin films. A combination of *nanoindentation* testing, *AFM*, *Scanning Electron Microscopy* (SEM), *micro-Raman Spectroscopy*, *Focused-ion Beam* (FIB) and *Transmission Electron Microscopy* (TEM) was used to study phase transformations in semiconductors under contact loading. The peculiarities in the indentation load-displacement behaviors of Si and Ge ("*elbow*" and "*pop-out*") were assigned to a phase transformation upon pressure release. In GaAs, GaN, GaSb and InP, "*pop-in*" events were observed during loading, which can be attributed to the dislocation nucleation. Also, the metastable high-pressure phases were observed in Si and Ge, suggesting that the nanoindentation-induced transformation to a metallic phase. On the contrary, phase transition of GaAs, GaN,

GaSb and InP were not displayed in nanoindentation.

MD simulations are based on interatomic potentials that accurately reproduce many properties of semiconductors. Nanoindentation simulations were performed by means of Tersoff's potential with an ideal Berkovich indenter that was held rigid during the simulation. To reduce the computing time, the predictor-corrector method will be adopted to calculate the positions as well as speeds of atoms. We will analyze the interactions among molecules using the arithmetic method of local interactions. Theoretically characteristics of the nanoindentation and nanoprocessing system will be obtained by a great number of numerical calculations performed by computers. The hardness and Young's modulus were calculated from the load-displacement curves. Results of MD simulations will then be compared with the experimental records and, the qualitative behavior of the theoretical analysis is consistent with the experimental observations as well.

Keywords

Nanooxidation、Nanoindentation、Molecular Dynamics Simulations、Atomic Force Microscopy、micro-Raman、Focused-ion Beam、Transmission Electron Microscopy、Scanning Electron Microscopy、Auger Electron Spectroscopy、Si、Ge、GaAs、GaN、GaSb and InP.

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