奈米碳材料和金屬氧化物之電子結構及其化學調控之研究

中文摘要

在奈米尺度下，表面尺寸和其形狀將會影響材料的電子結構組成，所產生新穎的電性表現將會提供未來應用性。在這篇論文中，我討論三種不同奈米材料和其化學特性調控，第一類為一維碳奈米管 (Carbon NanoTubes)，第二類為二維石墨烯 (graphene)，第三類為奈米氧化銅線 (CuO)。為了增加其應用性，利用雷射光和高能質子束來加以改質，在其反應過程中可出現新化學鍵結和表面結構重組。在同步輻射中心(NSRRC)中，利用具有空間解析度的掃描式電子顯微術 (Scanning PhotoEelectron Microscopy) 和光電子顯微術 (PhotoElectron Emission Microscopy)，來研究其奈米表面的電子結構和其化學調控。

在碳奈米管 (CNTs) 樣品，利用雷射光和反應氣體來控制其電子結構重組，可產生表面形貌變化和化學氣體攙雜。在大氣下利用雷射照射 CNTs 樣品，其結果上顯示，介於在 CNTs 頂端和側壁位置上，碳 1s 軌域中出現明顯 0.9 eV 的化學位移(chemical shift)。另一方面，在價帶 (Valence Band) 中可發現外層電子混成軌域之轉移，例如 C 2p-π 到 C 2s 和 C 2s/2p 電子軌域。另外，雷射光照射在不同氣體 (如真空，氮氣，和氧氣環境中) 中的碳奈米管，亦出現不同化學鍵結和化學位移變化，並在價帶分布上，也產生與氣體直接有關的電子密度重新分布。因而可發現，雷射光造成表面結構破壞而產生結構缺陷，當外界氣體進入將因而產生共價鍵結，因而影響到電子結構的形成。在價帶中，因化學鍵結和物理吸附效應可同時地存在於表面缺陷結構上，而產生不同的電子軌域轉移和其重新混成。其結果將提高碳奈米管的應用範圍，如場發射系統，電性傳輸和氣體偵測系統。

在石墨烯 (graphene) 的系統中，利用高能質子束影響六元碳結構重組和化學鍵結形成。其結果可發現，經過高能質子的轟擊，樣品表面可產生空間膨脹，但石墨烯仍有部分可存留在表面上，且在外部環邊界裡產生sp^3混成軌域和減少 C-SiC鍵結。當觀察graphene分子鍵結軌域時，發現原先碳結構在產生空缺後，平面晶格中π電子雲變成傾斜地分布，但在外部環邊界中π電子雲仍可以維持住其垂直方向性，並不受晶格缺陷的影響。此質子束產生具有不同化學鍵結所組成的表面圖案，並影響到π電子雲的方向分布，將有助以未來graphene中電性傳導應用，並可以提供磁性碳元素的可能產生原因。

一維奈米金屬氧化銅 (CuO) 為p-type 半導體，在電子組態控制上，可利用聚焦雷射來產生化學態改質。在研究結果中，發現經過雷射改質可以出現局部化學還原機制，如氧化銅奈米線頂端出現氧化譜線 (O^{2-}) 強度變弱和金屬銅特性之表現。並利用X光光譜 (EDS) 研究，我們發現在金屬銅球內部仍存在部分未還原氧化銅線，因此可解釋 Cu^{2+} 還原機制來自局部加熱所產生熱脫附效應或是光激發過程所造成氧鍵結破壞，因而所產生的異質材料(CuO-Cu)；此項研究提供了，

未來在奈米半導體中基本電性傳輸元件，並可以用來當作新的催化位置來生長新複合材料。

在這論文中，主要是利用物理方法加以改變奈米材料的電子結構，並利用光電子顯微技術來辨別其空間上的化學結構和電子組態變化，針對未來奈米材料應用上，提出電子結構調控之可能性和其影響的物理機制。

關鍵詞：奈米材料，奈米碳管，石墨烯，氧化銅，光電子能譜術，X 光吸收近緣能譜術，掃描式電子顯微術，光電子顯微術。

Electronic Structures and Chemical Modifications of Nano-material Systems: Carbon Nanotubes, Graphene, and Metal Oxide Materials

Cheng-Hao Chuang

Abstract

In the nano-material systems, the electronic property of materials is dependent on the construction of quantum confinement involving the size and shape. For the composition of electronic structure, it is attractive to study the novel behaviors of the chemical and physical property for the future application. This work is to study the electronic structures and its chemical modifications of the nanoscaled materials, including carbon nanotubes (CNTs), graphene, and CuO nanowires. In order to expand its utilization, the focused laser or energetic proton beam is introduced into the nanoscaled materials for engineering the electronic structure. The interaction between the injected particles and materials leads to various performances in physical and chemical fields. The irradiation effect can effectively modify its surface morphology, electronic structure, chemical composition, and chemical binding species. The electronic structure of materials and its chemical modification is resolved by X-ray photoelectron spectroscopy (XPS). Due to the localized surface functionalization, Scanning PhotoElectron Microscopy (SPEM) equipped with XPS and PhotoElectron Emission Microscopy (PEEM) equipped with near-edge X-ray absorption fine structure (NEXAFS) provide the chemical and elemental information with the spatial resolution of 100 nm.

In the CNTs materials, a He-Ne laser beam through the optic microscope could concentrate the beam on the surface of CNTs arrays. The result shows that the electronic structure was able to be adapted by binding various gas species on the CNTs surface. The laser beam was able to pattern the morphology on as-grown

CNTs array for the purpose of patterned morphology in the CNTs-related application. Behind that, the laser-induced defect site actually offer the potential area to chemisorb gas atom. The proof of C-N and C-O bond in the chemical binding environment were identified by XPS. After laser pruning removed the top region of CNTs in air and N_2 environment, the modified region showed an enhanced chemical shift of 0.9 and 0.6 eV in carbon 1s state, respectively. However, while CNTs is trimmed in vacuum environment, the laser-induced defect in carbon 1s state revealed a small chemical shift (< 0.1 eV). In the air-treated CNTs, the distribution of valence band demonstrated the configuration transfer from C 2s and C 2s/2p band to C 2p-π band, which was mostly derived from the correlation of defects and gas contribution. Due to the study of oxygen-treated CNTs, the structural defect with oxygen species tended to produce the decreasing C 2s and C 2s/2p band and increasing C 2p-π band. The modification of electronic structure was strongly dependent on the gaseous environment. We demonstrated an effective post-growth process to modify the electronic structure of CNTs for further applications.

One-atom-thick graphene layer is a promising materials for its outstanding transport property, in particular π electron channel. The π electron formed by sp^2-bonded carbon plays the important rule in the chemical and physical performance. The energetic proton beam was irradiated onto the epitaxial graphene (EG)/SiC sample, for the purpose of modification in the electronic character. While the bulk SiC by proton bombardment was raised the top of EG layer upward, the sp^2-bonded carbon of EG sheet was partially removed on the entirely irradiated area. The boundary of laser-irradiated area showed a new form of sp^3 configuration. The isotropic angular dependence of π state in NEXAFS spectrum indicated a rather random orientation of the remaining EG due to a loss of carbon atom, whereas the EG at the boundary area almost retained its orientation perpendicularly. The structural and chemical modification at different sites could be resolved by the space-resolved basis, which accounted for the ferromagnetic origin of proton-irradiated highly ordered pyrolytic graphite (HOPG). The molecular reconstruction of carbon and hydrogen atoms through proton irradiation might lead to the application of graphene-based device. The ability to locally manipulate the structure and properties of EG using

focused ion beam will help to open up a new route to engineering EG with potential for graphene-based electronics

One-dimensional copper oxide (CuO) nanowires is one of promising metal oxide materials. We demonstrated the capability of chemical modification in semiconducting CuO nanowires associated by focused laser. When laser beam was used to trim as-grown CuO nanowires, it could heat and re-solidify nanowirs into the drip-shaped microball. The unique spectral features which are assigned to CuO and Cu configuration in O 1s state and VB spectra was distinguished from the Cu-CuO nanowire synthesis. Due the elemental analysis in energy dispersive X-ray spectroscopy (EDS), we speculated that the chemical reduction of CuO to Cu existed locally at the microball. Therefore, laser beam could lead some chemical reactions such as thermal annealing and oxygen vacancy, in the case of the removal of oxygen amount in the CuO nanowires. This unique hybrid-material involving metal Cu and semiconductor CuO can be used as a basic item for further nanoelectric devices.

In this work, the different physical methods were used to modify the electronic property of materials. Using the ability of the position-resolved chemical analysis in SPEM and PEEM, we can distinguish the difference of chemical binding environment and speculate the physical mechanism. Our findings open up a new field in controlling electronic structure for further application.

Key words

Nano-materials, CNTs, Graphene, CuO, XPS, NEXAFS, SPEM, PEEM.