

摘要

本論文主要的研究方向在分析討論氧化鋅(ZnO)一維奈米結構的成長機制，並探討金在 ZnO 成長時所扮演的角色及其影響。實驗主要分為兩部分，第一部分是利用 ZnO 和碳粉的混合粉末在高溫爐管系統中以熱蒸鍍法來成長 ZnO 一維奈米結構，亦即以物理氣相傳輸方式來成長 ZnO。實驗中嘗試改變基板溫度、成長時間及選用不同基板等參數，探討 ZnO 的成長情形與金的影響。第二部分是以 $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ 為前驅物利用金屬有機化學氣相沉積系統 (Metalorganic chemical vapor deposition, MOCVD)，分別選用鍍金與不鍍金之矽晶片、石英玻璃與 Sapphire (氧化鋁單晶)等各式基材來成長 ZnO，探討金對 ZnO 成長的影響。並利用電子顯微鏡來觀察並分析 ZnO 的形狀、成分與結構。

高溫爐管系統實驗結果方面，在不同基板上成長的 ZnO 奈米帶或奈米柱，尺寸皆隨著基板溫度增加而變大。而成長時間愈長，奈米柱與奈米帶之尺寸亦隨之增加，另外觀察在 Al_2O_3 基板成長之 ZnO 隨時間增長，由奈米柱轉變成奈米帶。由穿透式電子顯微鏡 (TEM) 的分析結果可知 ZnO 奈米帶均為單晶之 Wurtzite 結構，而奈米帶之形狀是以一固定寬度延伸，但愈至末端可發現寬度漸減，另外在奈米帶之末端有一形狀較不規則的金粒，此金粒形狀具有刻面 (facets) 特徵，且與 ZnO 相接之界面平整。

MOCVD 實驗結果方面，鍍金之基板均可長出具有方向性之 ZnO 奈米柱，其形狀之特徵為頂端呈現尖錐狀，並無金球在上面。在沒有鍍金之基板，則成長出 ZnO 薄膜。在 $\text{Si}(100)/\text{Au}(10\text{nm})$ 基板上除成長一層均勻具方向性之 ZnO 奈米柱外，另有一部分為尺寸較大之奈米柱，且隨著時間增加，

其相對尺寸差異更明顯。但整體來說隨著時間增加，ZnO 奈米柱的尺寸均會明顯增加，TEM 分析奈米柱無論尺寸大小均為單晶之 Wurtzite 結構，成長方向為[0001]。而 ZnO 與基板之界面處有一層金，由 HRTEM 分析後發現金和氧化鋅之關係為 $[01\bar{1}]_{\text{Au}} \parallel [2\bar{1}\bar{1}0]_{\text{ZnO}}$ 及 $(111)_{\text{Au}} \parallel (0001)_{\text{ZnO}}$ 。由上述觀察顯示以 MOCVD 成長之 ZnO 奈米柱並非以氣相-液相-固相 (Vapor-liquid-solid, VLS) 機制形成。



Abstract

In this study, the growth process of one dimensional (1-D) Zinc Oxide (ZnO) nanostructures and the effect of Au on the growth were investigated. Two methods were used to grow ZnO: In the first section, 1-D ZnO nanostructures were synthesized on Si, polycrystalline Al₂O₃, and sapphire by thermal evaporation of ZnO and graphite mixed powders in a tube furnace system. The growth process of ZnO was varied by changing the experimental parameters inclusive of substrate temperatures, and growth time. Secondly, zinc acetylacetonate hydrate (Zn(C₅H₇O₂)₂ · xH₂O) was used as precursor to grow ZnO nanostructures by metal-organic chemical vapor deposition (MOCVD) system. Si, quartz glass, and sapphire substrates with and without Au coated were used to investigate the influence of Au on the growth process of ZnO. Electron Microscopy was used to characterize the morphology, compositions, and nanostructures of ZnO.

For the thermal evaporation of ZnO, the size of all ZnO nanobelts or nanorods grown on the different substrates increased with substrate temperature and the growth time. In addition, ZnO nanostructures grown on Al₂O₃ substrates have been found to be from nanorods to in the initial stage of growth, and gradually change to nanobelts as the growth time increased. TEM and selected area diffraction (SAD) analyses showed that ZnO nanobelts were single crystalline and wurtzite structure. ZnO nanobelts had uniform width but decreased at the tip. Also, it is observed that there is an irregular Au particle with the characteristic facets at the end of the nanobelt, and it has a smooth interface with ZnO.

For the MOCVD growth, well-aligned ZnO nanorods in a size of 40-90 nm were grown only on Au-coated substrates at 500°C. The top of ZnO nanorods has a cone-like shape and no Au particles on them. The Au remained in the substrate. On the other hand, continuous ZnO thin films were grown on substrates without Au. The size of the ZnO nanorods increased with the growth time. From TEM and SAD, ZnO nanorods were all single crystalline with wurtzite structure and the growth direction in [0001]. High-resolution TEM shows that the orientation relationship between Au and ZnO is $[01\bar{1}]_{\text{Au}} \parallel [2\bar{1}\bar{1}0]_{\text{ZnO}}$ and $(111)_{\text{Au}} \parallel (0001)_{\text{ZnO}}$. Thus, it demonstrates that ZnO nanostructures grown by MOCVD were not via the vapor-liquid-solid growth mechanism.



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