

## 氧化鋅奈米結構製作及特性分析之探討

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本研究以寬能帶的二六族半導體材料中的氧化鋅(ZnO)為主要的研究與探討的目標；在奈米結構的定義上，本研究採用維度限制的觀念，亦即在三個方向(x, y, z 三軸)受到奈米尺度限制(長度在 100 奈米以下)時稱為三維奈米結構(3D-nanostructure)，兩個方向受到限制則稱之為二維奈米結構，如本研究所著重的氧化鋅奈米線，若只有一個維度受到奈米尺度的限制，則為一維奈米結構如現今許多研究中所提到的奈米薄膜；本研究針對氧化鋅奈米線的製作方式，物理性質，化學性質，光學特性及電學特性等作一個全面性的研究與探討，試圖提出幾個氧化鋅奈米線的成長模型與其光學與電學特性的相互影響關係，並且研究其作為場發射平面顯示元件時所須要具備的電學特性指標，同時提出解決的方式與未來研究可進行的方向與內容。

文中採用兩階段氣液固法(2 step Vapor-Liquid-Solid process)來成長氧化鋅奈米線，相較於一般傳統的氣液固法而言，這個改進式的成長方式利用兩階段的升溫方式可以有效的將在基板表面的觸媒金屬薄層形成一些有規則或是尺寸相對較小的奈米金屬觸媒點，接著其後的快速升溫過程可以將溫度迅速的提升到鋅蒸氣產生的溫度範圍，以一個穩定的溫度環境進行飽和析出的氧化鋅奈米線成長過

程，如此可以將其成長出來的氧化鋅奈米線幾何尺寸維持在 80 nm 的直徑與約 5  $\mu\text{m}$  長度的大小。

在金屬觸媒的使用上，也有很多不同的選擇，傳統的金觸媒較不易成長具有一定有序的氧化鋅奈米線，這是因為金觸媒在與矽基板之共晶溫度時，極易形成不規則的奈米級顆粒，為一個多晶的結構體，造成在氣液固法成長時氧化鋅過飽和析出時的不規則性，以致形成較為雜亂分佈的氧化鋅奈米線。而實驗中所選擇的銅奈米顆粒觸媒點則可以在其與矽基板的共晶溫度形成非常規則的觸媒點，有助於氧化鋅奈米線的有序成長。

在載氣氣氛的選擇上，使用高純度的氬氣作為成長上的氣流控制，不同的氣流流速將會影響到氧化鋅奈米線成長過程中的鋅蒸氣含量多寡與成長，速率較快的流速對於成長出線徑較小的奈米線較有幫助，同時長度上也增長許多，其幾何關係比可以到達的程度，相對於流速較低的環境所成長出的奈米線，其缺陷也因為快速成長而變得較多，在選用高純度氬氣氣氛後，更可以發現因為氬氣本身的黏滯係數較小，進一步加速了氧化鋅奈米線的成長速率，也提高了幾何比，對於光學與電性特性都有一定程度上的增強作用。

肇因於尋求更好的光學激發與電性特性，也有鑒於成長方向雜亂的原因可能為基板與氧化鋅之間的晶格不匹配所致，因此藉著超薄氧化鋅緩衝層的引入，先在矽基板上成長一單晶優選方向(002)的超薄氧化鋅氧化層，接著再依循先前的氣液固方式成長氧化鋅奈米線，發現藉由氧化鋅緩衝層的幫助可以有效的解決晶格不匹配所導致的方向不均與缺陷機制，使氧化鋅奈米線可以垂直的成長於基板之上，不再受到基板方向與晶格的限制，如此可以元件化的氧化鋅奈米線製作成為可能，更可以有效的整合至現今的半導體製程內。

以上的各式不同製程的氧化鋅奈米線其光學激發特性研究方面，藉由光致發光的頻譜配合材料分析工具可以知道當激發光為 325 nm 時其在 380 至 400 nm 的範圍內會有一極為顯著的紫外光激發峰，此峰值的位置反映了氧化鋅奈米線中的結晶情形與雜質分佈，同時也與結晶的缺陷有相當程度的關係，其他的特徵峰值則說明了氧缺陷或是氧空缺以及鋅原子的移動情況。

在場發射特性的探討中，針對不同成長條件下的氧化鋅奈米線測量其場發射特性，可以發現具有垂直方向成長的奈米線其激發電場(trun-on electric field)約為 0.83 V/ $\mu\text{m}$ ，是一項很優異的成果，歸因於相當均一的奈米線成長型態與幾何大小且是完美的單晶晶體，才可以得到如此低的激發電場值，此一數值的有效降低頗具實用價值，意即可以運用較低的電壓來使場發射平面顯示器達到場發射激發的效果，不但可以節省電能更可以提升產品的使用壽命與兼顧環保的需求。藉由分析 Fowler-Nordheim 圖所計算出的場發射增強因子(field emission enhancement factor,  $\beta$ )可以達到 7,180，此以數值與其他場發射奈米線如奈米碳管( $\beta \sim 1,100$ )比較也較高，同時也已經達到實用化的範疇。

為了進一步增強氧化鋅奈米線的場發射特性與應用，吾人設法利用摻雜的方式降低氧化鋅本身的阻抗，經實驗證明加入微量的錫(Tin, Sn)有助於降低氧化鋅

奈米線的有效阻抗，此一摻雜證明確實可以降低奈米線的內部阻抗(由未摻雜的 85.43 k $\Omega$  降至 8.53 k $\Omega$ )，另一方面由於低熔點金屬錫的加入也間接的降低了氣液固法在成長氧化鋅奈米線時的溫度(由原先的 900 度降至 805 度)，其在場發射特性的表現上，經由摻雜的結果也將原先的機發電場由 0.83 V/ $\mu\text{m}$  大幅降低至 0.07 V/ $\mu\text{m}$  附近，藉著良好的低阻抗高方向性成長的錫摻雜氧化鋅奈米線的製作也將場發射幾何增強因子增加到  $6.67 \times 10^5$  左右，是一個很好的結果。

此外，利用元件製作的技術，吾人成功的製作出一具備有閘極控制的氧化鋅奈米現場發射元件，利用不同的閘極電壓，可以有效的控制氧化鋅奈米線的場發射行為，在量測的數據顯示最佳的控制操作電壓約為 35 伏特，同時最佳的電壓與電流比(Transconductance,  $g_m$ )位於  $3.88 \times 10^{-4}$  S，這樣的特性將可以初步的證明氧化鋅奈米線其在接受控制之後可以具備較佳的場發射特性與極為穩定的場發射電流密度，對於未來的場發射顯示元件而言相當的具有實用性的潛力。

經過觸媒金屬選擇，載氣氣氛控制，光學激發特性分析以及場發射性質的研究，可以對現階段的氧化鋅二維奈米結構的成長機制與結晶過程給予一個較為明確的探討，同時也針對未來的場發射平面顯示元件的基礎性研究提供了清楚的模型，證明場發射元件材料可以朝著寬能代半導體材料的領域發展，運用其寬能帶的優良激發特性與奈米結構微型化的相輔相成而早日達到實際應用的領域。



# The Synthesis and Characteristics of ZnO Nano Structure

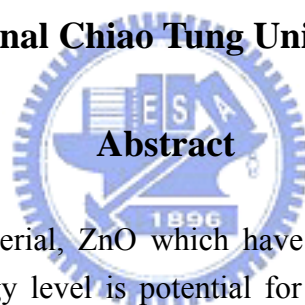
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The wide band gap material, ZnO which have 3.37 eV energy band gap and about 60 meV excitation energy level is potential for nano laser application and flat display applications in the future. This research is focus on the 2-D nanostructure which means the x and y axis was limit by the nano size (<100 nm). The characteristics of the ZnO nanowires are paying attention in growth mechanism, optical emission, and electric properties. Furthermore, the field emission devices are also been focus on the low turn-on electric field and more stability current density.

Here we report for the first time the ZnO-nanowire-growth on p-type Si (100) substrates using a VLS process catalyzed by copper instead of gold. This is a new method for preparing ZnO NWs through a rapid and cost effective thermal process. The two-step VLS growth method, used in this study reduced the liquid metal size and content efficiently to promote the growth of ZnO NWs. Furthermore, in this process we introduce the thermal annealing steps to make ZnO NWs approach vertically on the Si substrate.

Among various preparation methods, the metal catalytic VLS growth process provides a cheap and speedy route for large-area deposition of nanowires. The physical structures of the nanowires are affected strongly by the fabricating parameters such as starting materials, temperature, time and atmosphere. However,

the effect of atmosphere on the structure and property of ZnO nanowires was scarcely studied. In the present study, we grow ZnO nanowires on Si (100) p-type substrate by using Cu catalyzed VLS with Ar and N<sub>2</sub> carrying gases. The effects of atmosphere on the morphology, structure and optical property of those nanowires were studied.

The nanowire growth process was controlled by surface morphology and orientation of the epitaxial ZnO buffer layer, which was deposited by radio-frequency (rf) sputtering. The copper catalyzed the vapor-liquid-solid growth of ZnO nanowires with diameter of ~ 30 nm and length of ~ 5.0 μm. The perfect wurtzite epitaxial structure (HCP structure) of the ZnO (0002) nanowires synthesized on ZnO (002) buffer layer/Si (100) substrate results in excellent optical characteristics such as strong UV emission at 380 nm with potential use in nano-optical and nano-electronic devices.

These ZnO nanowires show excellent field emission properties with turn-on field of 0.83 V/μm and corresponding current density of 25 μA/cm<sup>2</sup>. The emitted current density of the ZnO nanowires is 1.52 mA/cm<sup>2</sup> at a bias field of 8.5 V/μm. The large field emission area factor,  $\beta$  arising from the morphology of the nanowire field emitter, is partly responsible for the good emission characteristics.

The Sn doped ZnO (SZO) nanowires were fabricated by a vapor-liquid-solid (VLS) growth process. The reaction temperature for the formation of the nanowires can be reduced to ~100 °C due to Sn doping. The growth direction and morphology of SZO nanowires depend on the amount of Sn, which is attributed to different size between Zn and Sn atoms. The ultra-violet (UV) emission of SZO nanowires varies from 380 to 396 nm since Sn acts as a doubly ionized donor and introduces deep states in the band gap. In addition, the SZO nanowires exhibit significantly improved field emission characteristics with a turn-on electric field of 0.05 V/μm under a current density of 0.5 mA/cm<sup>2</sup> in comparison with undoped ZnO nanowires. The work function of the SZO nanowire decreases for the higher carrier concentration and the field enhancement factor increases for the smaller diameters.

The metal oxide NWs, especially ZnO NWs have potentials for much field application such as field emission display arrays or optical emission. Furthermore, the studies of the ZnO NWs are still narrow focus on the electric and optical applications. In the future, there are many kinds of subjects could be study which will increase the speed of commercialize.

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一切 是生命裡的一次轉彎。

桌上的雜亂如往常散落，工作與實驗的結束還是詫異的很難想像，滿滿的在心裡的是許許多多深深的祝福與感謝。曾老師俊元教授的指導與提攜，是最可貴的記憶，林老師鵬教授的細心與關懷是最溫暖的風，口試委員龔教授正、吳教授泰伯、王教授錫福、何教授孟書、陳教授三元多次的論辯與指正，更使得這一份工作愈趨完美。

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