行政院國家科學委員會專題研究計畫　成果報告

正型氧化鋅奈米棒和薄膜/積層膜的製備和它們性質的探討

計畫類別：個別型計畫
計畫編號：NSC92-2216-E-009-022-
執行期間：92 年 08 月 01 日至 93 年 07 月 31 日
執行單位：國立交通大學電子工程學系

計畫主持人：曾俊元

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫涉及專利或其他智慧財產權，1 年後可公開查詢

中　華　民　國 93 年 11 月 2 日

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中文摘要

由於氧化鋅具有寬能隙和直接能隙的特性，所以在光電工業中，以氧化鋅為材料的光電元件，都引起非常廣泛的興趣與注意，目前已經可以初步的掌握一些重複性高的氧化鋅奈米線製程及基礎物理上的特性，透過不同催化金屬(金、銅)的選擇，可以在經過 RCA 清洗的矽基板上成長出高度一致性近垂直方向具完美烏采(wurtzite)結構之氧化鋅奈米線，我們利用氣液固法的方式加上精確的氣流控制，成功製作出方向性極佳的氧化鋅奈米線，其場發射效應的量測結果相當優良，可以在約 0.83 V/μm 的啟動電場強度下擁有 25 μA/cm^2 的電流密度，在 8.5V/μm 的偏壓下激發電流密度為 1.52 mA/cm^2，這些優良的發射特性部份歸因於奈米線的型態。

Abstract

ZnO nanowires (NWs) synthesized by vapor-liquid-solid (VLS) growth mechanism with Cu and Au as the catalyst were investigated. The principal differences in morphology between Cu and Au catalyzed ZnO NWs are observed and lead to significant differences in their field emission and photo fluorescent characteristics. The Cu catalyzed ZnO NWs with a high-quality wurtzite structure were grown vertically on p-type Si(100) substrate along [0002] direction. A strong ultraviolet (UV) emission at 381 nm is observed. These ZnO NWs show excellent field emission properties with turn-on field of 0.83 V/μm and corresponding current density of 25 μA/cm^2. The emitted current density of the ZnO NWs is 1.52 mA/cm^2 at a bias field of 8.5 V/μm. The large field emission area factor, β arising from the morphology of the nanowire field emitter, is partly responsible for the good emission characteristics. The ZnO NWs with high emission current density and low turn-on field are expected to be used in field emission flat panel display.

Keywords: ZnO nanowires (ZnO NWs), photoluminescence (PL), and field emission (FE)

I. Introduction

Since CNTs were discovered in 1991, worldwide nanotechnology research has been extensive on one-dimensional (1-D) nanostructures, such as CNTs, oxide nanobelts, and NWs. Explorations of these nano-structured materials are focused on the field emission and photoluminescence properties. ZnO, a direct band gap (3.37eV) semiconductor with exciton binding energy of 60 meV, is a suitable material for optical and field emission application. In this study, the ZnO NWs are synthesized by the VLS process with Cu and Au as the catalysts in Ar atmosphere on p-type Si (100) substrate. The morphology, composition, photoluminescence, and field emission characterizations of these NWs were examined.

II. Experimental

Thin films of Au and Cu with the thickness of 70 Å were deposited on Si (100) substrate by rf-sputtering for the catalytic layer. Then, ZnO NWs were synthesized by VLS process with temperature of 900 ^{o}C with the temperature raising rate of 150 ^{o}C/min. under Ar atmosphere. A boat was filled with a mixture of ZnO and graphite powder and loaded in a furnace. A precisely controlling the carrying gas flow pattern (CGFP) method was employed to control the growth process of ZnO NWs. The appearance of Si substrate surface before VLS growth was observed by atomic force microscopy. The crystal structure and morphologies of the NWs was studied by X-ray diffraction, scanning electron microscopy and transmission electron microscopy, respectively. The chemical composition of the NWs was characterized by Auger Electron Microprobe. A photoluminescence analyzer with Xe lamp as an excitation source (320nm) was used for optical studies at room temperature. A Keithley 237 was used for measuring the field emission characteristic with the pressure of 1×10^{-5} Torr at room temperature.

III. Results and Discussion

Figure 1(a) shows that the surface morphology of Si substrate with Au thin film after heating process is an irregular island structure. The surface morphology (Fig. 1(b)) of Si substrate with Cu thin film is ordered square or hexagonal island structure. The different surface morphology of catalyst film will affect the distribution of the ZnO NWs on the Si substrate, which will be described in the later section.

Figure 2 shows the proposed VLS growth mechanism of ZnO NWs. There are at least four different stages involved in the formation of ZnO NWs: metal thin film deposition, catalytic nanoparticle formation, nucleation of ZnO and epitaxial growth of ZnO NWs. The substrate surface indicated a light or dark gray color after NWs growth.

Figure 3(a) illustrates the morphology of the ZnO NWs grown with Au as the catalyst. There exist randomly distributed hexagonal pillars on the Si substrate with lengths of 5 μm and diameters of 20 to 30 nm. The ZnO NWs with Cu as the catalyst (Fig. 3(b)) are well-aligned on the Si substrate with the length of 5 μm and diameter of 50 nm. The different morphology between Cu and Au catalyzed ZnO NWs is due to the different liquefaction temperature of the catalytic metal. The larger irregular island structure of the Au film formed at low temperature and the orientation of Si substrate affects the growth direction of the ZnO NWs. However, hexagonal Cu island structures formed at higher temperature The surface of the Cu catalyst film has many ordered square and hexagonal Cu island structures and, consequently, the ZnO NWs can vertically grow from Cu layer on the Si substrate with CGFP method.

As seen in the Fig. 3(a), there exist weak diffraction peaks identified as (100) and (002) of the ZnO NWs synthesized with Au as the catalyst, which is attributed to the random and disordered distribution of the ZnO NWs dispersed on the Si substrate (Fig. 3(a)). When the CGFP method was adopted, the NWs had higher (002) peak intensity. Furthermore, the ZnO NWs also have excellent preferred (002) orientation of Fig. 3(c) when replacing the

catalyst from Au to Cu by CGFP method.

The HRTEM image of Cu-catalyst NWs shown in Figure 5 indicates the lattice fringes along [0002] direction. The spacing of the lattice fringes along c-axis of the ZnO nanowire is 5.21 Å. The SAED pattern is shown in the inset of Fig. 5(a). The diffraction pattern of the ZnO nanowire reveals that this nanostructure is perfect wurtzite single crystalline structure. In Fig. 5(b), the bright view image shows the smooth sharp sidewall of the ZnO NWs, which proves the CGFP method is helpful for controlling the morphology of the ZnO NWs.

Figure 6 depicts the AES spectrum of the ZnO NWs, indicating that the chemical compositions of the ZnO NWs have two major elements, Zn and O, and one minor contaminant, C. The weak C signal peak is derived from the carbothermal route adopted for the synthesis of the ZnO NWs. After noise calibration and integrated calculation, the Zn and O atomic ratio is around 1:1.

According to the figure 7(a), a strong UV emission (~381 nm) for the near band edge emission of the wide band gap of ZnO, and weak green emission (~501 to 570 nm) caused by the singly ionized oxygen vacancies are observed in the PL spectrum of the ZnO NWs synthesized with Cu as the catalyst under the control of CGFP method. It is easy to perceive the contrast between the PL spectra of ZnO NWs synthesized with Cu and Au as the catalysts. That is, a little wavelength shift, from 381 to 368 nm, exists in the spectra of the shorter length (3 μm) and randomly distributed NWs synthesized with Au as the catalyst. This is because the rare catalyst materials, such as Cu and Au, which diffuse in the ZnO NWs and serve as the recombination centers.

Figure 8 displays the field emission I-V plots for the well-aligned and randomly grown ZnO nanowire array using different metal catalysts. The β value of Cu catalyzed ZnO NWs is about 7.18×10^3, and that of Au catalyzed with and without adopting CGFP method are 4.70×10^3 and 3.81×10^3, respectively. Our Cu catalyzed ZnO NWs exhibit higher β value than other reported ZnO NWs (β=847) mainly because of their vertical growth, better crystalline structure (Fig. 4) and lower density (Fig. 3). The Cu catalyzed ZnO NWs exhibit lower turn-on voltage and higher emission current densities. These results illustrate that the ZnO NWs array is sufficient for flat panel field emission display applications in the future.

IV. Conclusions

In summary, well-aligned and vertically grown Cu catalyzed ZnO NWs, which have an excellent wurtzite structure, less contamination and precise chemical composition, were successfully grown at 900 ^{o}C by adopting a CGFP method. The ZnO NWs exhibit excellent optical and field emission properties for the vertical direction growth of Cu catalyzed NWs. Such vertically grown ZnO nanowire array is a good candidate for the future flat panel display applications.

References

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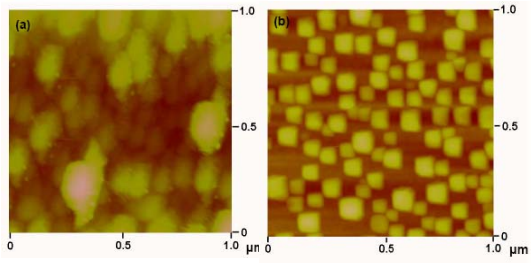

FIG. 1 AFM images of the (a) Au and (b) Cu thin film surface after heating process.

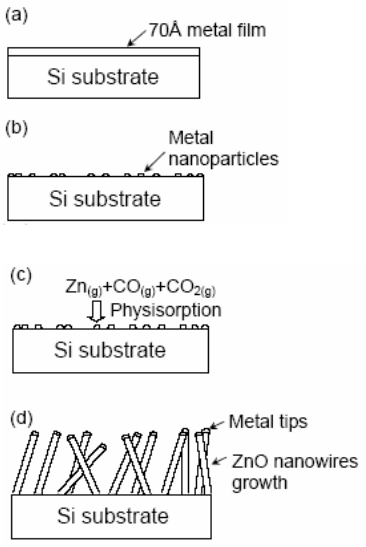

FIG. 2 Schematic illustration of VLS nanowire growth mechanism (a) metal film deposition, (b) metal nanoparticles formation, (c) absorption and nucleation, (d) epitaxial growth.

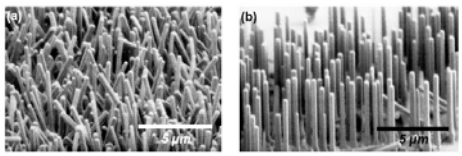

FIG. 3 FESEM photographs for (a) Au and (b) Cu catalyzed ZnO NWs synthesized on p-type Si (100) substrate with adopting CGFP method

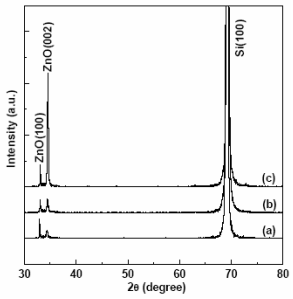

FIG. 4 XRD patterns of ZnO NWs synthesized with (a) Au as the catalyst, (b) Au as the catalyst by CGFP method, and (c) Cu as the catalyst by CGFP method.

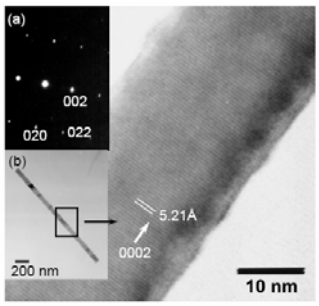

FIG. 5 HRTEM image of Cu catalyzed ZnO NWs. The selected area electron diffraction (SAED) pattern is shown in inset (a), while bright view image for side wall of the ZnO NWs, is indicated in inset (b).

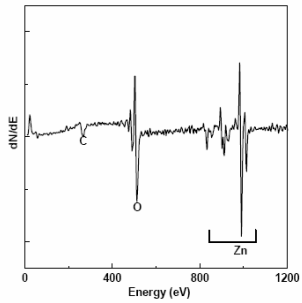

FIG. 6 Typical AES spectrum of Cu catalyzed ZnO NWs

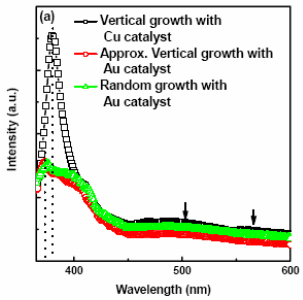

FIG. 7 PL spectra of the ZnO NWs grown on the p-type Si substrate.

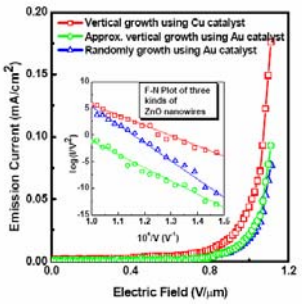

FIG. 8 Field emission characteristics of the ZnO NWs grown on p-type Si substrates. The inset reveals the F-N plots of the ZnO NWs.