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一維與二維的氧化鋅奈米材料之製作、結構與特性研究

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I. 中文摘要

氧化鋅奈米結構近幾年來已被廣泛的討論與製作，並針對其特殊的光學與電學性質作一系列的研究與討論，針對場發射特性研究上，吾人使用氣液固法(Vapor-Liquid-Solid, VLS)所製作的氧化鋅奈米線已經具備有相當良好的場發射特性與極佳的光學激發，為了更進一步提升其場發射電流密度與降低激發電場強度，採用了數個不同的金屬元素摻雜方式，經由實驗數據的分析結果發現，利用錫摻雜的氧化鋅奈米線不但具備有降低製程溫度的優點，更可以因為錫金屬進入氧化鋅奈米線取代了部分鋅原子的位置，可以有效的降低氧化鋅奈米線的串聯阻抗，使其擁有較低的場發射激發電場與較大的電流密度，經由實驗證明，吾人所製作的氧化鋅摻雜錫之奈米線其場發射激發電場約在 $0.05 \text{ V}/\mu\text{m}$ 可有 $0.5 \text{ mA}/\text{cm}^2$ 的電流密度，在激發電場為 $0.09 \text{ V}/\mu\text{m}$ 時可達到 $1.0 \text{ mA}/\text{cm}^2$ 的電流密度，同時，其摻雜後的串聯電阻更可以下降至 $8.53 \text{ k}\Omega$ ，對於未來的場發射平面顯示器元件應用有極佳的潛力。

II. Abstract

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 $\sim 100^\circ\text{C}$ 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 $0.05 \text{ V}/\mu\text{m}$ under a current density of $0.5 \text{ mA}/\text{cm}^2$ 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. Also, the resistance of the SZO nanowire is decreased for the higher Sn mole fraction. Therefore, the SZO nanowires are expected to be applicable to nano laser and flat panel display in the future.

Keywords: ZnO nanowire, SnO_2 , vapor-liquid-solid (VLS) process, Photoluminescence, field emission

III. Results and Discussion

ZnO, a direct band gap (3.37eV) semiconductor with exciton binding energy of 60 meV , is a suitable material for optical application. The interesting ZnO nano structures, such as nanowires, nanobelts, and nanoneedles have drawn much attention in the understanding of their growth mechanism, physical properties, optical characteristics and field emission applications. It is well known that the structural properties and dopants may determine the electronic and photoluminescence properties of the material. The Sn can serve as a doubly ionized donor when the incorporation of SnO_2 as a solute in ZnO and consequently provide high electron carrier concentration. It is, therefore, expected that the Sn doped ZnO (SZO) nanowires have higher electrical conductivity and better field emission properties compared to undoped ZnO nanowires.

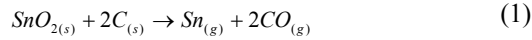
In this work, the effects of varying the concentration of Sn as a dopant on the surface

morphology, crystal structure, chemical composition, photoluminescence, and field emission characteristics of the undoped and SZO nanowires were investigated.

The ZnO nanowires were grown in a horizontal quartz tube furnace. The p-Si(100) substrate and ZnO, SnO_2 , and carbon ball mixed powders were loaded into the quartz tube. The p-Si(100) substrate that puts nearby the lower temperature zone of the furnace and makes sure loaded in the same position each experiment. During the synthesized process, high purity Ar gas as an auxiliary gas was induced into the fabrication system which flowing rate was $50\text{--}100 \text{ cm}^3/\text{min}$. The growth process continued at $800\text{--}900^\circ\text{C}$ for 12 to 20 min.

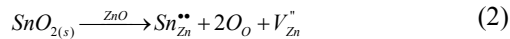
Figures 1(a), (b), and (c) indicate the XRD patterns of the ZnO nanowires with 0, 0.1 and 0.3 mole fractions of Sn, respectively. The pure ZnO nanowires synthesized at 900°C [Fig. 1(a)] are of hexagonal structure as reported in Joint Committee on Powder Diffraction Standards –

International Centre for Diffraction Data (JCPDS-ICDD) no. 80-0074. The reaction temperature for the formation of the SZO nanowires is not so high as that of the undoped ZnO nanowires. It is suggested that SnO₂ react with carbon to form the Sn vapor according to the following chemical reaction:



The generated Sn vapor would initiate a catalyst droplet-assisted growth in the early stage of VLS process. While we mixed SnO₂ and ZnO source powders with carbon, the synthesized temperature can be decreased to ~800°C.

The SZO nanowires synthesized at 800°C with 0.1 [Fig. 1(b)] and 0.3 [Fig. 1(c)] mole fraction of Sn have similar characteristic peaks as the pattern shown in the Fig. 1(a), but the 2θ of the (0002) peak has a little shift from 34.40° to 34.52°. The SZO nanowires are still of the hexagonal structure and possess shorter lattice parameter compared to the undoped ZnO nanowires. The lattice constants of the undoped ZnO nanowires are a = b = ~3.52 Å and c = ~5.21 Å, those of the 0.1 SZO nanowires are a = b = ~3.49 Å and c = ~5.19 Å, and those of the 0.3 SZO nanowires are a = b = ~3.43 Å and c = ~5.18 Å, which can be calculated according to the XRD patterns. If the addition of SnO₂ to ZnO forms a substitutional solid solution with the hexagonal structure, a possible reaction is:



Where Sn_{Zn}⁴⁺ means Sn substituted for Zn²⁺ in ZnO, O_o denotes O at oxygen site, and V_{Zn}^{••} indicates a vacancy at a Zn²⁺ site in the lattice of the SZO nanowires. It is shown in Eqn. (2) that the Sn⁴⁺ atom is substituted for Zn²⁺ atom and the Zn vacancy forms. The shorter lattice constants in the SZO nanowires may be attributed to smaller ionic radii of Sn⁴⁺ (r_{Sn⁴⁺} = 0.069 nm, r_{Zn²⁺} = 0.074 nm) and the formation of Zn-vacancy.

The tilted 45°-viewed FE-SEM images of undoped and SZO nanowires on p-Si(100) substrates are demonstrated in Fig. 2, indicating that the surface morphologies of the nanowires depend strongly on amount of the dopant, Sn. As shown in Fig. 2(a), the undoped ZnO nanowires have the smooth sidewalls, uniform diameter of ~50 nm and length of ~5 μm. Figures 2(b) and (c) show the geometrical appearances of the 0.1 and 0.3 SZO nanowires, respectively. Under the equal thickness of Au catalyst film (~60 Å), the geometrical appearances such as length and diameter of the ZnO nanowires should be similar due to the same thermal synthesized process and carrier gas flowing rate. But a very interesting aspect is the different morphologies for 0.1 and 0.3 SZO nanowires. These two nanowires have the rugged sidewalls, smaller diameters and

longer lengths. The 0.1 SZO nanowires have a diameter of ~30 nm and length of ~10 μm, while the 0.3 SZO nanowires have a diameter of ~80 nm and length of ~2 μm. The individual average volume of the undoped, 0.1, and 0.3 SZO nanowires are of the same order and comparable. The values are ~9.817×10⁻³, ~7.068×10⁻³, and ~10.053×10⁻³ μm³, respectively. According to the alloy phase diagram of Au and Sn, at the temperature of ~282 °C, Au and Sn form an eutectic Au-Sn alloy (20 wt% Sn and 80 wt% Au). Therefore, the 0.1 SZO nanowires have the smaller diameter and longer length because of the low partial pressure of Sn in vapor phase in the upstream that leads to the deposition of Sn as small droplets that alloying with Au on the substrate, thus initiating the growth of longer nanowires in the presence of sufficient Zn vapor in the VLS process. On the contrary, the 0.3 SZO nanowires have larger diameter and shorter length due to the presence of abundant Sn vapor that leads to the formation of larger Au-Sn catalyst droplets under an lower Zn vapor pressure. The Sn-assisted growth mechanism of undoped and SZO nanowires is schematically shown in Fig. 3. The Sn in the alloy droplets can diffuse into ZnO nanowires through the thermal process. The content of Sn in the SZO nanowires can be measured by EDS spectra as demonstrated in a later section. This indicates that the fraction of Sn to Zn can influence the morphologies of the SZO nanowires.

Figure 4(a) shows the room temperature (298 K) photoluminescence (PL) spectra of undoped ZnO and SZO nanowires. A strong UV emission at 380 nm and a green light emission at 520 nm are observed in the PL spectrum of the undoped ZnO nanowires. The UV emission is due to the direct band gap of ZnO, and the green light emission is corresponding to the oxygen vacancies in the ZnO nanowires. On the other hand, it illustrates that the SZO nanowires exhibit four photoluminescence bands centered at 380, 396, 461 and 502 nm. Corresponding to the band gap value of the SZO nanowires shown in Fig. 4(b), those two emission peaks at 380 nm (E_λ = 3.26 eV) and 396 nm (E_λ = 3.13 eV) could be attributed to (1) the recombination of electrons in valence band with holes in conduction band, and (2) the recombination of electrons in deep traps with holes in conduction band, respectively. These processes are shown in Fig. 4(c). It is suggested that the first peak of 380 nm correspond to the band gap of ZnO, and the second peak of 396 nm may be due to the response for the Sn atom that performs the role of a doubly ionized donor and introduces deep states in the energy band gap [see Fig. 4(c)]. As a result, the peak intensity of 396 nm caused by 0.3 SZO nanowires is higher than that of the 0.1

SZO nanowires. There are other two broad photoluminescence emissions, 461($E_\lambda = 2.68$ eV) and 502($E_\lambda = 2.47$ eV) nm in the spectra of the SZO nanowires, which may be associated with a complex luminescent centers such as $(V'_{Zn} - Sn^{2+})^*$ or Zn_i . Other minor unknown peaks in Fig. 4 possibly result from the phonons or photons emission process associated with the thermal atomic vibration in the nanowires.

The field emission characteristics of the undoped ZnO and SZO nanowires are shown in Fig. 5(a). At the current density of 0.5 mA/cm², the turn on electric fields of undoped, 0.1 and 0.3 SZO nanowires are 0.83, 0.07 and 0.05 V/ μ m, respectively. While the electric field is remained at 0.05 V/ μ m, the electron number densities from the field emission mechanism of the ZnO nanowires are 2.97×10^{15} for 0.3 SZO, 9.93×10^{14} for 0.1 SZO, and 3.77×10^{14} for undoped ZnO nanowires. The released electrons may be increased due to the increase in electric field, and Sn dopant as proposed in Eqn. (1). The lower turn on electric field and higher electron number density again provide evidence of the substitution of Zn by Sn in the SZO nanowires. The SZO nanowires exhibit the better field emission properties than that of the undoped ZnO nanowires. After the I-V measurement, the Fowler–Nordheim (F-N) relation ($\ln(I^2/E)$) is plotted as a function of I/E is applied in order to realize the properties of those emitters. The F-N plots [indicated in Figs. 5(b), (c) and (d)] of those nanowires indicate that the field emission properties of those nanowires follow the F-N equation:

$$J = \frac{A\beta^2 E^2}{\phi} \exp\left(\frac{-B\phi^{3/2}}{\beta E}\right) \quad (2)$$

where J is the current density, E the applied field, ϕ the work function of the emitter, β the field enhancement factor, $A=1.56 \times 10^{-10}$ (AV^{-2} eV) and $B=6.83 \times 10^3$ ($VeV^{3/2}$ V μ m⁻¹). Therefore, the field enhancement factor and work function can be obtained respectively from the slope and the intercept of the $F-N$ plot. The work functions Φ of undoped, 0.1, and 0.3 SZO nanowires are 7.26, 7.16, and 6.92 eV, respectively, while field enhancement factor, β , of those nanowires are 2.07×10^4 , 4.45×10^5 and 6.67×10^5 , respectively. The better experimental results are obtained for 0.3 SZO nanowires : $\beta = 6.67 \times 10^5$ and $\Phi = 6.92$ eV. The field enhancement factors increase and the work function decreases due to the addition of Sn. The larger field enhancement factor is attributed to the smaller diameter of the SZO nanowires. Moreover, it can be concluded from the result that the Sn dopant acts as the donor, which increases the carrier concentration and reduces the work function of the SZO nanowires.

To investigate the difference of electronic characteristic between undoped and SZO nanowires, the stability of the field emission current-voltage characteristic is compared, as shown in Fig. 6. The saturation behavior has been observed on individual undoped, 0.1 and 0.3 doped ZnO nanowires. The saturation of the field emission current has occurred in those nanowires, that is, each ZnO nanowire has its highest resistance under the turn on electric field. In this case, the voltage drop (IR) across such resistor would lead to decrease in the effective applied voltage, and therefore to cause a flattening of the characteristics. The resistance in series with the ZnO nanowires can be estimated by using

$$I = a(V - IR)^2 \exp[-b/(V - IR)] \quad (3)$$

where I and V are field emission current and applied voltage, respectively, a , b are constant, and R is resistance in series with the ZnO nanowires. Firstly, assuming $R = 0$, a and b can be evaluated by Eqn.(3) fitting to the low emission current part of the measured data. The resistances corresponding to undoped, 0.1 and 0.3 SZO nanowires are estimated to be 85.43, 24.53, and 8.53 k Ω , respectively, as shown in Fig. 10. This decrease in resistance is proportional to the increase in Sn dopant concentration. The lower resistance of SZO nanowires is also attributed to that Sn-enhanced the electron density and consequent increase of the conductivity of the ZnO nanowires.

IV. Conclusion

In summary, the single crystalline SZO nanowires are fabricated at 800 °C under the conditions of a vapor-liquid-solid (VLS) growth process. This Sn addition also affects the ultra-violet (UV) emission of SZO nanowires. Furthermore, the 0.3 SZO nanowires exhibit good field emission characteristic of 0.05 V/ μ m as the turn-on electric field and 0.5 mA/cm² as the current density. The lower work function of the SZO nanowires is due to the higher carrier concentration and the smaller diameters that result in the higher field enhancement factor. Therefore, the SZO nanowires could be used for fabricating optoelectronic and field emission devices.

V. Reference

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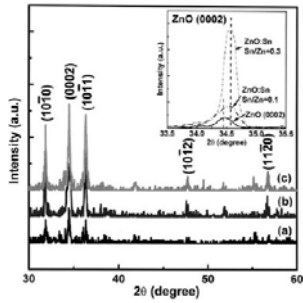


Fig. 1 XRD patterns of the (a) ZnO, (b) 0.1, and (c) 0.3 SZO nanowires. The inset is (0002) peak shifted by Sn dopant.

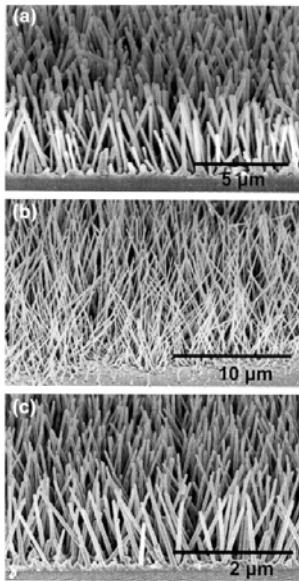


Fig. 2 SEM images of the (a) ZnO, (b) 0.1, and (c) 0.3 SZO nanowires.

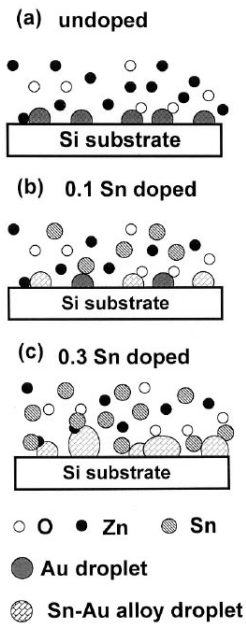


Fig. 3 VLS growth process mechanism for, (a) undoped, (b) 0.1 and (c) 0.3 SZO nanowires.

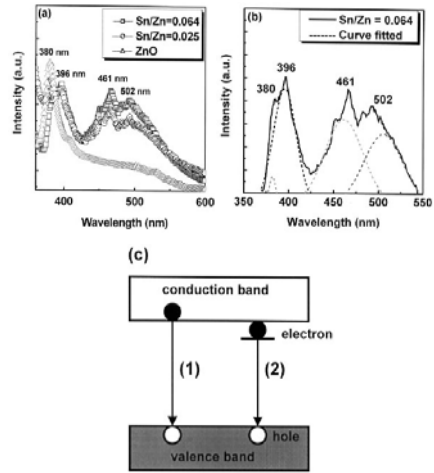


Fig. 4 (a) PL emission spectra of the up-doped and SZO nanowires. (b) PL emission curve fitted analysis for 0.3 SZO nanowires. (c) proposed energy band structure of the undoped and the SZO nanowires.

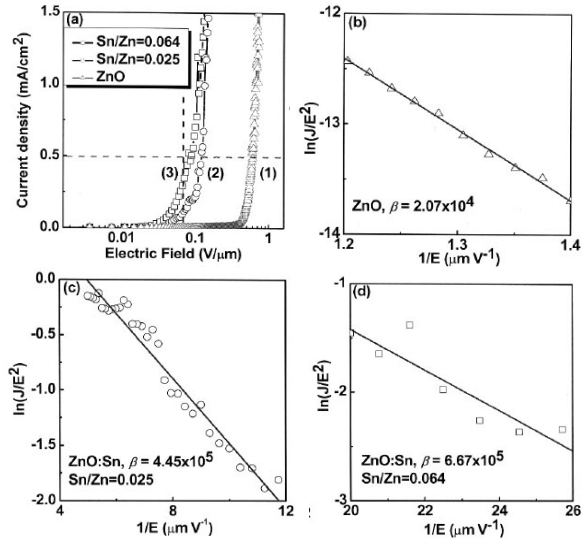


Fig. 5 (a) Field emission characteristics of the ZnO, (b) F-N plots of undoped ZnO, (c) F-N plots of 0.1 Sn doped, and (d) F-N plots of 0.3 Sn doped ZnO nanowires.

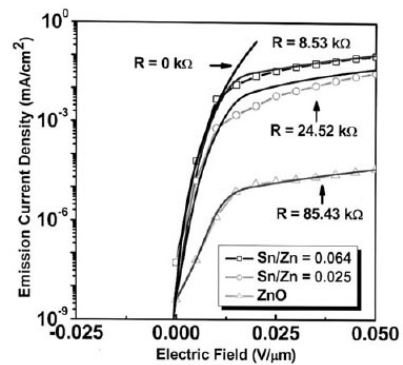


Fig. 6 Emission current density vs. electric field of the undoped, 0.1, and 0.3 SZO nanowires.