PHOTOLUMINESCENCE OF ZnO NANOSTRUCTURE PREPARED BY CATALYST - ASSISTED VAPOR - LIQUID - SOLID TECHNIQUE

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ABSTRACT

ZnO semiconductor nanostructures have been synthesized by thermal evaporation of mixture of ZnO and graphite powders. The thin layer of gold coated on Si substrates was used as a catalyst. The structure analysis shows high crystallinity of ZnO, their preferred orientation along the (0 0 2) plane of the wurtzite phase and their chemical purity. The scanning electron microscopy (SEM) images of products indicate that ZnO nanowires have a diameter of about 40 - 150 nm and a length of up to tens of micrometers. The morphology and structure of ZnO nanowires and nanorods depend on the thicknesses of the Au layers. The fact that Au nanoparticles are located at the tips of the nanowires represents a strong evidence for a growth process dominated by the vapor - liquid - solid mechanism. The low temperature photoluminescence spectra of the ZnO nanowires indicate a group of the ultraviolet narrow peaks and a blue - green very broad peak at 500 nm.

Keywords: Photoluminescence, ZnO nanostructure, vapor-liquid-solid mechanism

1. INTRODUCTION

Zinc oxide (ZnO) has been one of the most promising oxide semiconductor materials because of its good optical, electrical, piezoelectric properties and potential application. Numerous studies on the preparations and physical properties of ZnO films and, specially, nanoparticles have been reported.

Nanowires have been successfully fabricated by using various approaches including the vapor transport process, chemical vapor deposition, electrochemical deposition technique, and sol - gel *etc.*

In this work, we report on the fabrication, mechanism and features of ZnO nanowires using a vapor transport process via the vapor - liquid - solid mechanism. The origin of the luminescent peaks will be discussed.

2. EXPERIMENTS

ZnO nanostructures were synthesized by means of a vapor transport process on Si substrates (n -

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type, (1 0 0)) by using an Au as a catalyst. The Si substrates were ultrasonically cleaned in acetone for 30 min. The cleaned Si substrates were coated with a layer of Au using a sputtering technique. Source materials are mixture of ZnO and C powder (molar ratio is 1:0.1). Arrangement of experiment is shown in Fig. 1. The flow rate of argon was 500 sccm. The furnace was heated up to 1000°C and kept at the temperature for 60 min. After reaction at the temperature range of 500 - 800°C, the substrate surface was coated by white wax - like materials.

The crystal structure, composition of the ZnO nanostructures was analyzed by X - ray diffraction (XRD Bruker - AXS D5005) and energy dispersive X - ray analysis (EDX; Oxford Isis 300). The morphology of the ZnO nanostructure was characterized by scanning electron microscopy (SEM; JEOL - JSM 5410 LV). The photoluminescence measurement was done by using a spectrofluorometer (FL3 - 22 Jobin Yvon Spex, USA).

Fig. 1: Experimental set up for synthesis of ZnO nanostructures

3. RESULTS AND DISCUSSION

XRD patterns of ZnO products are given in Fig. 2. Most of the samples indicated a growth along the (0 0 2) direction. No peaks of Zn, but two peaks of Au (1 1 1) and (2 0 0) have been detected in the XRD patterns.

Fig. 2: XRD patterns of ZnO nanostructures on substrates coated with Au layers of 25 nm (a, b); 50 nm (c); 100 nm (d) in thickness

Fig. 3: EDX spectrum of ZnO nanowires on substrate with an Au layer of 25 nm in thickness

Figure 3 shows the EDX pattern of the ZnO nanowires, showing peaks due to Zn, O. The EDX spectrum clearly indicates that the nanostructures consist of pure ZnO.

The thickness of Au films played an important role in the growth of the nanowires. It was observed that when the thickness of the Au film increased from 25 to 100 nm, the diameter of the wires is increased as shown in Fig. 4.

Fig. 4: SEM of ZnO nanostructures deposited on substrates coated with Au layers of different thicknesses: (a, b) 25 nm, (c) 50 nm and (d) 100 nm

Figure 5 illustrates SEM images of ZnO nanowires ending with spherical nanoparticles. The presence of spherical nanoparticles at the end of the nanowires represents strong evidence for a growth process dominated by the VLS mechanism (Fig. 6). In the present work, carbon was used for reducing sublimation temperature of ZnO. The Zn and ZnO_{1-x} vapor is deposited on the Si substrate located downstream, and reacted with the Au catalyst to form Au - ZnO alloy droplets.

Fig. 5: SEM images of ZnO nanowires

Fig. 6: Mechanism of the growth of nanowires, nanorods

As the droplets become supersaturated in Zn and ZnO_{1-x}, ZnO nanostructures are formed. The size and shape of the nanocomposite Au - ZnO droplets directly control the diameter of the 1D nanostructure. Smaller diameter of the Au droplets favors the growth of thinner nanowires, whereas larger Au droplets help to grow thicker nanorods.

Fig. 7: PL spectrum of ZnO nanowires measured at 61.6 K

The photoluminescence (PL) measurements at low temperature were done for the ZnO nanowires (Fig. 7). Most of PL spectra have a blue - green broad peak and a group of ultraviolet (UV) narrow peaks.

The blue - green emission band was commonly attributed to a deep - level (oxygen vacancies, interstitial zinc), trap-state or surface state emission. Because, even at low temperature, ZnO is a nonstoichiometric oxide and presents deep defects such as oxygen vacancies (V_o^0), interstitial zinc (Zn_i^0), ionized oxygen vacancies (V_o^+), ionized interstitial zinc (Zn_i^+) [1].

In this work, we concentrate on the investigation and explanation of the origin of UV emission peaks. PL spectra of the ZnO nanostructure measured in the temperature range from 15 K to 300 K are shown in Fig. 8.

Fig. 8: The low temperature PL spectra of ZnO nanowires

It can be seen that the PL spectra exhibited one broad peak at about 3.113 eV (peak IV) and three narrow peaks (III, II, I) at around 3.243 eV, 3.316 eV, 3.362 eV, respectively. As the temperature increases, these peaks are shifted toward the low energy side, while their intensity decreases. Peak I disappeared at temperature approximate to 166.1 K, whereas two peaks II, III exist until room temperature.

In order to clarify the origins of emission peaks, the experimental data were fitted by symmetric Pearson VII function (reliability factors > 99.3%).

$$y = A \frac{2\sqrt{m}e^{\Gamma(2^{1/m}-1)}}{\pi w_h e^{\Gamma(m-0.5)}} \left[1 + 4 \frac{2^{1/m}-1}{w_h^2} (x-x_C)^2 \right]^{-m}$$

where A is integrated intensity, w_h is full width at half maximum (FWHM), m is peak flack parameter, x_C is peak position, and Γ is function defined as:

$$\Gamma(a) = \int_0^\infty t^{a-1} e^{-x} dt \quad (a > 0)$$

From the fitted results, we have found the position, integrated intensity and FWHM of UV peaks.

Fig. 9 shows the position of these peaks as a function of temperature. As it can be seen from this figure, the experimental values of peak I are fitted rather well to the Varshni's curve calculated by using Varshni's semiempirical formula [2]:

$$E(T) = E(0) - \frac{\alpha T^2}{T + \beta}$$

where $E(0)$ is position peak at 0 K, α and β are fitting parameters.

By curve fitting the experimental data in Fig. 10, we found that $\alpha = -9.8 \times 10^{-4}$ eV/K, $\beta = -800$ K and $E(0) = 3.369$, 3.324 and 3.251 eV for peaks I, II, III, respectively.

Based on fitting results, peak I can be ascribed to a neutral donor - bound exciton (denoted by D^0X).

Fig. 9: The observed peak energy of UV peak as a function of temperature

Peak II is still maintained up to room temperature, and its position varies with temperature more slowly than the energy band gap. Thus, this peak is attributed to the recombination of bound charge carriers on impurities with free carriers in the allowed bands (BF). In our case, the sample is an n - type semiconductor, so peak II can be the result of recombination between an electron bound on a donor and a free hole in the valence band (BF) [3]. The energy distance between peaks II and III at different temperatures is about 73 meV, this value is approximate to long optical (LO) - phonon energy of 72 meV. Hence, peak III can be attributed to the phonon replica of peak II (BF - LO).

Figure 10 shows the integrate PL intensity of D^0X and BF peak as a function of temperature. It was found that the integrated PL intensity could be fitted by formula [4]:

$$I(T) = \frac{I(0)}{1 + Ae^{\frac{E}{k_B T}}}$$

where $I(0)$ is the emission intensity at 0 K, A is a constant, E is activation energy of the thermal quenching process and k_B is Boltzmann constant.

Fig. 10: The temperature dependence of integrated intensity of $D^\circ X$ and BF peaks

By curve fitting the experimental data in Fig. 10, we found that $E = 13.5$ meV and 42.3 meV for $D^\circ X$ and BF peaks, respectively. The value of 13.5 meV is close to the value of the binding energy of the exciton bound to the neutral donors, experimentally obtained to be 12 meV [5]. The value of 42.3 meV being larger than thermal activation energy at room temperature (~ 26 meV) indicates the possibility of existence of the BF peak at high temperatures.

Fig. 11: The observed FWHM of $D^\circ X$ and BF peak as a function of temperature

FWHM (Γ) of peak $D^\circ X$, BF as a function of temperature is shown in Fig. 11. It was found that FWHM could be fitted by following [6]:

$$\Gamma(T) = \Gamma(0) + \Gamma_{LA}T + \frac{\Gamma_{LO}}{e^{\frac{E_{LO}}{k_B T}} - 1}$$

where $\Gamma(0)$ is the broadening parameter at 0 K, Γ_{LA}, Γ_{LO} are parameters measured by

weighting of LA, LO phonons, respectively, and E_{LO} is the energy of LO phonons.

From the fitting we obtain $E_{LO} = 73.9$ and 72.5 meV for D⁰X and BF peak, respectively. Such values are in good agreement with the previously reported value of 72 meV.

The broad peak at about 3.113 eV (peak IV) is interpreted as a donor - acceptor pairs (DAP) emission. The position of DAP emission is described as:

$$h\nu = E_g - (E_A + E_D) + \frac{q^2}{\epsilon r}$$

where E_g is the band gap, E_A and E_D are the acceptor and donor binding energy, respectively, q is the electrical charge of the acceptor and donor ions, ϵ is the dielectric constant, and r is the donor - acceptor distance.

With increasing temperature, carriers on donor-acceptor pairs with small distance r are released into the band, which results in extinguishing the high-energy side of DAP emission line, and the line is shifted to the low-energy side as observed in our experiment.

4. CONCLUSIONS

The ZnO nanowires have been fabricated by controlling the conditions of the vapor - phase transport. The ZnO nanowires with diameter of about 40 - 150 nm and length to tens of micrometer show the typical wurtzite crystal structure. The growth process is explained by means of a VLS mechanism. The PL spectra of ZnO nanowires in the near band edge region were investigated in temperature range from 14.5 K to 300 K. Four UV emission peaks were attributed to neutral donor - bound exciton (D⁰X), recombination of an electron bound on donor with a free hole in the valence band (BF), phonon replica of the peak BF with one LO - phonon energy (BF-LO), donor - acceptor pairs (DAP).

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