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CHANGING THE SHAPE OF ZnO NANOSTRUCTURES BY CONTROLLING Zn VAPOR RELEASE

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Abstract. Our fabrication of ZnO nanostructures was based on a thermal evaporation process of ZnO powder without the presence of a catalyst. The source material was pure ZnO powder mixed with different contents of graphite (molar ratio 1:1.2; 1:1.1; 1:1; 1:0.8, respectively). Temperature is the critical experimental parameter for the formation of different morphologies of ZnO nanostructures, Zn or Zn suboxide plays a crucial role for the nucleation of ZnO nanostructures. The structure of the deposited materials was investigated by X-ray diffraction, scanning electron microscopy. Photoluminescence measurements were performed.

1. Introduction

ZnO nanostructures are very promising for applications in field emission displays and photonic devices operating in blue and UV spectral ranges due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV) [1]. Therefore, fabrication and properties of ZnO nanostructures have attracted considerable attention recently [2,3].

In this work, we fabricated ZnO nanowires from a mixture of ZnO and carbon in order to investigate the change in the shape of obtained structures by varying the release rate of Zn vapor.

2. Experiments

ZnO nanowires array was fabricated by a thermal evaporation process of the ZnO - C powder mixture. The mixture of zinc oxide and graphite powders was loaded in a quartz boat and placed in the center of a horizontal quartz tube furnace, where the temperature, pressure and evaporation time were controlled. The thermal evaporation of the ZnO + C powder source was performed at 1000 °C for 1 h under an argon flow with the rate of 500 standard cubic centimeters per minute (sccm) maitaining a constant pressure of 0.2 atm in the furnace chamber. Several cleaned silicon substrates were placed in sequence at the downstream in the quartz tube for collection of the products.

The as-synthesized products were characterized by X-ray diffraction (XRD) (Siemens D505 with Cu K$_\alpha$ radiation), Scanning electron microscope (SEM) (JSM 5410 LV) for the analysis of the microstructure. Photoluminescence measurements were performed by using a FL 3 - 22 spectrometer with a Xenon lamp as the excitation source at room temperature.

3. Results and discussion

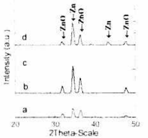

Fig.1. XRD patterns of the as - made ZnO nanowires with different ratio of ZnO (a) x = 0.8; (b) x = 1.0; (c) x = 1.1; (d) x = 1.2

Fig.1 shows the XRD patterns of as synthesized ZnO nanowires with the source material with different contents of graphite (molar ratios of pure ZnO and graphite are x = 0.8, 1.0, 1.1 and 1.2, respectively).

The crystallinity of the ZnO nanowires, the existence of zinc flakes in the as-made sample as x = 0.8 and 1.0 were studied by X - ray diffraction. From these spectra, it is found that both samples with x = 0.8 and 1.0 show a typical wurtzite hexagonal structure like bulk ZnO with unitcell constants of a = 3.248 Å and c = 5.206 Å.

A representative energy dispersive X-ray (EDS) spectrum of the nanowires is depicted in Fig.2. Only the peaks associated with Zn and O atoms are seen in the EDS spectrum, leading to the obvious fact that the nanowires are indeed ZnO material.

The SEM images in Fig.3 exhibit the side view of different shapes of ZnO nanowires grown on a Si substrate in the temperature range (650-500^{0}C). These images show that the nanowires are grown not from the Si substrate but from a thick layer of ZnO polycrystalline material on the top of the Si substrates, indicating that the thick layer is formed before the formation of the nanowires.

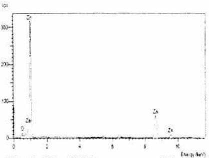

Fig.2. The EDS spectrum of the ZnO

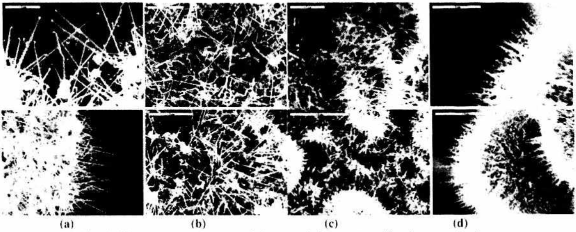

Fig.3. The side view images of the material grown on Si substrates in the temperature range (650 - 500 oC) with different ratio of ZnO and carbon powder (a) x = 1.2; (b) x = 1.1; (c) x = 1.0; (d) x = 0.8

Under the high temperature condition (~ 1000^{0}C), carbon reduced ZnO into Zn or Zn suboxide [1]. At the low temperature site (lower than 907 ^{o}C, i.e., the boiling point of Zn), ZnO vapor produced by the reactions:

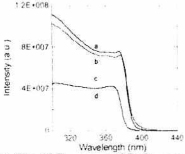

Fig.4. The PLE spectra of ZnO nanowires on Si subtrates with different contents of C (a) x = 0.8; (b) x = 1.0; (c) x = 1.1; (d) x = 1.2

$$ZnO + C \rightarrow Zn + CO_2$$

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Zn vapor should condense on the iner wall on the quartz tube forming liquid droplets, which are ideal nuclei of ZnO nanowires for the vapor-liquid-solid (VLS) reaction [1]. (Fig.3, a, b).

Figure 4 presents photoluminescence excitation (PLE) spectra of nanowires with different ratio of ZnO and C powder on Si substrates for the green emission monitored at 500nm. The peak of excitation spectra appears at 371nm (≈ 3.34 eV) approximated to the energy band edge.

Photoluminescence spectra of ZnO nanowires at room temperature were measured and shown in Fig.5. A weak UV band at 380 nm and a strong green band at 500 nm were detected from all ZnO products. The UV band emission of ZnO, maybe, has been understood to be related to the exciton emission, while the mechanism of green emission has been suggested mainly due to the present of various point defects, either extrinsic or intrinsic, which can easily form recombination centers.

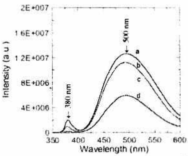

Fig.5. Room temperature PL spectra of ZnO nanowires with different contents of carbon (a) x = 0.8; (b) x = 1.0; (c) x = 1.1; (d) x = 1.2

4. Conclusions

Using zinc oxide and graphite powders as source materials, ZnO nanowires were farbicated on Si substrates at low temperatures. The growth process was attributed to a VLS mechanism. The ZnO nanowires exhibit an emission at UV and green region.

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