

Zinc Oxide Nanostructures synthesized by the Oxidation Reaction Method

การสังเคราะห์โครงสร้างนาโนซิงค์ออกไซด์โดยวิธีปฏิกิริยาออกซิเดชัน

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บทคัดย่อ

นาโนซิงค์ออกไซด์ที่มีลักษณะเหมือนไม้พายถูกสังเคราะห์ขึ้นโดยง่ายด้วยวิธีปฏิกิริยาออกซิเดชันของผงโลหะซิงค์ (99.9%) ที่อุณหภูมิ 900 องศาเซลเซียสเป็นเวลา 1 ชั่วโมง บนแผ่นซิลิกอน ลักษณะพื้นผิวและองค์ประกอบของนาโนซิงค์ออกไซด์จะถูกตรวจสอบลักษณะปั้งซ์ด้วยกล้องจุลทรรศน์แบบส่องกราด (SEM) และเทคนิคสเปกโตรสโคปีของอนุภาคอิเล็กตรอนที่ถูกปลดปล่อยด้วยรังสีเอกซ์ (XPS) ตามลำดับ ซึ่งมีการตรวจพบว่านาโนซิงค์ออกไซด์มีลักษณะเหมือนไม้พายที่สังเคราะห์ได้ปกคลุมกระจายทั่วบริเวณบนแผ่นซิลิกอน ผลจากสเปกตรัมของโฟโตลูมิเนสเซนส์ (PL) แสดงพีคเล็กๆ ที่ช่วงความยาวคลื่น 380 นาโนเมตร (3.26 eV) ซึ่งสอดคล้องกับแถบช่องว่างพลังงานของนาโนซิงค์ออกไซด์และความเข้มของพีคช่วงความยาวคลื่นของแสงสีเขียวที่ปรากฏเด่นชัดประมาณ 538 นาโนเมตรจะสอดคล้องกับตำแหน่งว่างของออกซิเจน (oxygen vacancy) จากคุณสมบัติโฟโตลูมิเนสเซนส์ของนาโนซิงค์ออกไซด์ที่สังเคราะห์ได้เป็นที่คาดหวังว่าจะสามารถนำมาประยุกต์ใช้ในตัวตรวจวัดแสงหรือจอแสดงผลในอนาคต

คำสำคัญ : ซิงค์ออกไซด์ โครงสร้างระดับนาโนเมตร ปฏิกิริยาออกซิเดชัน

Abstract

Zinc oxide (ZnO) nano-paddle-like nanostructures were synthesized by a simple oxidation reaction of metallic zinc powder 99.9% at a temperature of 900°C for 1 hour on a silicon substrate. Surface morphologies and compositions of ZnO nanostructures were characterized by field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) respectively. It was found that the surface of silicon was completely covered by ZnO nanostructures. Photoluminescence (PL) spectrum showed a small peak at 380 nm (3.26 eV), which corresponded to the band gap of ZnO nano-paddle-like. The high intensity green emission peak at around 538 nm was assigned to ionized oxygen vacancy defects. The photoluminescence properties have promising applications in the future, such as photo-detectors or flat display applications.

Keywords: Zinc oxide (ZnO); Nanostructure; Oxidation reaction

Introduction

Zinc oxide (ZnO) nanostructures have attracted a lot of study and active research for applications in electronics and optoelectronics due to their unique properties, such as a wide direct band gap of 3.2 eV and large exciton binding energy

of 60 meV at room temperature compared with 25 meV for GaN [1-6]. Moreover, ZnO is one of the materials that can be formed in a variety of nanostructures, including zero dimensional (0 D), one dimensional (1 D), and dimensional (2 D). The surface of nanostructures has importance because

it can determine the electrical and optoelectronic properties of nano-devices. The ZnO nanostructure is an especially interesting material because of its large surface-to-volume ratio. Due to these special properties, ZnO nanostructures are widely used in many applications, such as 1D ZnO nanostructures including nanowires, nanorods, nanobelts, nanowhiskers, and nanoneedles, all promising candidates for field emission display and excellent electronic transport properties [7 - 10]. 2D of ZnO nanostructures such as nanosheets, nanowalls, and nano paddle (less commonly reported) are good candidates for application as gas sensors, photo-detectors, and solar cells [11-12]. The morphology of ZnO nanostructure can be synthesized depending on the growth temperature, zinc source, and method. Up to now, nanostructures of ZnO can be synthesized by several techniques, such as chemical vapor-deposition (CVD), metal organic chemical vapor deposition (MOCVD), catalyst assisted vapor-phase transport, the porous template method, electrochemical deposition, and hydrothermal process [13- 17]. These above mentioned techniques are complicated and expensive. However, the oxidation reaction method is widely used in the synthesis of nanostructured materials because of its simplicity and low cost techniques [18-21]. Thus, this work reported the investigation of the ZnO nano-paddle-like using the oxidation reaction method. ZnO nanostructures were synthesized from metallic zinc powder 99.9%

at a temperature of 900°C for 1 hour on a silicon (100) substrate.

Experiments

The ZnO nano-paddle-like was synthesized on a silicon substrate by a simple oxidation reaction method. Prior to synthesis of ZnO nanostructures, the Si samples (2×2 cm² in sizes) were cleaned by using acetone, ethanol, and de-ionized water in an ultrasonic bath for a period of 30 minutes for each solvent and then dried with nitrogen gas. 0.2 g of Zn powder with purity 99.9% was put into an alumina boat, then the cleaned Si substrate was put on the upper side of zinc powder in the boat. Next, this boat was placed at the center of a reaction tube. ZnO nano-paddle-like was performed by heating the Zn powder at a temperature of 900°C for 1 hour in the ambience of oxygen at a flow rate of 20 standard cubic centimeters per minute (sccm) into the reaction tube. The pressure of this process was kept at 6.2×10^{-1} Pa under the gas flow. After the reaction tube cooled down to room temperature, it was observed that the color of the zinc powder changed from grey to white of ZnO nanostructures. The surface morphologies of the nanostructures were viewed under a field emission scanning electron microscopy (FE-SEM). X-ray photoelectron spectroscopy (XPS) was used for the chemical analysis investigation. The photoluminescence spectroscopy (PL) was performed at room temperature using a Jobin Yvon HR 800 UV.

Results and Discussion

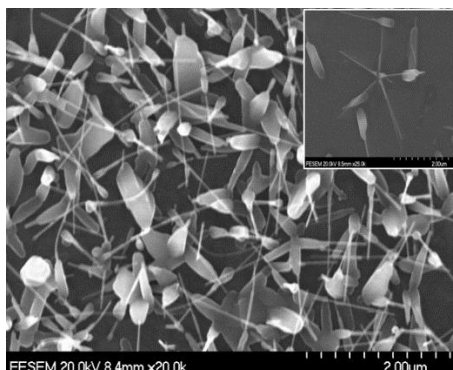


Figure 1 FE-SEM image of the ZnO nano-paddle-like that grew on the Si substrate. The inset shows a high magnification.

Figure 1 shows the FE-SEM images of the ZnO nano-paddles grown at 900°C for 60 minutes. As can be seen from the images, the head of the paddle is in the range of 100 to 140 nm in width and 400 to 600 nm long, the length of the handle being about 0.6 microns. We found that the ZnO nano-paddles were obtained at a temperature of 900°C for 60 min. Because the metallic Zn has a low melting point of 420°C, it exists in the form of large droplets at temperatures higher than its melting point because of its high surface tension. This leads to a reaction between the oxygen and Zn atom in these droplets and the formation of ZnO nanostructure was obtained. For the temperature of 500°C, we found that the oxidation reaction of Zn and O atom were not complete. When the temperature is increased above 900°C, the reaction process between metallic Zn and O atom is hardly controllable due to the high evaporation of Zn powder (boiling point: 907°C). Furthermore, ZnO with different nanostructures can be synthesized depending on the growth parameters, such as growth time, gas flow rate, pressure, and impurities of the zinc. All results have been reported in our previous research [22-25].

The compositions of ZnO nano-paddle-like nanostructures were determined by XPS techniques as shown in figure 2. The survey XPS spectrum shows that there are strong Zn and O peaks, with a small C peak suggesting that the synthesized product is pure ZnO as shown in figure 2(a). The Si peak disappeared from the XPS spectra because the ZnO nano-paddles cover the whole surface of the Si substrate [26]. The two peaks in figure 2(b) are located at 1022.45 eV and 1045.47 eV corresponding to the doublet of Zn 2p_{3/2} and Zn 2p_{1/2} respectively, as reported for ZnO [27-28]. The high intensity and sharp peak at 1022.45 eV for the Zn2p_{3/2} core level is associated with the Zn species in the completely oxidized state. Figure 2(c) show the oxygen 1s spectrum in ZnO nano-paddle-like nanostructures. The multiple peaks that form a curve to fit the Gaussian function are located at 529.3 eV, 531.05 eV, and 531.50eV. The intense peak at 529.3 eV corresponds to O²⁻ ion in wurtzite structure surrounded by Zn atom with a full complement of nearest neighbor O²⁻ ions. The two weaker peaks at 531.05 and 531.50 eV can be attributed to the chemisorbed oxygen (C-O bond). The proportion of Zn atom to O atom is close to

60:40 (3:2), after subtraction of the adsorbed oxygen species, indicating that an excess of Zn^{2+} in the product. The O^{2-} deficiency on the surface can capture and trap electron. These results can enhance photo-catalytic activity under visible-light irradiation.

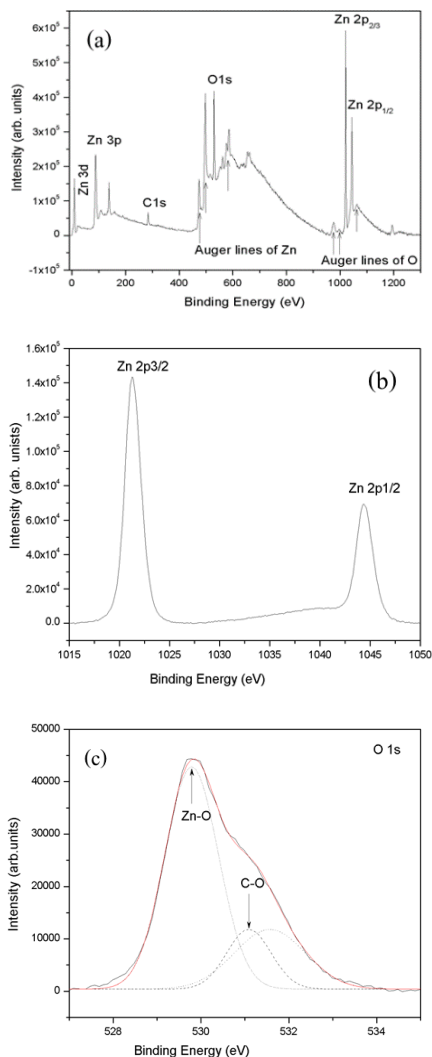


Figure 2 XPS spectra of the synthesized ZnO nano-paddles-like, (a) full range surveyed spectra, (b) zinc 2p spectra, (c) oxygen 1s spectra.

The room temperature PL spectra of the ZnO nano-paddle-like in the wavelength range of 350 to 700 nm is shown in figure 3. It was observed that the weak peak near band edge ultraviolet (UV) peak is located at 380 nm (3.26 eV). Another peak in the region of 450 to 650 nm is very strong. These two peaks correspond to near band-edge UV emission and the green emission respectively. The UV emission band can be explained by the near band-edge transition of the wide band gap of ZnO nano-paddle-like. The recombination of free excitons through an exciton-exciton collision process, the peak at 538 nm, is due to the deep-level emission related to the defects such as oxygen vacancies and Zn interstitials. A very strong defect emission peak shows that a large number of ionized oxygen vacancy defects present on the surface of ZnO nanostructures. These results correspond to trapped surface or subsurface oxygen vacancies. Due to the high surface-volume ratios of ZnO nanostructures and good results from PL spectra, the grown ZnO nano-paddle-like can offer applications in photo-detectors, gas sensing, and other devices.

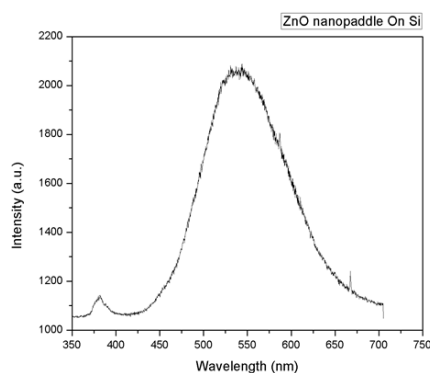


Figure 3 Photoluminescence spectra of ZnO nano-paddles-like grown on Si substrate.

Conclusion

ZnO nano-paddle-like nanostructures have been successfully synthesized on a silicon substrate by the oxidation reaction method at a temperature of 900°C for 1 hour. The surface morphology of the ZnO nanostructure was investigated using FE-SEM, XPS and PL. The high intensity peak around 538 nm in the visible light region was observed by PL spectra. The large surface to volume ratio of ZnO nano-paddles and the O²⁻ deficiency on the surface can capture and trap electron, thus enhancing photo-catalytic activity under visible-light irradiation. These results are ideal materials for use in photo-sensors or photo-detectors.

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