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Influence of annealing ambient on the structure, photoluminescence and photocatalytic activity of low temperature grown ZnO nanowires

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ABSTRACT

ZnO nanowires were synthesized via a low-temperature (90 °C) hydrothermal route on glass substrates pre-deposited with a ZnO seed layer. The influence of different annealing ambient conditions (air or vacuum) on the structure, photoluminescence and photocatalytic activity of ZnO nanowires was investigated by Raman spectroscopy, X-ray diffraction, photoluminescence (PL) and photochemical reactions etc. It was found that there existed graphitic carbons on the surfaces of ZnO nanowires after vacuum annealing. The PL intensity of ZnO nanowires with the graphitic carbons was significantly reduced while the photocatalytic activity was enhanced, indicating that the graphitic carbons could decrease the recombination probability of photo-induced carriers.

1. Introduction

Well-aligned ZnO nanowires with high surface areas have been extensively studied owing to their potential technological applications, such as laser diode [1], solar cell [2], photodetector [3], and photocatalyst [4]. Various methods have been developed to synthesize ZnO nanowires, including chemical vapor deposition, pulse laser deposition and hydrothermal method. Among them, hydrothermal

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method is an economical and low-temperature fabrication method. However, the large defect concentration is inevitable for the synthesis of ZnO nanowires during a low-temperature hydrothermal route, such as surface defects, near surface traps and surface adsorbed species [5,6], which maybe result in passivation or inefficient electron transport [7]. In general, a post annealing treatment is a effective way to modify the surface defects. Although the effects of post-annealing in forming gas (90% N_2/10% H_2), oxygen and air on the optical properties of low-temperature grown ZnO nanowires were studied [8–11], the investigation on the influence of air and vacuum ambient during the post-annealing process on the photoluminescence and transport mechanism of photo-induced carriers of low temperature grown ZnO nanowires has not been reported yet. In this paper, the effects of different annealing ambient conditions (air or vacuum) on the structure, photoluminescence and photocatalytic activity of ZnO nanowires are investigated. It is found that graphitic carbons are detected in the nanowires after vacuum annealing at 500 °C. The effects of the graphitic carbons on the photoluminescence and photocatalytic activity of ZnO nanowires are discussed.

2. Experimental

2.1. Preparation of the samples

ZnO nanowires were synthesized from zinc nitrate in an aqueous solution. The procedure included two steps: coating ZnO seed layers on glass substrates first, then growing ZnO nanowires on the ZnO seed layers. The ZnO seed layers were prepared from the zinc acetate solution [12] by sol–gel spin coating, then were sintered in air at 500 °C for 2 h. The ZnO nanowires were obtained by putting the glass substrates with ZnO seed layers into a 20 ml aqueous growth solution with 0.0004 mol zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and 0.0004 mol hexamethylenetetramine (HMTA, $C_6H_{12}N_4$), and keeping at 90 °C for 3 h. Then the samples were rinsed with de-ionized water and dried in air at 90 °C. As-grown samples were annealed under air or vacuum at 500 °C for 1 h. The vacuum level was about 1.5×10^{-1} Pa.

2.2. Characterization

The Raman spectra were acquired by a Renishaw in Via Raman spectrometer with the backscattering geometry using the 514 nm line of an Ar ion laser as an excitation source at room temperature. X-ray diffraction (XRD) measurements were carried out by using a PANalytical X'pert MPD PRO with Cu Kα radiation (45 kV, 35 mA). Photoluminescence properties at room temperature were measured by using Gangdong F-320 photoluminescence spectrophotometer at an excitation wavelength of 325 nm. The morphologies of the samples were obtained by scanning electron microscope (SEM, MIRA3 XMU).

2.3. Photocatalytic measurements

The photocatalytic activities of the ZnO nanowires were evaluated by the photo-degradation of methyl orange (MO) in aqueous solution under 500 W high-pressure Hg lamp (λ = 365 nm) irradiation. The photo-degradation of MO was carried out in 3 quartz tubes with volume of 70 ml each. The substrate-supported samples were vertically immersed in the organic dye solution (50 ml, 20 mg/l) at the same suspension height, respectively. Before irradiation, the solutions were stirred for 20 min to ensure that adsorption/desorption equilibrium had been reached. The changes of MO concentration were estimated by the samples taken out from the solutions at intervals of 10 min. The photo-degradation efficiency was monitored by measuring the absorbance of the samples at its maximum absorption wavelength of 464 nm with ultraviolet–visible spectrophotometer (Jasco UV–vis spectrophotometer U4802) at room temperature. The concentration of MO as a function of time was calculated by the absorbency values of the original and measured samples.