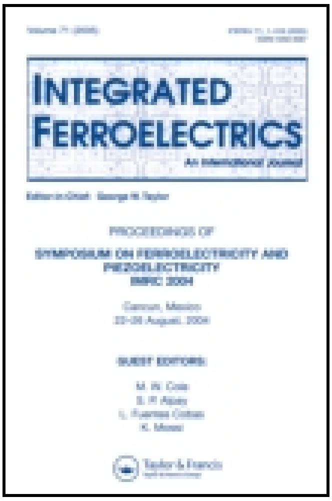

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Xing Wang[a], Xueying Chu[a], Haifeng Zhao[b], Shanshan Lu[a], Fang Fang[a], Jinhua Li[a], Xuan Fang[c], Zhipeng Wei[c], Xujie Wang[a], Peng Du[c] & Xiaohua Wang[c]

[a] Changchun University of Science and Technology, Changchun 130022, China

[b] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Dongnanhu Road, Changchun 130033, People's Republic of China

[c] State Key Laboratory of High Power Semiconductor Laser, Changchun University of Science and Technology, 7089 Wei-Xing Road, Changchun 130022, China

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Controllable Growth of Functional Gradient ZnO Material Using Chemical Vapor Deposition

XING WANG,[1] XUEYING CHU,[1,*] HAIFENG ZHAO,[2] SHANSHAN LU,[1] FANG FANG,[1,*] JINHUA LI,[1] XUAN FANG,[3] ZHIPENG WEI,[3] XUJIE WANG,[1] PENG DU,[3] AND XIAOHUA WANG[3]

[1]Changchun University of Science and Technology, Changchun 130022, China
[2]State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Dongnanhu Road, Changchun 130033, People's Republic of China
[3]State Key Laboratory of High Power Semiconductor Laser, Changchun University of Science and Technology, 7089 Wei-Xing Road, Changchun 130022, China

As a kind of semiconductor material, the morphology of zinc oxide directly affects its physical properties. By adjusting the ratio of the reaction source and the rate of the incoming gas flow, we obtained one-dimensional nanowire and two-dimensional nanoflag-like functional gradient material (FGM) using chemical vapor deposition (CVD) method. Compared with the one-dimensional nanowires, the growth of the two-dimensional ZnO FGM not only c-oriented, but other directions are also appeared. Photoluminescence results show that the FGM has a higher visible/UV emission intensity ratio than the nanowires for several orders of magnitudes. Meanwhile, the growth mechanism of these nanostructures were discussed in details.

Keywords ZnO; chemical vapor deposition (CVD); functional gradient material (FGM)

1. Introduction

Functional gradient material (FGM) is a kind of material whose composition and structure in a particular orientation (one-dimensional, two-dimensional, three-dimensional) changes continuously to other orientations. FGMs usually present new types of performances and functions. In the late 1980s, Japanese researchers Newfield Masayuki first proposed the concept of functionally graded materials [1]. Then, great concerns were attracted in many areas of science [2]. During the past three decades, FGM has impressive achievements in the organizational structure, performance, preparation, material application and other aspects. FGM prepared by chemical vapor deposition (CVD) method usually add different energy

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*Corresponding authors. E-mail: chuxy608@163.com; fang_fang0131@126.com

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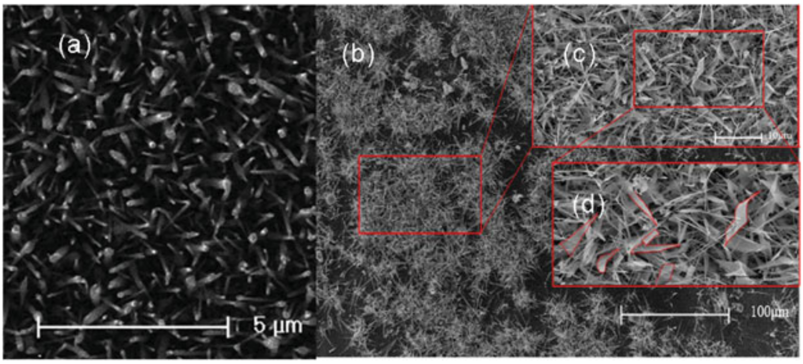

Figure 1. (a) SEM image of ZnO nanowires obtained by ZnO/C ratio at 2:1. (b)–(d) different resolution SEM images of ZnO nanoflags obtained by ZnO/C ratio at 1:1.

to raw gas, mixed in a reactor, then produce a solid phase film deposited on a substrate by a chemical reaction. By selecting synthesis temperature, adjusting the raw gas flow and pressure to control the gradient composition and structure of the deposited material, researchers have prepared C/C, Si/C and TiC/C series FGM by CVD[3].

Zinc oxide (ZnO) is a II–VI group semiconductor material with a hexagonal Wurtzite crystal structure. It has a wide and direct bandgap of 3.37 eV (at 300 K), a large free-exciton binding energy (60 meV), a strong cohesive energy of 1.89 eV, and a high optical gain (300 cm^{-1}). Simultaneously, it has high mechanical and thermal stabilities and radiation hardness. These excellent optoelectronic properties make ZnO become one of the most promising materials for optoelectronic devices, including display devices, UV-light emitters [4], transparent power electronic devices, gas-sensing sensors[5, 6], surface acoustic wave (SAW) devices and piezoelectric transducers [7]. So far, some groups have received zinc oxide nanostructures like nanowires [8], nanoribbons [9], nanorods [9], nanotubes [10], branched [11], flower-like [12], a hollow structure [9] and other different morphologies of ZnO. However, the synthesis method about nanoscale ZnO FGM is few reported.

In this article, the reaction source ratio and the rate of the gas flow were changed in a CVD process. Experimentally, we obtained two kinds of materials: one-dimensional nanowire and two-dimensional nanoflag-like FGM. The structure, the optical properties and the growth mechanism were discussed, respectively.

2. Experiments and Analysis

Firstly, 2g ZnO/C (2:1 or 1:1, wt%) mixed powder were prepared. The powder was placed in a quartz boat for two experiments. The quartz boat containing the mixture was placed in the central hot zone of the quartz tube. Then, a Au coated Si substrate were placed on another invert empty quartz boat. The distance between the sources and the substrate was kept as 5 cm. In experiment I (ZnO/C = 2:1), the flow rate of Ar gas was 20 sccm and the rate of oxygen was 10 sccm. In contrast, the flow rate of Ar carrier gas was varied from 20 to 10 sccm at a fixed oxygen flow rate of 10 sccm in experiment II (ZnO/C = 1:1). In these two experiments, the reaction temperature was controlled at 900°C for 30 min,

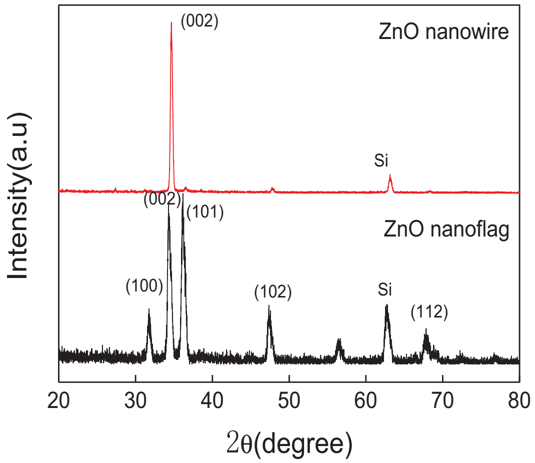

Figure 2. XRD patterns of ZnO nanowires and nanoflags.

and keeping the vacuum of 19 Pa. After reaction at 900°C, substrates were cooled down to room temperature naturally under the forming gas.

The morphologies of the nanowires and the FGM were examined by scanning electron microscopy (SEM). The crystalline quality was investigated by X-ray diffraction (XRD). For photoluminescence (PL) measurements, a He-Cd laser (325 nm) was used as an excitation source.

Figure 1 shows the SEM images of the samples we obtained. It can be found that ZnO nanowires can be obtained when the ratio of ZnO and C was kept as 2:1 (sample I, Fig. 1(a)). The diameter of the nanowire is between tens to one hundred nanometers. Figures 1(b–d) are SEM images of sample II (ZnO/C = 1:1) at different resolution. As shown in Fig. 1(d), at the top of the nanowires, there is another lateral growth blade structure (flag-like structure), which sized in few hundred nanometers.

The structure and the crystallinity of the samples are investigated by X-ray diffraction (XRD) (as shown in Fig. 2). Because of the one-dimensional structure, nanowire only (002)

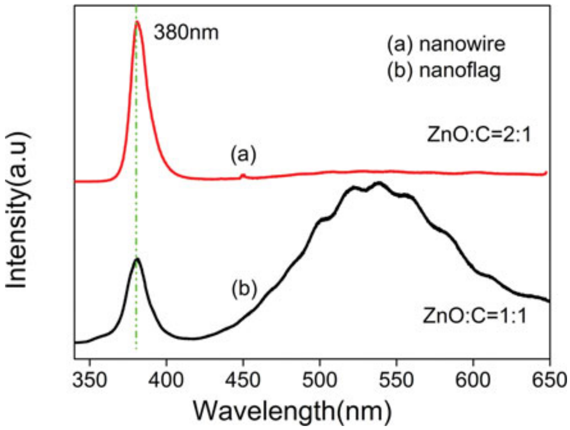

Figure 3. Room temperature PL spectra of ZnO nanowire (a) and nanoflag (b).

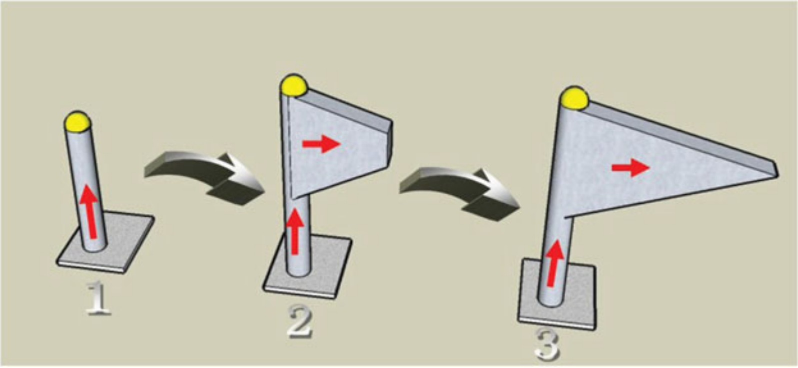

Figure 4. The schematic diagram of the growth mechanism of nanoflag-like FGM.

diffraction peak of wurtzite ZnO can be found in the XRD spectrum of sample I, which indicated that the crystals grow along a certain direction. This is in complete accord with the nanowire morphology observed in SEM image. In contrast, the XRD patterns of the flag-like FGM, we can observe the intensities of the diffraction peaks in two directions are very evidently, which are (002) and (001). It means that ZnO FGM growth not only along C-axis. We infer that the change of the morphology may mainly come from the changing of the gas flow rate. The reaction sources carried by the gas should be increased when the gas flow rate was enhanced in experiment II. There are more surface states at this excess source situation, which is beneficial to lateral nucleation growth and chemical adsorption.

In order to further evaluate the optical properties of the samples, the room temperature PL spectra of the ZnO nanowire (plot (a) in Fig. 3) and the flag-like nano structure (plot (b) in Fig. 3) were recorded, respectively. We can observe an intrinsic emission in the near UV region at 380 nm in the PL spectrum of ZnO flag-like FGM [13]. A visible light emission is very strong at 500–550 nm [14]. Since the FGM is composed of one-dimensional nanowire and two-dimensional nanoflag-like structures, higher surface states should be present in the ZnO FGM structure. It results in a strong response in the visible light region. In contrast, the ratio of the visible/UV emission of the ZnO nanowires is lower than that of the FGM for several orders of magnitudes. This feature of the ZnO FGM will greatly enlarge the application in the visible range such as light response devices, light detection devices, etc.

3. Growth Mechanism

Many researches indicate that gas flow rate is vital for the growth of FGM by CVD. In our experiments, Ar gas plays an important role in the transport of the reaction source. At a certain temperature and vapor pressure, more O_2 flow will make more Zn source deposited onto the substrate, which leading the growth rate increased. But the transport gas does not play the main role on powder reaction. When the gas reacted with the powder source, the disposition speed of the material will be decided by the reaction rate. Compared the growth of the nanoflag-like structure with the nanowires, we reduced Ar flow from 20 sccm to 10 sccm and keeping O_2 stable, result in the O_2 ratio greatly increasing to 50%.

During the one-dimensional nanowire growth process (ZnO and C in a quality ratio of 2:1), the (002) crystal plane has the minimum energy. This lead the nanowires grow along the corresponding direction. During the two-dimensional nanoflag-like structure growth process, we infer that the sheet structures are produced in the cooling down process. Such growth process includes two main steps: the adsorption process and the re-evaporation process to achieve dynamic equilibrium in the first step. It is good for the depositing of the nanowires. Adsorption process and the re-evaporation process are broken down during the cooling process at the second step. Meanwhile, we changed the gas ratio and enlarged the source bias, which supplied sufficient source for the lateral growth. Figure 4 exhibits the growth mechanism of the nanoflag-like FGM.

4. Conclusions

In conclusion, we obtained one-dimensional nanowire and two-dimensional nanoflag-like FGM by regulating the reaction source and the rate of the gas flow. Due to the high surface states, the intensity ratio of the visible/UV emission of the two-dimensional ZnO nanoflag-like FGM is higher than that of the one-dimensional nanowires for several orders of magnitudes. So far, few reports were concentrated on investigating of the ZnO FGM structure. This will greatly improve the FGM application in visible light detection and visible light response devices.

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