Growth of Low-dimensional ZnO Materials on Graphite Substrate

ZHANG Zhi-Kun1, ZHANG Yu-Zhi2, BIAN Ji-Ming1,2, SUN Jing-Chang3, QIN Fu-Wen1, LIU Wei-Feng1, LUO Ying-Min1

(1. School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China; 2. Key Laboratory of Inorganic Coating Materials of Chinese Academy of Sciences, Shanghai 200050, China; 3. School of Physics and Electronic Technology, Liaoning Normal University, Dalian 116029, China)

Abstract: Low-dimensional ZnO materials, (1-dimensional ZnO nanorods (NRs) and 2-dimensional ZnO films) were grown perpendicularly on graphite substrates. The crystalline structure, morphology, and optical properties of the as-grown low-dimensional ZnO materials were investigated with X-ray diffraction (XRD), field effect scanning electron microscope (FESEM), photoluminescence (PL), and the relative reflection spectra measurements. The high optical qualities of both ZnO NRs and ZnO films on graphite substrates were demonstrated by the dominant near-band edge emission and nearly undetectable deep level emissions of photoluminescence spectra under room temperature. The extremely low average reflectance was obtained from the low-dimensional ZnO materials/graphite structures in the spectra range from 300 nm to 800 nm, indicating that the obtained low-dimensional ZnO materials/graphite structures have significant opportunity for potential application in high-performance photovoltaic devices.

Key words: ZnO; graphite; photoluminescence; high power optoelectrics devices

As semiconductor devices become smaller dimensions of new electronics components are reaching nanometer scale. Understanding the fundamental properties of these nanostructure materials will provide opportunities to design advanced materials and to fabricate novel nano-devices for future applications. ZnO is probably the richest family of low-dimensional structures among all materials, which exhibits the most splendid and abundant configurations of nanostructures. The large direct band gap of 3.37 eV along with the large exciton binding energy of 60 meV, make ZnO a strong candidate for the next generation of ultraviolet (UV) light-emitting diode (LED) and lasing devices operating at high temperatures and in harsh environments[1-2]. Recent improvements in the control of background conductivity of ZnO and demonstrations of p-type doping have intensified interest in this material for applications in optoelectronic field[3]. As a material, ZnO can be grown as bulks, thin films and nanostructures. Especially, low-dimensional ZnO materials are of particular interest due to its excellent material characteristics and potential applications in constructing novel performance optoelectronic and electronic devices. Despite the considerable interests and rapid developments in low-dimensional ZnO materials, some essential issues with regards to the fundamental properties deserve further investigation. For example, an important and key challenge for the technological applications of high-power ZnO based devices is the severe heat dissipation problem, which might significantly affect the power persistence of a high-power device based on low-dimensional ZnO materials[4]. So far, a variety of methods have been employed to fabricate high-quality low-dimensional ZnO materials on various single-crystal substrates, such as sapphire, ZnO, and Si[5-7]. Nevertheless, the heat dissipation performance would not be satisfied due to the relatively high thermal resistance of these substrates. In addition, for some special applications such as large area foldable and high-power devices, it is necessary to transfer crystalline ZnO onto foreign substrates, such as flexible plastic or metal substrates[8-9]. However, it is difficult to separate the ZnO NRs from the above mentioned single-crystal substrate because of strong bonding between them, this presents one of the
major limits for such applications. Graphite substrates are considered to be a good solution to this issue, and the advantage of graphite lie in its low cost, non-toxic, excellent mechanical and chemical stability, especially the superior electrical and thermal conductivity even higher than copper\cite{10}, as well as the potential advantage for transferable optoelectronics devices since it consists of multi-layer system with nearly decoupled 2D graphene planes. All these features of the graphite substrate provide significant opportunities for fabricating various transferable and low thermal resistance high-power electronic and optoelectronic devices. In addition, the excellent heat dissipation performance of the graphite-insulator-semiconductor (GIS) diode compared with conventional sapphire based devices has been systematically demonstrated in our previous work, indicating that the GIS structure would be of special interest for the development of high-power semiconductor devices with sufficient power durability\cite{11}.

In this study, low-dimensional ZnO materials, including 1-dimensional ZnO nanorods (NRs) and 2-dimensional ZnO films were grown perpendicularly on graphite substrates. Considering the excellent material characteristics of low-dimensional ZnO materials and the versatile and fascinating features of graphite substrates, the achievements make it possible for the development of high performance ZnO based optoelectronic devices with sufficient power durability.

1 Experimental

ZnO NRs were grown on graphite substrates by the simple wet chemical base deposition (CBD) method, which was a high performance growth technique for ZnO nanostructures due to its obvious advantages of low-cost, low temperature operation and environmental friendliness\cite{12}. Detailed process by CBD technique can be found in our previous work\cite{12}. ZnO films were grown with the relatively simple process of ultrasonic spray pyrolysis (USP), which was successfully employed to grow p-type ZnO (ZnMgO) films and ZnO p-n homojunction LEDs in our previous study\cite{13}. The morphology and crystal structure of the obtained ZnO NRs and films were investigated by field effect scanning electron microscope (FESEM) on JEOL JSM 6700F, and X-ray diffraction (XRD) on SHIMADZU XRD-6000. Photoluminescence (PL) measurements were performed at room temperature by a Jobin Yvon HR320 spectrometer using a He-Cd laser (30 mW) with an excitation wavelength of 325 nm. The relative reflection spectra were measured on UV-VIS-NIR spectrophotometer (UV-3600) with integrated sphere.

2 Results and discussion

2.1 Structure characters of ZnO nanorods and films on graphite substrates

Figure 1 shows the typical XRD patterns of low-dimensional ZnO materials grown on graphite substrates. As shown in Fig. 1(a), a dominant ZnO (002) diffraction peak at 34.511° companied with a high intensity graphite (002) diffraction peak at 26.476° are observed, no peak from other compounds is detected besides that of ZnO. This means that the c-axis preferentially oriented ZnO NRs are vertical to the graphite substrate. As shown in Fig. 1(b), three diffraction peaks are obviously observed and can all be indexed to ZnO (100), (002) and (101). This indicates that ZnO films deposited on graphite substrate exhibit polycrystalline structure with no preferred orientation. It should be noted that it is nearly impossible to grow epitaxial ZnO single crystal film directly on amorphous graphite substrate due to the extremely large lattice mismatch between ZnO and amorphous graphite substrate as well as the relatively low growth temperature of USP, therefore only wurtzite ZnO polycrystalline films are successfully obtained and will be employed as buffer layer for transferable optoelectronics devices.

![Fig. 1 XRD patterns of low-dimensional ZnO materials grown on graphite substrates](image-url)

(a) 1-dimensional ZnO NRs; (b) 2-dimensional ZnO films
2.2 Morphology of ZnO nanorods and films on graphite substrates

Figure 2 shows the typical top-view and corresponding cross-sectional SEM images of low-dimensional ZnO materials grown on graphite substrates. ZnO NRs grown with CBD method at 95°C for 3 h and ZnO films grown with USP technique at 500°C for 5 min. As shown in Fig. 2(a), it is clearly seen that high density and random-aligned ZnO NRs with the average diameter and length to be ~55 nm and ~2.3 μm are synthesized on the graphite substrates. Furthermore, it shows that each ZnO NR has a uniform diameter along its entire length, indicating that the growth anisotropy is constantly maintained. Moreover, it should be noted that nearly all the individual ZnO NRs present well defined hexagonal prism shape with homogeneous diameter and smooth side facets, which will be particular beneficial for the formation of a natural whispering-galley-mode (WGM) nanocavity based on the total internal reflection at the cavity boundary. As for the ZnO films grown with USP technique (Fig. 2(b)), it can be seen that the ZnO films on graphite substrates present an irregular surface structure comprised of pyramidal-shaped ZnO nanosheets. The corresponding cross-section SEM images show that the ZnO films present uniform thickness and dense distribution.

2.3 Optical properties of ZnO nanorods and films on graphite substrates

Optical properties of ZnO NRs are important for many of their technological applications. Figure 3 presents the typical room-temperature PL spectra of low-dimensional ZnO materials grown on graphite substrates. Generally, the UV emission in ZnO PL spectra is accepted as the near-band-edge (NBE) emission which has an exciton nature[14]. On the other hand, the green emission band in ZnO PL spectra was usually observed for most ZnO samples reported in literature, which was believed to be closely related to the defect level induced by the defects of O vacancies, Zn interstitials or their complexes[15-16]. In this study, however, it should be noted that only strong NBE UV emission peaks were observed for the low-dimensional ZnO samples grown on graphite, yet the usually observed defect related deep level emissions were nearly undetectable, indicating high optical quality low-dimensional ZnO materials were successfully
achieved via this simple USP approach. Such low-dimensional ZnO materials with high optical quality are synthesized only by physical techniques like molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), and gold-catalyzed vapor-phase-transport (VPT). However, those are expensive and energy consuming processes since they are operated under extreme conditions. Here, high optical qualities low-dimensional ZnO materials were fabricated by simple low-temperature process.

Figure 4 shows the measured relative reflection spectra from 300 nm to 800 nm of graphite substrates (black solid line), the ZnO NRs/graphite, and the ZnO films/graphite samples (red solid line), respectively. The extremely low average reflectance of 0.196% and 3.7625% are obtained for the ZnO NRs/graphite and ZnO films/graphite structures in the spectra range from 300 nm to 800 nm. The lower reflectance compared with graphite substrates should be attributed to the enhanced incident light trapping by the scattering effect of surface nanostructure [17]. Given the fact that the transmission of graphite substrates was nearly zero, the correspondingly absorption in solar spectra would be rather high. Therefore, the reported ZnO NRs/graphite and ZnO films/graphite structures have significant opportunity for potential application in commercial photovoltaic devices due to its distinctive low reflectivity and correspondingly high absorption in solar spectra.

3 Conclusions

High optical quality low-dimensional ZnO materials, including 1-dimensional ZnO nanorods (NRs) and 2-dimensional ZnO films, were grown perpendicularly on graphite substrates. NBE UV emission were observed in room-temperature photoluminescence spectra for the annealed samples, yet the usually observed defect related deep level emissions were nearly undetectable, indicating high optical quality low-dimensional ZnO materials could be achieved on graphite substrates. Considering the excellent material characteristics of low-dimensional ZnO and the versatile and fascinating features of graphite substrates, the achievement makes it possible for the development of high performance ZnO based devices with sufficient power durability, especially for commercial photovoltaic devices due to its distinctive low reflectivity and correspondingly high absorption in solar spectra.

References:


石墨衬底上低维 ZnO 纳米材料的生长

张志坤 1, 章俞之 2, 边继明 1,2, 孙慧昌 3, 秦福文 1, 刘维峰 1, 骆英民 1
(1. 大连理工大学 物理与光电工程学院, 大连 116024; 2. 中国科学院特种无机涂层重点实验室, 上海 200050; 3. 辽宁师范大学 物理与电子技术学院, 大连 116029)

摘 要：本研究成功地在石墨衬底上制备了低维 ZnO 材料，即一维的 ZnO 纳米棒和二维的 ZnO 薄膜。采用 X 射线衍射、场发射扫描电镜、光致发光谱和反射谱等测量技术对石墨衬底上制备的低维 ZnO 纳米材料的晶体结构、形貌和光学特性进行了表征，结果发现在室温条件下，准一维的 ZnO 纳米棒和二维的 ZnO 薄膜都表现出了较好的近带边发射，基本探测不到由杂质和缺陷等引起的深能级发光，并且这种低维 ZnO 材料石墨衬底复合结构在 300–800 nm 光谱范围内具有较低的反射率。本实验结果对于 ZnO 基光电子器件性能的提高以及在太阳能电池领域的应用具有重要意义。

关 键 词：ZnO; 石墨; 光致发光; 高功率光电子器件
中图分类号: TB34 文献标识码: A