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Synthesis of One-Dimensional ZnO Nanorods by Oxidating Zinc Films Deposited with Magnetron Sputtering*

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Abstract: One-dimensional ZnO nanorods are synthesized by oxidating thin metal zinc films deposited on Si(111) substrates with radio frequency magnetron sputtering. The crystal structure, surface morphology, and optical properties of nanorods are investigated. X-ray diffraction (XRD) pattern, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses show that the synthesized single-crystal ZnO nanorods develop like hairpins along different radials, with a hexagonal wurtzite structure. The diameters of nanorods range between 30 and 60nm and lengths up to micrometers. Photoluminescence (PL) analysis shows that, under 280nm light excitation, a strong and sharp near band-edge UV light emission band at 372nm and a relatively weak green deep-level light emission band at 516nm are observed from the ZnO nanorods, which indicates excellent crystallization and optical quality of the fabricated ZnO nanorods.

Key words: magnetron sputtering; thermal oxidation; ZnO; nanorods; properties
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1 Introduction

One-dimensional nanostructures such as nanowires, nanotubes, and nanorods have attracted extraordinary attention for their potential applications in device and interconnect integration in nanoelectronics and molecular electronics[1,2]. Zinc oxide (ZnO) is a wide-gap (E_g= 3.37eV at 300K) compound semiconductor with large exciton binding energy (60meV) that is suitable for short-wavelength light emitting materials[3,4]. Thin ZnO films have been extensively investigated. Fu Zhuxi, et al[5] studies the cathodoluminescence of ZnO films deposited on Si substrates by reactive DC sputtering. Wang Qingpu, et al[6] studies the violet and UV photoluminescence of thin ZnO films deposited by radio frequency (RF) magnetron sputtering. Due to the promising application of ZnO materials in the nanoscale optoelectronic devices, it is of great significance to synthesize ZnO nanomaterials in single crystalline form and study their optical properties. Most of the ZnO nanomaterials studied are in the form of nanoparticles although needle crystals and polycrystalline ZnO nanowires have been previously reported[7~9]. But majority of the methods are based on vapor-liquid-solid (VLS) catalytic reaction growth mechanism, which will introduce contaminates unintentionally. In this paper, we report the synthesis of one-dimensional single crystalline ZnO nanorods with excellent optical properties by simple and novel method: thermal ox-

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idation of thin metal zinc films deposited on Si substrates by RF magnetron sputtering. Furthermore, the method can overcome the contaminated shortcomings of VLS catalytic reaction growth mechanism.

2 Experiment

First, thin metal zinc films were prepared in JCK-500A magnetron sputtering system with sputtering frequency of 13.56MHz. N-type Si(111) wafers were used as substrates in this study. High-purity (99.999%) metal zinc of 64mm in diameter was used as sputtering target. The sputtering chamber was pumped down to a basic pressure of about 6×10^{-4}Pa prior to sputtering process, then high-purity (99.999%) Ar and O_2(Ar∶O_2= 10∶1) were introduced to achieve a pressure of 1.1Pa. The output power of the RF power source was 150W. The distance between the target and the substrates was 80mm. Pre-sputtering was carried out for 5min and the sputtering deposition lasted for 50min. Thin metal Zn films with thickness of about 300nm were deposited on Si substrates at room temperature. Subsequently, the as-deposited films were placed on a quartz carrier and annealed in an open tube furnace in air at 700℃ for 1h. XRD measurements were carried out on Rigaku D/max-rB X-ray diffraction spectroscopy with CuKα line (40kV 100mA). PL spectrum measurements were carried out with a fluorescence spectrophotometer (FLS920) at excitation of 280nm from a 300W Xe lamp excitation source. SEM and TEM were measured on HITACHI H-8010 scanning and transmission electron microscopy. Energy-dispersive X-ray (EDX) analysis was also performed to analyse the samples. All measurements were carried out at room temperature.

3 Results and discussion

Figure 1 shows the XRD patterns of the as-deposited thin zinc films (a) and the sample annealed at 700℃ in air for 1h (b), respectively. The diffraction peaks in panel (a) located at 2θ= 36.3°, 38.9°, 43.1°, and 54.2° correspond to the ZnO(101), Zn(010), Zn(101) and Zn(012) planes, respectively, revealing that the sputtering layer is mainly composed of polycrystalline metal zinc. However, a small quantity of ZnO has already formed in the sputtering process. For a little oxygen is introduced into the sputtering chamber, we think, zinc atoms sputtered from the target may collide with oxygen atoms to form a small quantity of ZnO, which might act as the precursor for the post-growth of ZnO nanorods during thermal oxidation. Due to lower crystalline temperature, ZnO can be partly crystallized on substrates without purposive pyrogenation. The peaks in panel (b) located at 2θ= 31.6°, 34.3°, 36.2°, 47.4°, and 56.5°correspond to hexagonal wurtzite ZnO (100), (002), (101), (102), and (110) planes, respectively. No diffraction peaks corresponding to zinc have been identified, which suggests that thin zinc films have been completely oxided and translated into crystalline ZnO in the hexagonal wurtzite phase.

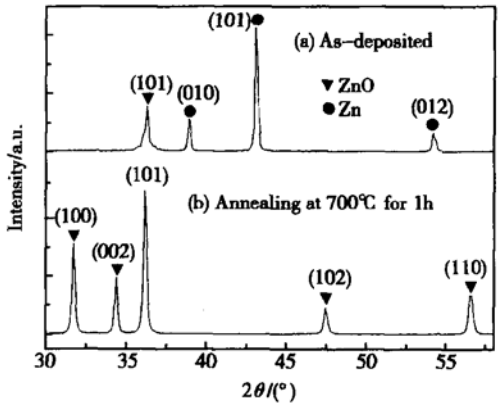

Fig. 1 XRD patterns of the as-deposited sample and the sample annealed at 700℃ for 1h

Figure 2 shows the SEM images of sample annealed with different magnifications at 700℃ for 1h. The results show that glazed and flat ZnO nanorods develop like hairpins along different radials, the diameters of which range between 30 and 60nm and the lengths are up to 2~ 8μm. EDX analysis of an individual nanorod (not shown here) in-

dicates that the ZnO nanorods are composed of Zn and O elements with an atomic ratio about 1 ∶ 1, corresponding to the chemical composition of ZnO, which further testifies the nanorods growing from the thin zinc films after thermal oxidation are ZnO nanorods.

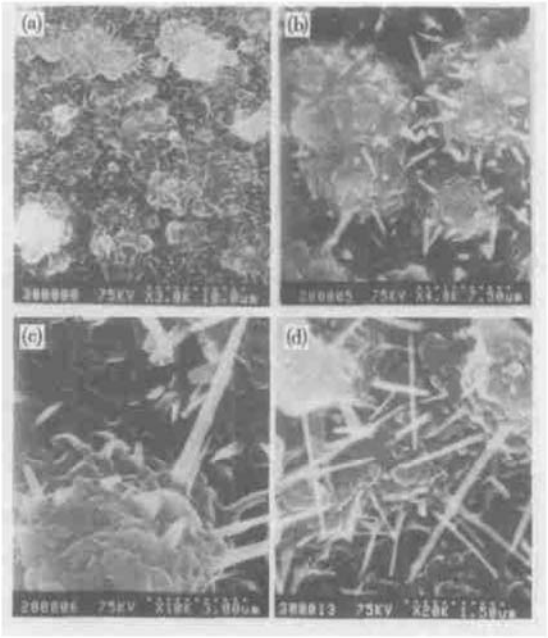

Fig. 2　SEM images of the sample annealed at 700℃ for 1h with different magnifications　(a) 3K; (b) 4K; (c) 10K; (d) 20K

In order to understand fully the crystalline structures of the ZnO nanorods, we turn to TEM with different amplified multiple of 20K (a) and 100K (b) in Fig. 3, which shows the high-magnification TEM images of the selected ZnO nanorod. It can be seen that the diameters of ZnO nanorods are about 50nm and the surface is glazed and flat without any curve and intertwist, indicating that the one-dimensional ZnO nanostructures are solid rods but not hollow tubes. The inset shows a selected area electron diffraction (SAED) pattern of the corresponding ZnO nanorod. Regular diffraction spots show that the one-dimensional nanorods are single crystalline ZnO nanorods with hexagonal wurtzite structures.

Figure 4 shows the PL spectrum of the sample annealed at 700℃ for 1h. Under 280nm light excitation, a very strong and sharp UV light emission

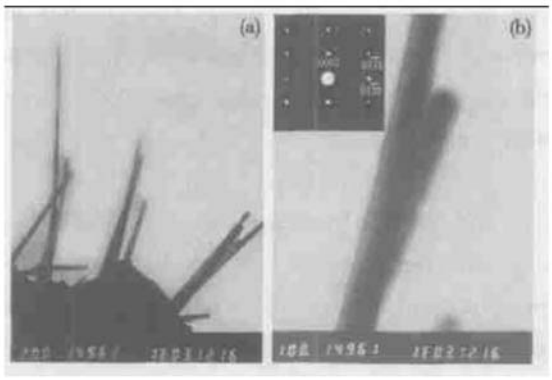

Fig. 3　TEM image of the sample annealed at 700℃ for 1h with different magnifications　(a) 20K; (b) 100K　The inset in (b) is the SAED pattern of the corresponding ZnO nanorod.

band at 372nm results from near band-edge excitons transition. Compared with bulk ZnO (at about 381nm), a small blue-shift is observed due to size confinements of nanomaterials. A relatively weak green light emission band at 516nm due to deep-level defects is also observed. The ratio of intensity of UV light and green light is up to 15, which indicates excellent crystallization and optical quality of the fabricated ZnO nanorods.

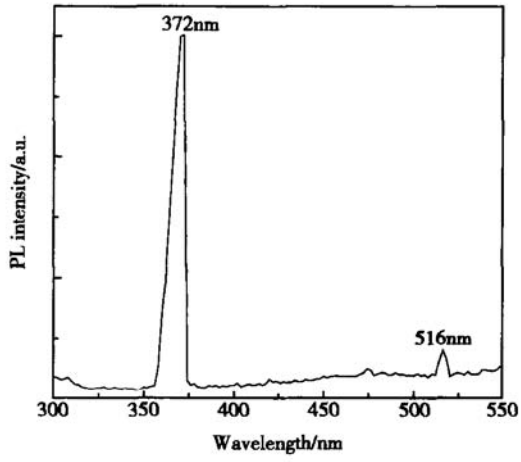

Fig. 4　PL spectrum of the sample annealed at 700℃ for 1h under 280nm light excitation at room temperature

4　Conclusion

Polycrystalline thin metal zinc films have been deposited on Si(111) substrates by RF magnetron sputtering. Because of O_2 introduced during sput-

tering process, a small quantity of ZnO has been formed in the as-deposited samples. After annealing in air at 700℃ for 1h, zinc films have been completely oxided and translated into thin polycrystalline ZnO films. SEM and TEM results show that glazed and flat ZnO nanorods develop like hairpins along different radials with diameters about 30~ 60nm and length up to 2 ~ 8μm. Regular diffraction spots of SAED show that the one-dimensional nanorods are single crystalline ZnO nanorods with hexagonal wurtzite structures. Under 280nm light excitation, a strong and sharp near band-edge UV light emission band at 372nm and a relatively weak deep-level green light emission band at 516nm were observed from the ZnO nanorods, which indicates excellent crystallization and optical quality of as-grown ZnO nanorods and makes them potential applications for optoelectronic nanodevices.

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热氧化磁控溅射金属锌膜合成一维 ZnO 纳米棒*

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摘要: 利用退火热氧化射频磁控溅射金属锌膜的方法在 Si(111) 衬底上制备了一维 ZnO 纳米棒, 同时用多种测试手段对样品的晶体结构、表面形貌和光学性能进行了研究. XRD, SEM 和 TEM 的测试结果表明, ZnO 纳米棒为单晶相六方纤锌矿结构, 呈头簪状向外发散生长, 直径在 30~ 60nm 左右, 其长度可达几 μm. PL 谱测试结果表明: 在波长为 280nm 光的激发下, 在 372nm 处有强的近带边紫外光发射和 516nm 处的较微弱深能级绿光发射. 说明合成的一维 ZnO 纳米棒的结晶质量和光学性能优良.

关键词: 磁控溅射; 热氧化; 氧化锌; 纳米棒; 特性

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