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Na-doped ZnO nanorods fabricated by chemical vapor deposition and their optoelectrical properties

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ABSTRACT

Na-doped ZnO (ZnO:Na) nanorods have been grown on Si substrates by a catalyst-free chemical vapor deposition method. Element analysis reveals that the doping concentration of Na is in the range of 0.5 −3.7 at.%. Morphological and electrical properties of the ZnO nanorods were found to be highly dependent on the Na concentration. Hall measurement indicates the realization of p-ZnO:Na nanorods with hole concentrations in the order of 10^{15} cm^{-3}. Temperature dependent photoluminescence measurement down to 10 K confirms the shallow acceptor level, which is ~132 meV. Desirable rectifying behavior has also been observed from the *I-V* characteristic of the p-ZnO:Na nanorods/ZnO/n-Si structure and the turn on voltage is ~2.5 V.

1. Introduction

ZnO has drawn tremendous attention due to its wide direct band gap (~3.37 eV at room temperature), large exciton binding energy (60 meV), and promising applications in short-wavelength optoelectronic devices [1]. It is essential to develop high-quality n- and p-type ZnO to realize these applications. Generally, ZnO is an n-type semiconductor due to its native defects, such as oxygen vacancies and zinc interstitials [1]. The electron concentration can be further increased by doping group III elements, such as Al [2], Ga [3] and In Ref. [4]. Furthermore, extensive efforts have been made in the preparation of ZnO-based heterojunctions by using p-GaN [5], p-Si [6] and p-SiC [7] for optoelectronic applications. However, heterostructured devices have poorer performance than those of homojunctions due to the reduced lattice mismatching, which could avoid introducing more defects in the fabrication of devices. Therefore, the ZnO homojunction is necessary for the optoelectronic application of ZnO, and the realization of stable p-type ZnO is particularly essential [8,9]. Recently, research on p-type ZnO has been carried out by various doping techniques, including chemical vapor deposition (CVD) [10], the hydrothermal method [11], metal organic chemical vapor deposition (MOCVD) [12], pulsed laser deposition (PLD) [13] and sol-gel deposition [14]. Currently, group V (N, P, As, and Sb) and IA (Li, Na and K) elements have been considered as p-type dopants of ZnO by many research groups [8,9]. Group IA elements, especially, have been regarded as ideal dopants due to their shallow acceptor levels according to theoretical prediction [15]. Also, Na has a shallow acceptor level of 170 meV in ZnO when Na substitutes for Zn [15]. Recently, much research has been conducted regarding p-type Na-doped ZnO films fabricated by using different growth techniques [16–19]. However, the studies about Na-doped ZnO nanostructures are limited [13,20–22], and further discussion is needed on the electrical and optical properties of Na-doped ZnO nanostructures. Liu et al. reported on Na-doped p-type ZnO microwires created by a vapor-liquid-solid process with a hole concentration of 1.3×10^{16} cm^{-3} and a carrier mobility of 2.1 cm^2 V^{-1} S^{-1} [20]. Huang et al. created Na-doped p-type ZnO nanorods on a molecular beam epitaxy (MBE) ZnO layer seeded Si through a quartz tube furnace system [21]. Lei et al. demonstrated the successful growth of Na-doped ZnO nanorod arrays by MOCVD [22]. Qiu et al. reported on Na-doped ZnO nanowires grown on gold catalytic Si substrates by the high pressure PLD process [13]. However, among these fabrication techniques, CVD is one of the most powerful and economical methods for oxide nanorod growth. In this work, Na-doped ZnO nanorods on ZnO layer seeded Si

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substrates were prepared using the CVD method. Detailed influence of Na concentration on morphological and electrical properties of the Na-doped ZnO nanorods have been investigated by SEM, HRTEM, XPS and Hall measurement. Low temperature-dependent photoluminescence (PL) properties of Na-doped ZnO nanorods have been studied carefully. The p-type conductivity of Na-doped ZnO nanorods was demonstrated by the Hall measurement and I-V characteristics of ZnO:Na nanorods/ZnO/n-Si structure.

2. Experimental

Na-doped ZnO nanorods were synthesized on ZnO layer seeded Si substrates through a simple vapor-phase transport process in a conventional horizontal tube furnace. The detailed growth process has been reported in our previous work [23]. In brief, ~200 nm-thick ZnO seed layers were fabricated by a sputtering technique. A mixture of ZnO (Alfa Aesar, 99.99%), graphite powder (Alfa Aesar, 99.995%) (0.1 g, molar ratio 1:1), and sodium pyrophosphate powder (Amethyst Chemicals, 99.9%) (0, 0.01, 0.02, 0.03 and 0.05 g) was used as the source materials. The temperature and pressure in the tube were kept at 1000 °C and 1800 Pa, respectively, during the whole growth process. Two hundred standard cubic centimeters per minute (200 sccm) of N_2 and 3 sccm of O_2 were inlet to the furnace tube during growth. In order to avoid the interference signal originated from Si substrates during the Hall effect testing, AlN buffered sapphire substrates were put side by side the Si substrates.

Morphological, compositional and crystal properties of the as-prepared samples were characterized by field-emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 430), X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), transmission electron microscopy (TEM, JEOL 2100F), and X-ray diffraction analysis (XRD, PANalytical X'pert PRO with a standard Cu-Kα radiation source, $\lambda = 0.15418$ nm). Room temperature PL spectra were measured by a stabilized UV laser system (LEOPTICS, excitation wavelength was 266 nm). The low-temperature PL spectra were performed on an Edinburgh FLS 920 luminescence spectrometer (Xe lamp, excitation wavelength was 325 nm). The electrical property of Na-doped ZnO nanorods was measured using an Accent Hall system (HL5500). Electrical measurements were tested using a Keithley 2600 semiconductor characterization system.

3. Results and discussion

Fig. 1(a)–(c) illustrate the SEM images of the as-prepared undoped and the representative Na-doped ZnO nanorods, where the concentrations of Na determined by XPS are 0%, 0.5 at.% and 2.1 at.%, respectively. As shown in Fig. 1(a), the average diameter and the length of undoped ZnO nanorods are about ~120 nm and several micrometers, respectively. ZnO nanorods gradually shrink at the top and become tapered at the tip with an increasing Na concentration, showing sharpened-pencil-like morphology [Fig. 1(c)]. The incorporation of Na into the ZnO lattice plays an important role in morphological evolution. A similar phenomenon has been observed by Yang et al. [24].

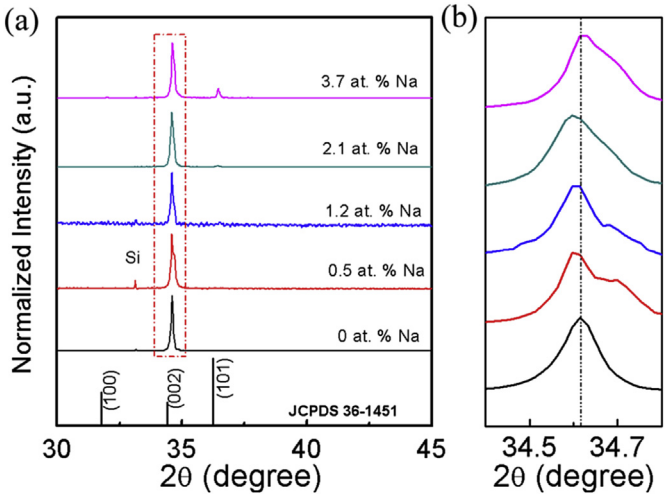

Fig. 2. XRD patterns of the undoped ZnO nanorods and the Na-doped ZnO nanorods. (a) Full range XRD patterns, and (b) Magnified (002) peaks.

Fig. 2 displays XRD spectra of as-prepared ZnO nanorods samples. With the exception of the diffraction peak arising from Si substrate, all other diffraction peaks in the spectra are consistent with the hexagonal ZnO (002) plane (JCPDS 36-1451). ZnO nanorods grow preferentially along the *c*-axis. Moreover, there are no diffraction peaks of Na-related impurities, indicating the phase purity of the samples. It should be noted that the (002) peaks of Na-doped ZnO nanorods (0.5, 1.2 and 2.1 at.% Na) shift toward lower angles as compared with those of the undoped ZnO sample, as shown in Fig. 2(b), indicating the d-spacing expansion according to the Bragg formula. The ionic radius of Na^+ (0.102 nm) is larger than that of Zn^{2+} (0.074 nm), thus a lattice expansion would be caused by substitution of Na for the Zn site in ZnO. However, when Na concentration increases to 3.7 at.%, the diffraction peak does not

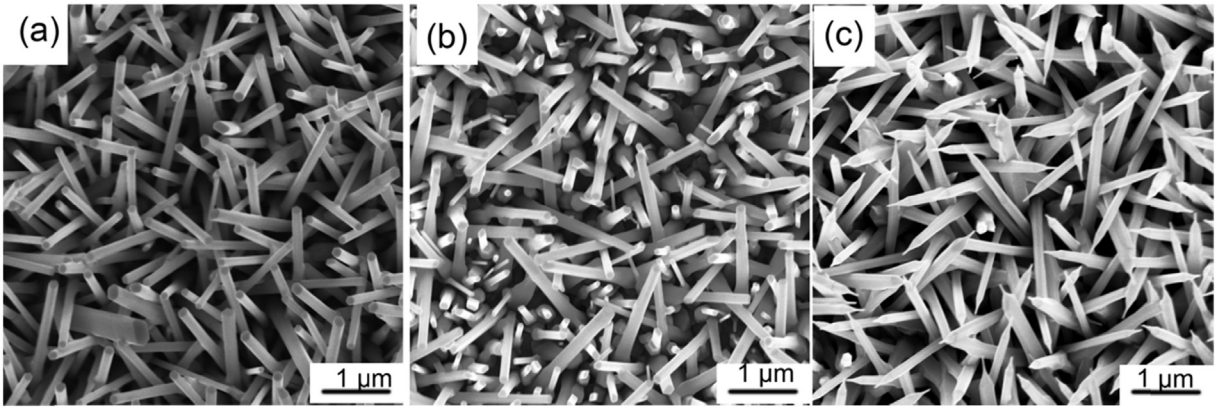

Fig. 1. The SEM images of the as-prepared undoped and the representative Na-doped ZnO nanorods. (a)–(c), the doping concentrations are 0%, 0.5 at.% and 2.1 at.%, respectively.