Self-assembly of Micro-structured ZnO-based Homojunction by Two-step Method

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ABSTRACT

Self-assembly of radial micro-structured ZnO homojunction were synthesized by a kind of two-step method. In-doped ZnO micro-rods were first fabricated by chemical vapor deposition method, and then a layer of undoped ZnO covers on the In doped ZnO rods via aqueous solution method. A epitaxial growth mechanism was provide to explain the growth process of the radial micro-structured ZnO homojunction. Room temperature photoluminescence (PL) spectra were measured for the In-doped ZnO film and the final junction structure. It clear reveals that the ultraviolet (UV) emission peak of the In doped ZnO micro-rods has an obvious blue-shift compared to that of the final junction structures. The intensity of the green emission obviously decreases after ZnO layer coating, which may ascribe to the capping treatment compensating the defects at the surface of In doped ZnO, and suppressing its defect luminescence. The PL measurement results also confine that the out layer is quite different from the inside of the radial micro-structured ZnO homojunction. This work provides a useful way to fabricate junctions, which are important for designing optic-electrical devices.

Keywords: ZnO-based homojunction, photoluminescence, growth mechanism, two-step method

1 INTRODUCTION

Zinc oxide (ZnO) is an important semiconductor material with a wide direct band-gap of 3.37 eV and possesses high exciton binding energy of 60 meV. It has great potential application in photodetectors, field-effect transistors, and other optoelectronic devices [1-3]. Recently, fabrication of microstructure and nanostructured ZnO homojunction has stimulated great interest due to their applications in nano-devices. Sun et al. synthesized ZnO nanowires by wet chemical method on various ZnO templates [4]. Chen et al. fabricated the catalyst-free p-n homojunction ZnO nanowires arrays in which the phosphorus and zinc served as p- and n-type dopants, respectively [5]. ZnO homojunctions were also synthesized by P-doped ZnO nanorods grown on undoped ZnO nanorods [6,7]. There were also some reports on nanostructured ZnO deposited on the p-type ZnO films to form the homojunctions [8,9]. Most of these reports were focused on the formation of axial nanostructured ZnO junction, while, there is few report on the radial ZnO homojunction. In this work, Self-assembly of radial micro-structured ZnO homojunction were synthesized by a kind of two-step method. The inside rods compose of In-doped ZnO micro-rods with In content of 2 at.%, and the outer layer is undoped ZnO. A epitaxial growth mechanism was proposed to explain the growth of the radial micro-structured ZnO homojunction. Room temperature photoluminescence (PL) spectra were also measured, and the results confine that a real junction are formed.

2 EXPERIMENTAL METHOD

A two-step route was present to fabricate radial micro-structured ZnO homojunction. First, In-doped ZnO micro-rods film was deposited on silicon substrate by CVD method. It was performed in a conventional horizontal tube furnace at atmospheric pressure. Pure Zn (500 mg) powder and mixture of In_2O_3 (32 mg) and C (8 mg) powders were loaded into a quartz boat. A cleaned silicon substrate was placed at the downstream with the distance of 10 mm far away from the sources. The boat was then loaded into the center of the tube furnace. The temperature was increased to 920℃ at the rate of 15℃/min under argon flow of 120 sccm and kept for 30 min. The sample was carried out when the furnace was cooled down to room temperature. Second, the micro-structured ZnO homojunction were obtained by aqueous solution method. The solution of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and methenamine ($C_6H_{12}N_4$) was prepared with the molar ratio of 1:1. The In-doped ZnO film grown on silicon substrate by CVD method was put into the solution with the film side facing downwardly. The solution was heat up to 90℃ and maintained at this temperature for 4 h. The sample was then carried out, cleared it in ethanol and dried it in air.

The structure, morphology and composition of the sample was characterized X-ray diffraction (XRD, Rigaku D/max-RB, Cu Kα) and field emission scanning electron microscopy (FESEM, SUPRA 55) equipped with energy dispersive spectrometry (EDS). The photoluminescence (PL) measurements were carried out on a HITACHI 4500-type visible–ultraviolet spectrophotometer with a Xe lamp as the excitation light source at room temperature, and the excited wavelength was 325 nm.

3 RESULTS AND DISCUSSION

The typical SEM image of the In-doped ZnO film deposited on Si substrate fabricated by CVD method was shown in Fig.1a, some micro-rods with the diameter of 1.2-2.0 μm deposit on the substrate. EDS results show that the

content of In is around 2 at.%. Fig. 1b shows that the micro-rods in Fig. 1a are coated with a layer of ZnO after solution method process, and some short "walls" encircle the top of the micro-rod, which makes the structure looks like castle. The thickness of the walls is about 250 nm.

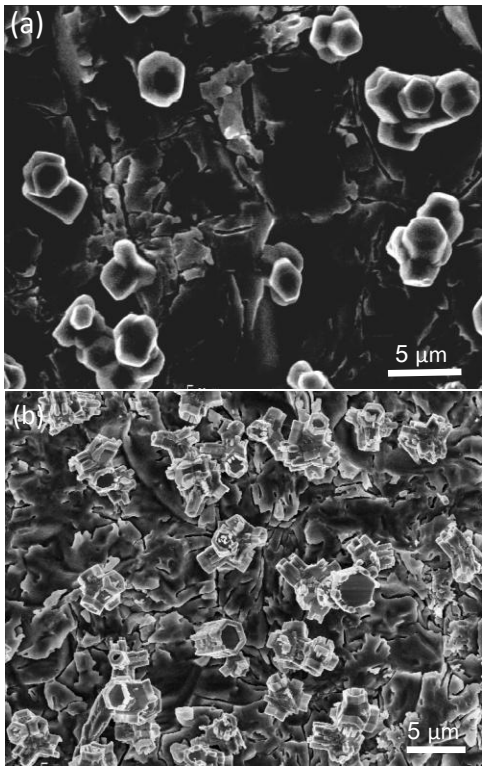

Figure 1: Typical SEM image of In doped ZnO microstructures fabricated by CVD method (a) and the radial micro-structured ZnO homojunction (b).

Fig. 2 shows the XRD pattern of the radial micro-structured ZnO homojunction grown on Si substrate. All the

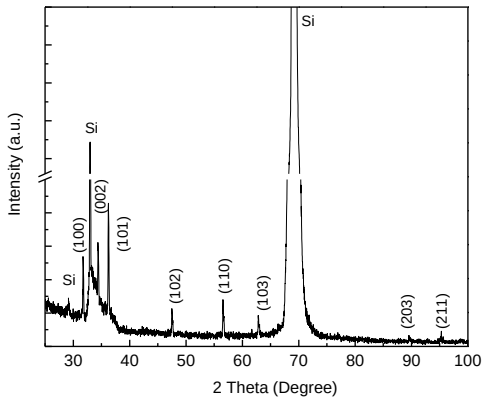

Figure 2: XRD pattern of the radial micro-structured ZnO homojunction.

diffraction peaks are well explained by the structure of hexagonal wurtzite ZnO. The EDS results exhibit that In content is too low to be detected by EDS measurement. Compared with the EDS results of the In doped ZnO micro-rods, it clearly shows that the content of In obviously decreases after the solution method process. The main reason is that the epitaxial ZnO layer covers on the In-doped ZnO film during the solution method process, the content of In is diluted with the increase of Zn and O elements.

Figure 3 shows the enlarged FESEM images of three kinds of the radial micro-structured ZnO homojunction. In Fig. 3a, the walls are composed of independent nanobricks with the thickness of 200 nm. In Fig. 3b, the nanobricks nearly coalesce into a integrate wall circled around the top of the micro-rod. Fig. 3c shows some isolated nanorods grown on the top of the micro-rod beside the wall. Why is the nanobricks epitaxial growth along the In doped ZnO micro-rods instead of other places (Fig.3a and 3b)? Why are there many isolated nanorods exist on the top of the micro-rods (Fig.3c) while the top of other micro-rods are nearly flat (Fig3a and b)? Fig. 3d may provide the answer. It clearly shows that some nanobricks formed at the interface between the inside rod and the outside layer. It is well known that nucleation is very easy formed at the places of the surface defects, which may provide the nucleation sites for the growth of nanobricks. The nanobricks then grow up and at last coalesce into a circled wall. These nanobricks coalesce into a wall with hexagonal-shape because the inside micro-rods supply a hexagonal model. If many defects exist on the top of the micro-rod, many isolated nanorods will form (Fig. 3c), and the number of isolated nanorods correlates to the number of defects on the top of micro-rods. The isolated nanorods randomly distribute on the top of the inside rod because the defects are randomly formed. However, if there are few defects at the surface of the micro-rod, no nanorod is deposited on it (Fig. 3b).

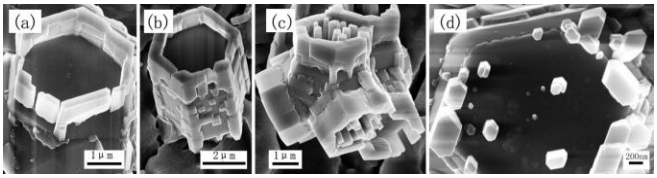

Figure 3: Enlarged FESEM images of the radial micro-structured ZnO homojunction. (a), (b) and (c) are three typical morphologies; (d) top-viewed image of a radial micro-structured ZnO homojunction.

The growth mechanism of the radial micro-structured ZnO homojunction is sketched in Fig. 4. First, In-doped ZnO micro-rods film deposits on the silicon substrate (Fig. 4a). Second, a layer of un-doped ZnO is covered on the In-doped ZnO micro-rods and film during the solution growth process (Figure 4b and 4c). At the same time, some of ZnO nucleate at the interface between the inside rod and the outer layer

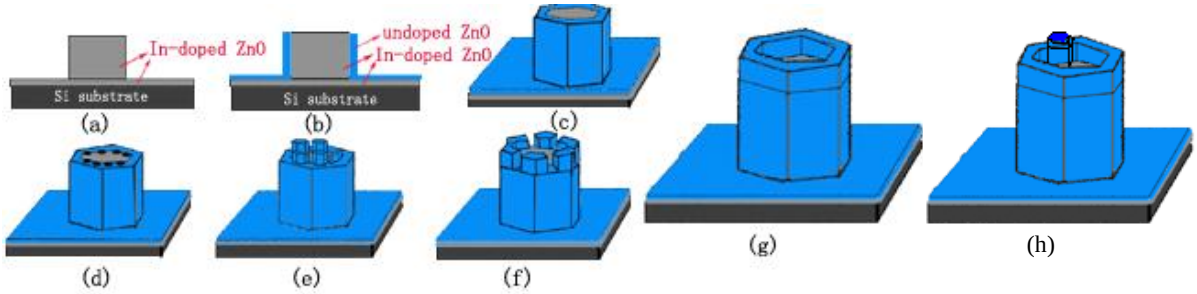

Figure 4: Schematic diagram of the proposed growth mechanism of the radial micro-structured ZnO homojunction. (a) In doped ZnO micro-rod on Si substrate, (b) undoped ZnO covered on In doped ZnO micro-rods and film, (c) A rotated view of (b), (d) ZnO nanobricks nucleated from the defects at the interface between the inside and the out layer, (e) Nanobricks grow up from the interface, (f) Lateral growth of the nanobricks, (g) Perfect radial micro-structured ZnO homojunction, (f) Some isolated nanorods grown on the top of the inside rod.

(Figure 4d). They grow up and at last coalesce into hexagonal wall (Figure 4e, 4f, and 4g). if defects exist on the top of the inside rod, some isolated nanorods will form on it (Figure 4f).

Room temperature PL spectra were shown in Fig.5. Curve 1 is the PL spectrum of the In-doped ZnO film, and curve 2 is that of the radial micro-structured ZnO homojunction formed by aqueous solution method. Two emission peaks exist in both curve 1 and 2. One of them is ultraviolet emission, centered at around 380 nm, corresponding to the near band-edge emission, and another one is green emission, which is commonly ascribed to defects, particularly those native defects such as ionized

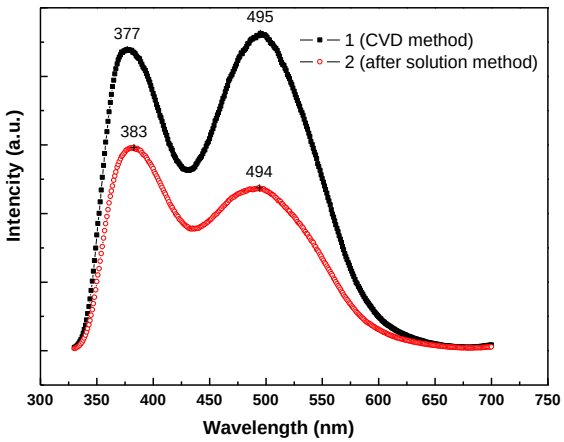

Figure 5: Photoluminescence spectra of the In doped ZnO film (curve 1) and radial micro-structured ZnO homojunction (curve 2).

oxygen vacancies and zinc interstitial.[10,11] Fig.5 shows that the UV peak position (377 nm) of curve 1 shift to short wavelength compared with that (383 nm) of curve 2, which agrees with the previous report that the UV emission of ZnO nanorods shifts to high energy side with the increase of In content.[12] In curve 2, the intensity of UV emission is stronger than green emission, while in curve 1, it is reverse. It means that the ratio of intensity of UV emission to that of green emission increases after aqueous solution process, which may be ascribed to the coating of ZnO layer suppressed the surface defects of the In-doped ZnO film. Shi et al. also reported that SnO_2 capping treatment leads to improve the near band-edge emission and suppress the defect luminescence of ZnO nanowires.[13] These differences of the PL spectra also suggest the outer layer is quite different from the inside of the radial micro-structured ZnO homojunction, which indicates that the real junction structure forms. This kind of structure may have great potential application for optic-electrical nano-devices.

4 CONCLUSIONS

Radial micro-structured ZnO homojunction was successfully synthesized by two-step method. The inside is In doped ZnO micro-rod, while the out layer is ZnO. A epitaxial growth mechanism is proposed to explain the growth of radial ZnO homojunction. The nanobricks form at the interface of the inside rod and the out-layer, and then they coalesce into a wall with hexagonal-shape. Some isolated nanorods form on at the top of the some inside rod. Moreover, the PL spectra suggest that the outer layer is quite different from the inside one. This kind of structure has great applications for the optic-electrical devices.

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