Growth of branched In-doped ZnO nanowires: Structural and Optical Properties

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Abstract. Well-crystallized branched Indium (In)-doped ZnO nanowires were grown on silicon substrate via simple thermal evaporation process by using metallic zinc and indium powders in the presence of oxygen. The as-grown branched nanowires were examined in terms of their morphological, structural and optical properties using field emission scanning electron microscopy (FESEM) attached with energy dispersive spectroscopy (EDS), X-ray diffraction and room-temperature photoluminescence (PL) spectroscopy. The morphological and structural characterizations confirmed that the as-grown products are branched nanowires, grown in high-density and possessing well-crystalline structures. The room-temperature photoluminescence (PL) spectrum exhibited a very small UV emission and a broad band in the visible region indicating the presence of structural defects due to insertion of In-atoms in the lattices of as-grown nanowires. The presence of a strong green emission in the room-temperature PL spectrum demonstrates that these structures can be used for specific applications of ZnO-based phosphors, such as field emissive display technology, etc.

INTRODUCTION

Due to exotic properties and wide applications of semiconductor nanostructures, especially nanowires, this area of research has received a great attention. Therefore, recently, many research groups have put their active efforts in this area of research. Among various semiconductor materials, the II-VI metal oxide semiconductor, i.e. zinc oxide (ZnO) has received a special attention due to its various superior properties which made this material distinct from any other material. The properties of ZnO includes, its direct and wide band gap energy (3.37 eV), large exciton binding energy (60 meV), negative electron affinity, high surface-to-volume ratio, high mechanical strength and thermal stability [1-10]. Due to the excellent and versatile properties of ZnO, it has been used in various high-technological applications such as dye-sensitized solar cells (DSSCs), field effect transistors, field emission devices (FEDs), p-n-heterojunction diodes, gas, chemical and bio-sensors, UV-detectors and so on [5-9]. Due to aforementioned properties and wide applications, a variety of methods have been demonstrated for the growth of ZnO nanostructures such as thermal evaporation process, chemical solution method, hydro-thermal reaction process, metal organic chemical vapor deposition (MOCVD) method, microwave technique, sonochemical techniques and so on [1-12].

Various attempts have been made to enhance the properties of ZnO nanomaterials and for this doped ZnO nanostructures were prepared and characterized and reported in the literature [10-16]. In this regards, various transition metals are used for doping to enhance the electrical, optical, magnetic and structural properties for variety of applications. Recently, indium doped ZnO (In:ZnO) nanostructures were prepared and characterized and reported in the literature [15, 16]. Huang et al. synthesized In-doped ZnO nanowires by thermal evaporation process [15]. They demonstrated that the In-doped ZnO nanowire exhibits better field emission characteristics as compared to bare undoped ZnO nanowires [15]. Jie et al. synthesized In-doped ZnO nanobelts by thermal evaporation with gold catalyst. It was observed that UV emission peak of In-doped ZnO nanobelts was red shift as compared to undoped ZnO in photoluminescence spectra [16].

In this paper, we report the growth of branched In-doped ZnO nanowires on silicon substrate via simple thermal evaporation process using metallic zinc and indium powders in the presence of oxygen. The synthesized products were characterized in detail in terms of their morphological, structural and optical properties.
EXPERIMENTAL DETAILS

Branched indium doped zinc oxide (In:ZnO) nanowires were synthesized via simple thermal evaporation process by using metallic powders of zinc and indium in the presence of oxygen. The evaporation of metallic powders was performed in horizontal quartz tube IR furnace. The deposition of the nanowires was done on Si (100) substrate which was washed with DI water, alcohol and acetone, sequentially, before use. In a typical reaction process, high purity metallic Zn (99.9 %) and In (99.9%) powders were well-mixed with weight ratios of 10:1, and put into a silica boat which subsequently positioned at the center of the quartz tube furnace. The silicon substrates were then placed adjacent to the source material. After this arrangement, the furnace was started to heat up to 950 °C under the continuous flow of high purity (99.999 %) nitrogen gas, which was used as a carrier gas to transfer the evaporated species from the boat to the substrate and as a source to create an inert atmosphere inside the tube furnace. Once, the temperature of the furnace was reached to 950 °C, high purity (99.999 %) oxygen gas was flowed as source gas for oxygen. During the reaction, the evaporated metallic zinc powders were reacted with oxygen and finally In-doped ZnO nanowires were obtained. The temperature of the furnace was kept constant at 950 °C during the whole reaction process. The reaction was terminated in 90 min. After terminating the reaction, gray colored products were deposited on the silicon substrate which was characterized in detail in terms of their morphological, structural and optical properties.

The morphological and structural characterizations of the as-grown In-doped ZnO nanostructures were done by using field emission scanning electron microscopy (FESEM) and X-ray diffraction pattern, respectively. The composition of as-synthesized nanowires was examined by using energy dispersive spectroscopy (EDS) attached with FESEM. The room-temperature photoluminescence (PL) spectroscopy was done to investigated the optical property of as-grown In-doped ZnO nanostructures.

RESULTS AND DISCUSSION

To examine the general morphologies of as-synthesized In-doped ZnO nanostructures, FESEM was done and the results are demonstrated in figure 1. Figure 1 (a) demonstrates the low-magnification images of as-synthesized nanostructures. It is clear from the low-magnification images that the synthesized products are grown in high density and possess nanowire-shaped morphologies. Interestingly, it is seen that the nanowires are arranged in beautiful urchin-like morphologies. The full size of the nanowires based urchins are in the range of 30 ± 5 μm. By high-resolution FESEM images shown in fig. 1 (b) and (c), it is clear that the diameters of the as-grown nanowire in urchin-like morphologies are not uniform. The nanowires possess larger diameter at the bases and smaller diameters at their tips. It is fascinating to see that the large diameter bases are joined with each other at one common point and finally beautiful urchin-like morphologies were obtained. The diameters of the nanowires at the bases and tips are in the ranges of 350 ± 50 nm and 150 ± 35 nm, respectively. The lengths of the nanowires are in the micrometers. The clear view of as-grown products is shown in figure 1 (d) which confirmed that the surfaces of the nanowires are not uniform. It is interesting to see that small spikes (branches) are grown in both sides of the nanowires. In other words, one can state that the nanowires possess spikes or small branches on both side of their surface and resemble with double side comb structures. The sizes of the spikes are not uniform and are in the range of 250 ± 30 nm.

To check the crystallinity and crystal structure of as-synthesized branched In-doped ZnO nanowires, powder X-ray diffractometry (XRD) analysis was carried out with monochromated CuKα radiation (45 KV, 30 mA), scanned in step size of 0.02° for the angular range 10-60° of 2θ. The general aspect of the XRD patterns (Figure 2), in particular, the presence of strong and sharp peaks and the absence of diffraction halo, indicate the presence of crystalline phase only and show the absence of amorphous or crystalline-amorphous phase formation. The obtained values of d-spacing for In-doped ZnO nanowires are in good agreement with that of reported values [17], confirming that as-synthesized In-doped ZnO nanowires has hexagonal structure. The diffraction lines (Figure 2) have been indexed with the help of JCPSDs data files 36-1451. The obtained positions of Bragg diffraction angle for pure and In-doped ZnO nanowires were found to be very close to each other. This clearly shows that the synthesis of ZnO with In-doping does affect the morphology to a certain extent but not the crystal structure. No peaks of indium (In) were found in the X-ray diffraction pattern (Figure 2) which indicates that the dopant (In) atom occupied the vacant sites available inside the unit cell of ZnO without disturbing the existing structure.

To check the composition of the as-grown branched In-doped ZnO nanowire, energy dispersive spectroscopy (EDS), attached with FESEM spectroscopy was done and shown in figure 3. Figure 3 (a) exhibits the...
typical SEM image of single urchin-like indium-doped ZnO nanowires and further confirms that the products are
grown in very high-density over the whole substrate surface. Figure 3 (b) shows the corresponding EDS spectrum of
selected branched In-doped ZnO nanowires.

Figure 1. Typical (a, b) low and (c, d) high-magnification FESEM images of well-crystallized branched In-doped
ZnO nanowires grown by simple thermal evaporation process on Si(100) substrate.

The selected portion is surrounded by rectangular lines. The observed spectrum demonstrates the
corresponding peaks for zinc, indium and oxygen which clearly reflect that the synthesized materials are made of
zinc, indium and oxygen. No other peak related with any impurity were detected in the EDS spectrum, up to the
detection limit of the EDS machine, which further confirms that the synthesized products are In-doped ZnO.

Two basic mechanisms are known for the formation of nanostructures grown especially by thermal
evaporation process, i.e. vapor-liquid-solid (VLS) process and vapor-liquid (VS) growth process. In VLS growth
process, the source vapor reacted with the metal particles, which acts as a catalyst, and formed the alloy droplets.
After reaching the supersaturation state, the grown droplets lead to the formation of nanostructures [18]. It is
important to state that the typical characteristic of VLS mechanism is the presence of metal particles capped at
the end of the grown nanostructures. In our synthesis process, no metal catalyst or additives were used and after the
growth no metal droplets were seen at the tips of as-grown branched nanowires. Therefore, vapor-solid (VS) growth
mechanism has been proposed instead of conventionally and widely used VLS growth process for the growth of
branched In-doped ZnO nanowires.
To check the optical properties of as-grown branched nanowires, room-temperature PL spectroscopy has been performed using He-Cd (325 nm) laser line as the exciton source. Figure 4 shows the typical room-temperature PL spectrum of the as-grown branched In-doped ZnO nanowires. Normally, two distinct peaks have been observed in the room-temperature PL spectrum of pure ZnO nanowires, i.e. a peak in the UV region also called as near band edge emission (NBE) and a peak in the visible region, also known to be as deep level emission (DLE). The origination of NBE in the PL spectrum is due to the recombination of free excitons through an exciton-exciton collision process [19] while the DLE is appearing in the spectrum due to the radial recombination of a photo-generated hole with electron of the singly ionized oxygen vacancies in the surface lattices of the ZnO [20]. The room-temperature PL spectrum of our synthesized branched nanowires exhibits a much suppressed UV emission at 378 nm and a broad visible emission at 561 nm. Egehaaf et al. reported that the radiative transitions between shallow donors (related to oxygen vacancies) and deep acceptors (zinc vacancies) can create defects in the luminescence spectra [21]. As the ZnO was doped with In ions which infiltrate and sit into the lattices of ZnO and hence create structural defects which is believed are the major cause for the suppression of UV emission and broadening of visible emission. Due to the enhancement of green emission in the formed nanowires, these structures show great interest for typical applications of ZnO-based phosphors, such as field emissive display technology.
Figure 3. Typical (a) SEM image and; (b) corresponding EDS spectrum of as-grown well-crystallized branched Indoped ZnO nanowires grown by simple thermal evaporation process on Si(100) substrate.
CONCLUSION

In conclusion, large-quantity growth of branched Indium (In)-doped ZnO nanowires was done on silicon substrate via simple thermal evaporation process by using metallic zinc and indium powders in the presence of oxygen. The detailed morphological and structural characterizations confirmed that the synthesized products are well-defined branched nanowires and possessing well-crystalline structures. X-ray diffraction analysis revealed that the doping of indium (In) does affect the morphology to some extent but keep the original hexagonal crystal structure of zinc oxide (ZnO). A broad green emission was observed from the room-temperature PL spectrum which is believed to be mainly due to the insertion of Indium atoms into the lattices of the as-grown branched nanowires. Due to presence of strong green emission in the room-temperature PL spectrum, it is assumed that the synthesized products can be utilized in some specific applications of ZnO based devices, especially in ZnO-based phosphors, such as field emissive display technology.

ACKNOWLEDGEMENTS

Authors acknowledge the financial support of the Deanship of Scientific research, Najran University, Najran, Kingdom of Saudi Arabia for financial support (grant project number NU 12/10). Authors acknowledge the Higher Ministry of Education, Kingdom of Saudi Arabia for granting a Collaborative Research Centre on Sensors and Electronic Devices, dated 24/3/1432 H, 27/02/2011.
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