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Growth and optical properties of ZnO–In_2O_3 heterostructure nanowires

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Abstract

ZnO–In_2O_3 heterostructure nanowires were grown on a Si (111) substrate using the thermal evaporation method. Scanning electron microscopy results showed that the ZnO nanowires had spherical caps. The X-ray diffraction (XRD) pattern and energy-dispersive X-ray (EDX) spectrum indicated that these caps were In_2O_3. An analysis of the early growth process revealed that indium oxide might have played a self-catalytic role. Therefore, it was plausible that the vapor–liquid–solid mechanism (VLS) was responsible for the growth of the ZnO–In_2O_3 heterostructure nanowires. The optical properties of the products were characterized using a photoluminescence (PL) technique. The PL results for the ZnO–In_2O_3 heterostructure nanowires showed a strong peak in the ultraviolet region as a result of the near band emission and a negligible peak for the visible emissions that occurred as a result of the defects. Based on these PL results, it was found that the In_2O_3 nanostructures not only introduced the caps at the tips of the ZnO nanowires but also partially passivated the nanowire surfaces, leading to an improved near band edge emission and the suppression of the defect luminescence.

Keywords: C. Optical properties; Passivation; Thermal evaporation method; ZnO–In_2O_3 heterostructure nanowires.

1. Introduction

Zinc oxide (ZnO) is an n-type metal oxide semiconductor with a wide band-gap (3.36 eV) and large excitation binding energy (60 meV). These characteristics generate interest in the use of this material in numerous applications such as solar cells [1] and field emission materials [2]. The key factors affecting these applications are the shape, size, impurities, doping, structures, and phases of the material. To obtain the desired properties, many researchers in recent years have focused on the synthesis of doped and pure nanocrystalline materials such as ZnO. Doping semiconductors with various elements is known to greatly affect many of their basic physical properties, including their electrical, optical, and magnetic properties, which are crucial in most practical applications. In addition to our group, many other groups have also reported the synthesis of doped ZnO nanostructures with various morphologies using different methods [3–6]. Typically, group III (Al, Ga, and In) elements are used as donor impurities to dope ZnO. Accordingly, many studies have already been performed on the synthesis and characterization of ZnO nanostructures doped with these elements [7,8]. However, In-doped ZnO nanostructures are reported several times more often than the use of other group III elements as dopant materials in ZnO nanostructures. Moreover, for technological applications, many research groups have focused on the development of In-doped ZnO nanostructures, because In-doped ZnO is a very important material in the semiconductor industry [9,10]. We also investigated the self-catalytic role of indium oxide in relation to the growth process for ZnO/ZnInO heterostructure nanowires grown using a thermal evaporation setup and studied the effect of indium on the optical properties of the products [11]. In addition, it was found that by changing the indium source position in the thermal evaporation setup, the passivation role of indium in the ZnO nanostructure growth process could be observed [12].

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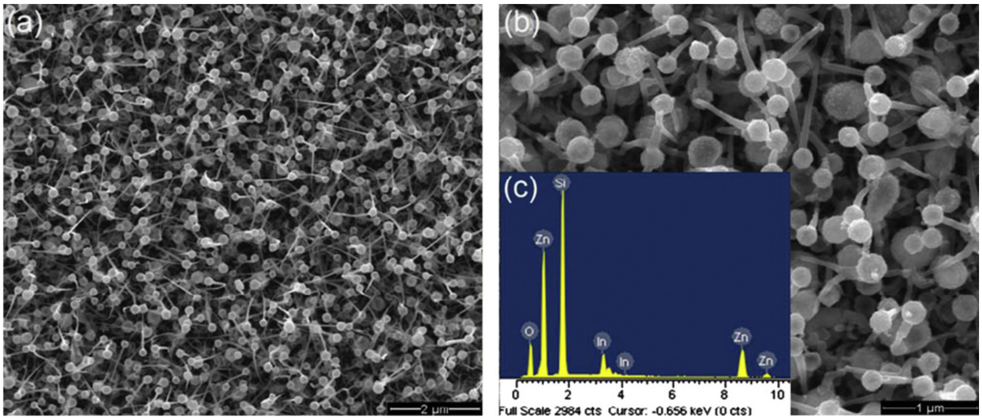

Fig. 1. (a) Low magnification and (b) high magnification FESEM images of In-doped ZnO nanowires grown for 90 min. (c) EDX spectrum of In-doped ZnO nanowires.

Unfortunately, the luminescence properties of these doped nanomaterials were likely to degrade when using a dopant material such as indium. This decrease in the optical properties of doped ZnO nanostructures can be explained by the formation of band tiling in the band gap, which is often induced by the introduction of impurities into semiconductors. Surface passivation is one of the best methods for increasing the optical properties of nanostructures. Materials with larger band gaps (compared to that of the core material, ZnO in this case) are usually chosen for the surface passivation layer, in order to efficiently confine the electrons and holes within the core material [13]. Successful demonstrations of enhanced photoluminescence from ZnO by surface passivation/modification using physical/chemical approaches have been reported in the recent literature [13–17]. In addition, it should be noted that real device applications also require the formation of junctions, which may not exist in most of the as-grown nanostructures. A metal–semiconductor–metal junction nanowire serves as a basic unit for an optoelectronic nanodevice. In addition, this junction provides an ideal system to study the transport behavior of the nanowires without considering the uncertainties of the external contact.

By combining surface modification to improve the optical properties of doped ZnO nanostructures and junction formation, we designed a two-junction nanowire configuration, using In-doped ZnO nanowires grown on a Si substrate with In_2O_3 caps on their tips. In the present work, we demonstrated that the ZnO–In_2O_3 heterostructure nanowires could be achieved via a thermal evaporation method. A strong enhancement of the ZnO–In_2O_3 heterostructure nanowires band edge emission was observed as compared to that from undoped ZnO nanowires.

2. Experimental

The ZnO–In_2O_3 heterostructure nanowires were fabricated in a conventional horizontal furnace without using a metal catalyst. First, a Si (111) substrate was ultrasonically cleaned using ethanol and de-ionized water. It was then lightly etched with HF (43%) and de-ionized water mixture (1:10) for about 10 min to remove the native oxide layer. Zinc oxide (99.99%) and indium oxide powder (99.99%) were mixed in a molar ratio of 10:2. To synthesize the wires, the appropriate powders were put in an alumina boat and inserted into a horizontal tube furnace to serve as an evaporation source. The prepared silicon substrate was located downstream from the source material. A vacuum of 800 Pa was maintained inside the furnace tube during deposition. The source material was heated up to 950 °C and the temperature of the substrate was kept at 600 °C during the growth. High purity Ar and O_2 gases were fed at about 100:10 sccm into the furnace tube at one end, while the other end was connected to a rotary pump. The growth process was allowed to proceed for 90 min.

The crystal morphology and structure of the nanowires were investigated using field emission scanning electron microscopy (FESEM) (Quanta 200 F) and X-ray diffraction (XRD) (Siemens D5000). Studies of elemental contents of products were undertaken using energy dispersive X-ray (EDX, Quanta 200 F) spectroscopy. A room temperature photoluminescence spectrometer (PL, Jobin Yvon Horiba HR 800 UV) was employed to study the optical properties of the products. A He–Cd laser with a wavelength of 325 nm was used for the PL measurement.

3. Results and discussion

Fig. 1(a) and (b) shows FESEM images of the obtained nanostructures at different magnifications. It can clearly be seen that the nanostructure morphology contains capped nanowires. The average diameters of the nanowires and caps are about 85 and 200 nm, respectively. Fig. 1(c) shows the EDX spectrum of the nanostructures. The EDX spectrum shows an indium content of about 12% (atomic). Fig. 2 shows a high magnification FESEM image of the capped nanowires. The EDX spectra were taken from

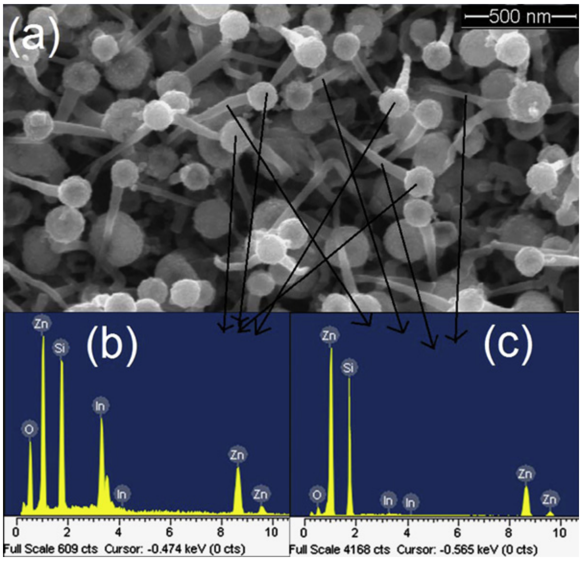

Fig. 2. (a) High magnification FESEM image of the In_2O_3 capped ZnO nanowires. (b) and (c) EDX spectra from different areas of the capped nanowires.

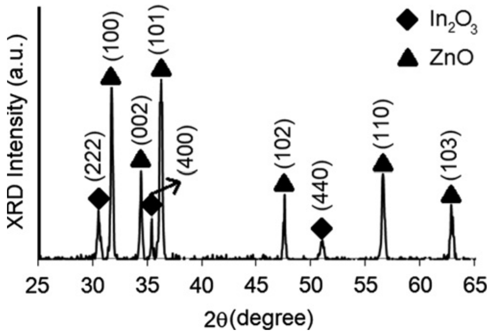

Fig. 3. XRD pattern of the In_2O_3 capped ZnO nanowires. The XRD shows that caps are In_2O_3 and the products are ZnO–In_2O_3 heterostructure nanowires.

different parts of the capped nanowires and show that the caps have a larger indium content (~22%) than the body of the nanowires (~6%).

Fig. 3 shows the XRD pattern of the capped nanowires. This pattern exhibits two material phases: one corresponding to the hexagonal phase of ZnO (JCPDS no. 800075) and the other to the cubic phase of In_2O_3 (JCPDS 6-0416). Therefore, the EDX and XRD results reveal that the caps could be In_2O_3 and the products could be ZnO–In_2O_3 heterostructure nanowires. However, the In_2O_3 caps also contain some zinc.

We synthesized In-doped ZnO nanowires under the same conditions as used in our previous work, where indium powders were mixed with ZnO powders and used as a source material [11]. We formed a pill of this mixture under high pressure. The pill was calcined and sintered in a box furnace in air, transforming it into a $Zn_xIn_yO_3$ compound [11]. Fig. 4(a) shows the In-doped ZnO nanowires that were grown by the method described here. The inset of Fig. 4 shows an FESEM image of a single nanowire. It can be seen that this nanowire is completely straight and tapered. The EDX measurements (not shown here), which were used to investigate the longitudinal indium distribution in a single nanowire, indicated a non-uniform distribution of the indium content along the nanowire (from part A to part D) [11]. In fact, the indium content decreased from part A to part D. We found that the $Zn_{x'}In_{y'}O_3$ played a self-catalyst role during the growth process for the In-doped ZnO nanowires. However, we also found that the $Zn_{x'}In_{y'}O_3$ droplets were unstable during the nanowire growth process. Therefore, the In-doped nanowires were grown with a tapered shape. Our proof for this claim were the undoped ZnO nanowires that were grown under the same conditions used to grow the In-doped ZnO nanowires (Fig. 4(b)). The inset of Fig. 4(b) shows straight nanowires with less tapering.

To understand the growth process for the capped nanowires in more detail, the nanowires were examined at an earlier stage of growth (15 min rather than 90 min) under the same conditions as described in the experimental section. Fig. 5 shows a top view FESEM image and the corresponding EDX spectrum of a sample that was grown for 15 min on the Si substrate. It can be seen that only scattered particles of indium oxide containing a small amount of zinc were deposited on the substrate. In comparison with our previous work [11], this sample exhibited larger indium content. In addition, the particles diameters were larger than those that were observed in the previous work.

Based on these results, the growth mechanism for the ZnO–In_2O_3 heterostructure nanowires can be tentatively proposed. We did not use any metal as a catalyst on the substrate. Therefore, the growth must have begun with nucleation sites. These sites were most likely established by In_2O_3 particles because the melting temperature of In_2O_3 is smaller than that of ZnO. In addition, by etching with HF acid the Si surface became very rough. Therefore, droplets of liquid In_2O_3, were deposited on the surface, clustered, and served as ideal nucleation sites. In_2O_3 may in fact play a self-catalytic role in the growth of the In_2O_3 capped ZnO nanowires. The FESEM results for the nanowires in Figs. 1 and 2 show self-catalyst particles as caps at the tips of the ZnO nanowires. In contrast with undoped ZnO nanowires (Fig. 4b), the growth process for the ZnO–In_2O_3 heterostructure nanowires cannot be based on the VLS mechanism. Therefore, we conclude that the unique morphology of the ZnO–In_2O_3 heterostructure nanowires may be attributed to the self-catalytic role of indium [16–18]. This supports the premise that the growth of the ZnO–In_2O_3 heterostructure nanowires was governed by the VLS mechanism. Generally, the VLS mechanism involves four important and successive steps: (1) the transport of reagent species in the vapor phase; (2) dissolution of species at the surface of droplet; (3) diffusion of species inside the droplets; and (4) precipitation and anisotropic crystal growth at the liquid–solid interface between catalyst droplet and nanostructure [19]. According

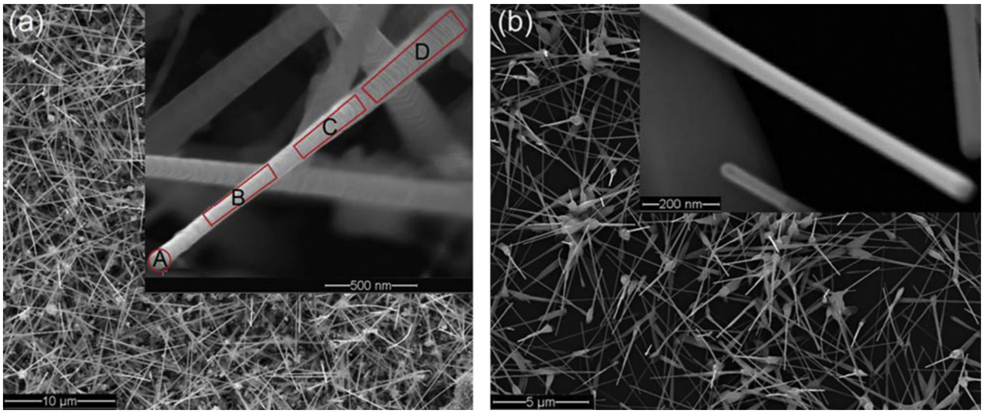

Fig. 4. (a) In-doped ZnO nanowires that were grown by mixed In+ZnO powders and (b) undoped ZnO nanowires that were grown under the same conditions.

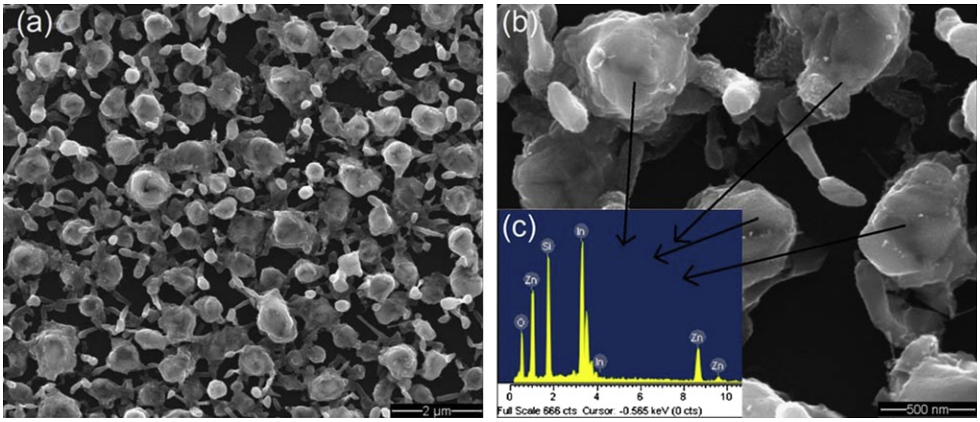

Fig. 5. FESEM image and EDX spectrum of the first grown for at 15 min.

to this mechanism, vapors of ZnO_x are absorbed by the self-catalyst, reach supersaturation, and finally solidify. Fig. 6 shows this mechanism schematically. However, one question arises here: why was the In_2O_3 catalyst more stable during the growth process for the ZnO–In_2O_3 heterostructure nanowires than the In_2O_3 catalyst in the In-doped ZnO nanowires grown under the previous conditions [11]? This could be a result of the independent role of the In_2O_3 powder under the current conditions in comparison to the previous conditions (Fig. 6). In the previous work, the source materials were Zn_xIn_yO materials that were obtained by sintering ZnO+In powders, while here ZnO and In_2O_3 could evaporate separately (Fig. 6). In fact, more In_2O_3 powder with a small amount of ZnO powder evaporated in the first step as a result of the lower melting point of the In_2O_3 powder compared to the ZnO powder. Therefore, the droplets were In_2O_3 particles with a small amount of Zn. These particles play a role as a catalyst when growing In-doped ZnO nanowires via the VLS method. The particles were stable during the growth process because of the stable conditions in the first step.

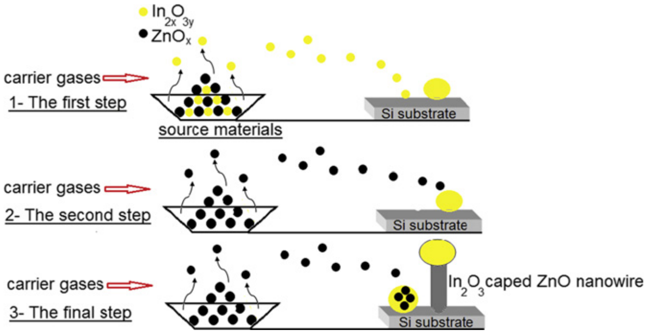

Fig. 6. Schematic illustrating the formation of the In_2O_3 catalyst and the ZnO–In_2O_3 heterostructure nanowires during the growing process.

PL study is a powerful method for investigating the effects of doping on the optical properties of ZnO nanostructures because doped ZnO nanostructures are expected to have different optical properties in comparison with undoped ZnO. Fig. 7 shows the room temperature PL spectra of the undoped ZnO nanowires and the ZnO–In_2O_3 heterostructure nanowires. The PL spectra of the nanowires show a strong peak in the ultraviolet (UV) region at 382 nm and a weak green emission (deep-level emission (DLE)) peak in the visible region at around 480 nm. This UV emission is also called the near band edge (NBE) emission and is caused by the recombination

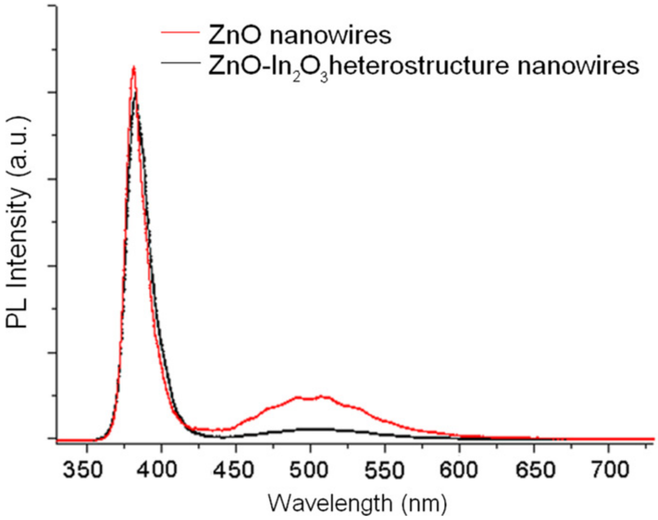

Fig. 7. PL spectra of the ZnO–In_2O_3 heterostructure nanowires and undoped ZnO nanowires.

of free-excitons via a process of exciton–exciton collision. It has been suggested that the green band emission is related to singly ionized oxygen vacancies in ZnO, and results specifically from the recombination of a photo-generated hole with the singly ionized charge state of this defect. The NBE/DLE ratio of the ZnO–In_2O_3 heterostructure nanowires, which is one of the main factors that is usually used for comparing the optical properties of samples, is larger than the NBE/DLE ratio of the undoped ZnO nanowires. Therefore, the ZnO–In_2O_3 heterostructure nanowires have a better relative crystalline quality and improved optical properties. In fact, the PL results that are presented here are in good agreement with other ZnO-semiconductor heterostructure nanostructures [13,20,21].

The improved NBE intensity and suppressed defect emission can be understood as follows. First, the larger band gap of In_2O_3 (3.6 eV) compared to that of ZnO (3.32 eV) more efficiently confines the electrons/holes in the ZnO nanowires, and the recombination of these pairs gives the near band edge emission. In addition, the surface dangling bonds and/or surface defect density of states can be reduced via the surface passivation. All of these contribute to the increased NBE and suppressed DLE. In addition, in comparison with the previous works, the UV peak of the In-doped ZnO nanowires is not shifted toward the blue region. This could be a result of the lower indium content of the body of the ZnO–In_2O_3 heterostructure nanowires. According to the FESEM results, the droplets were stable during the growth process for the In_2O_3 capped ZnO nanowires. Therefore, a lower amount of indium could be diffused in the nanowires (see Fig. 2(c)). The blue shift in the UV emission is believed to be a result of the Burstein–Moss effect because of the indium doping in the ZnO nanostructures that we observed in the previous works [11,12].

4. Conclusion

The thermal evaporation method was used to grow In_2O_3 capped ZnO nanowires. A comparison of the results from the previous studies and current study showed that the indium source position in the thermal evaporation setup played an important role in obtaining different morphologies. A study of the early stages of the growth process revealed that the In_2O_3 particles played a self-catalytic role. Experimental evidence demonstrated that the thermal evaporation method using ZnO + In_2O_3 powders not only induced the In_2O_3 cap growth in the tip region of the nanowires but also partially passivated the surface of the nanowires, both of which contributed to an improved near band edge emission and the suppression of the defect luminescence.

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References

[1] A. Qurashi, M.F. Hossain, M. Faiz, N. Tabet, M.W. Alam, N.K. Reddy, Fabrication of well-aligned and dumbbell-shaped hexagonal ZnO nanorod arrays and their dye sensitized solar cell applications, Journal of Alloys Compounds 503 (2010) L40–L43.

[2] R. Yousefi, F. Jamali-Sheini, M.R. Muhamad, M.A. More, Characterization and field emission properties of ZnMgO nanowires fabricated by thermal evaporation process, Solid State Sciences 12 (2010) 1088.

[3] F. Jamali-Sheini, M.A. More, S.R. Jadkar, K.R. Patil, V.K. Pillai, D.S. Joag, Observation of photoconductivity in Sn-doped ZnO nanowires and their photoenhanced field emission behavior, Journal of Physical Chemistry C 114 (2010) 3849.

[4] A. Khorsand Zak, R. Yousefi, W.H. Abd Majid, M.R. Muhamad, Facile synthesis, and X-ray peak broadening studies of $Zn_{1-x}Mg_xO$ nanoparticles, Ceramics International 38 (2012) 2059–2064.

[5] R. Yousefi, M.R. Muhamad, Effects of gold catalysts and thermal evaporation method modifications on the growth process of $Zn_{1-x}Mg_xO$ nanowires, Journal of Solid State Chemistry 183 (2010) 1733.

[6] F. Jamali-Sheini, D.S. Joag, M.A. More, Influence of process variables on growth of ZnO nanowires by cathodic electrodeposition on zinc substrate, Thin Solid Films 519 (2010) 184.

[7] S.Y. Bae, C.W. Na, J.H. Kang, J. Park, Comparative structure and optical properties of Ga-, In-, and Sn-doped ZnO nanowires synthesized via thermal evaporation, Journal of Physical Chemistry B 109 (2005) 2526.

[8] C.H. Jung, D.J. Kim, Y.K. Kang, D.H. Yoon, Transparent amorphous In–Ga–Zn–O thin film as function of various gas flows for TFT applications, Thin Solid Films 517 (2009) 4078.

[9] E. Pál, V. Hornok, A. Oszkoó, I. Dékány, Hydrothermal synthesis of prism-like and flower-like ZnO and indium-doped ZnO structures, Colloids and Surfaces A 340 (2009) 1.

[10] M.N. Jung, S.H. Ha, S.J. Oh, J.E. Koo, Y.R. Cho, H.C. Lee, T.I. Jeon, H. Makino, J.H. Chang, Field emission properties of indium-doped ZnO tetrapods, Current Applied Physics 9 (2009) e169.

[11] R. Yousefi, M.R. Muhamad, A.K. Zak, Investigation of indium oxide as a self-catalyst in ZnO/ZnInO heterostructure nanowires growth, Thin Solid Films 518 (2010) 5971.

[12] R. Yousefi, F. Jamali-Sheini, A.K. Zak, M.R. Mahmoudian, Effect of indium concentration on morphology and optical properties of In-doped ZnO nanostructures, Ceramics International 38 (2012) 6295–6301.

[13] L. Shi, Y. Xu, S. Hark, Y. Liu, S. Wang, L. Peng, K. Wong, Q. Li, Optical and electrical performance of SnO_2 capped ZnO nanowire arrays, Nano Letters 7 (2007) 3559–3563.

[14] J.M. Lin, C.L. Cheng, H.Y. Lin, Y.F. Chen, Giant, Enhancement of band edge emission in ZnO and SnO nanocomposites, Optics Letters 31 (2006) 3173.

[15] C.C. Lin, H.P. Chen, H.C. Liao, S.Y. Chen, Enhanced luminescent and electrical properties of hydrogen-plasma ZnO nanorods grown on wafer-scale flexible substrates, Applied Physics Letters 86 (2005) 183103.

[16] J.H. Li, D.X. Zhao, X.Q. Meng, Z.Z. Zhang, J.Y. Zhang, D.Z. Shen, Y.M. Lu, X.W. Fan, Enhanced ultraviolet emission from ZnS-coated ZnO nanowires fabricated by self-assembling method, Journal of Physical Chemistry B 110 (2006) 14685.

[17] A. Qurashi, T. Yamazaki, E.M. El-Maghraby, T. Kikuta, Fabrication and gas sensing properties of In_2O_3 nanopushpins, Applied Physics Letters 95 (2009) 153109.

[18] A. Qurashi, E.M. El-Maghraby, T. Yamazaki, T. Kikuta, Catalyst supported growth of In_2O_3 nanostructures and their hydrogen gas sensing properties, Sensors and Actuators B 147 (2010) 48–54.

[19] A. Qurashi, E.M. El-Maghraby, T. Yamazaki, Y. Shen, T. Kikuta, A generic approach for controlled synthesis of In_2O_3 nanostructures for gas sensing applications, Journal of Alloys and Compounds 481 (2009) L35–L39.

[20] I. Kazeminezhad, R. Yousefi, Growth and characterization of ZnO (microdisks)/W18O49 (nanorods) heterostructures, Solid State Sciences 14 (2012) 349–353.

[21] S. Kim, C.O. Kim, H.T. Oh, S.H. Choi1, Strong enhancement of near-band-edge photoluminescence from ZnO by assembling ZnO/SiO_x heterostructures, Journal of Physics D: Applied Physics 41 (2008) 235403.