The effect of Fe-dopant concentration on ethanol gas sensing properties of Fe doped ZnO/ZnO shell/core nanorods

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Abstract

In this paper, Fe doped-ZnO/ZnO shell/core nanostructures were synthesized through a simple two-step method and the effects of Fe dopant concentrations (between 0-9 at.%) on the structural, optical, electrical and gas sensing properties were investigated. The X-ray diffraction analysis revealed that all of the samples are crystallized in the same wurtzite hexagonal crystal structure with (002) peak as the main orientation. Nevertheless, the morphology of shell/core nanorods remained stable with increasing of Fe dopant, but the crystallinity improved. The Ultraviolet -Visible spectroscopy analysis showed that the Fe ions have coordination number of 3+ in the ZnO shell layer. The participation of Fe³⁺ ions into ZnO layer was also confirmed by Current-Voltage (I-V) curves where the resistance of nanorods was reduced with Fe concentration. Moreover, the ethanol-sensing properties of the Fe-doped ZnO/ZnO shell/core nanorod sensors were systematically investigated. According to the results, optimum gas sensing was obtained by the addition of 0.5 at.% Fe to ZnO shell layer which lead to significant enhancement in ethanol gas response.

Keywords: Zinc oxide nanorods; Encapsulation; Fe dopant; gas sensor; response.

1. Introduction

Ethanol is a hypnotic gas which has been widely utilized in the chemical, biomedical and food industries [1]. It has been proven that long-term exposure to potentially fast volatile alcohol vapor may cause carcinogenic and mutagenic injuries on human [1]. Therefore, there is a great demand for the monitoring of ethanol vapor at trace levels.

In the recent years, different metal oxide semiconductor (MOS) nanostructures such as SnO_2 , ZnO , WO_3 [2-4] are extensively investigated for ethanol vapor sensing aims. The function of MOS chemoresistive gas sensors is based on the physical absorption of trace species (with redox interactions) on the surface states and subsequent changes in their surface electron density and conductivity [5]. Among various MOSs, ZnO nanostructures are the most important candidates because of their preparation simplicity, low cost, thermal and chemical stability, high electron mobility and exquisite response to several gases or volatile organic compounds [6-8].

Up to now, a various kinds of ZnO nanostructures including nanoflowers [9], nanorods [10], nanofibers [11], nanobelts [12], and nanotubes [13] have been prepared by various physical and chemical methods. Among these, ZnO nanorods are particularly useful due to their large active surface area and persistent against aggregation. Moreover, nanorods with high aspect ratio and size confinement in two coordinates demonstrate better crystallinity, higher integration density, lower power consumption and consequently the highest compatibility with microelectronic processing industries [14]. In addition, they show superior gas sensing properties because of their large active surface area and small diameter comparable with Debye length (a measure of field penetration into the bulk) [14]. Recently, one-dimensional heterostructured nanorods have attracted a great deal of attentions in the fabrication of nanodevices ranging from (opto-)

electronic devices to chemical sensors due to their high specific surface area and special physicochemical properties [15-17]. Until now, several ZnO heterostructure nanorods have been developed in configuration of metal decorated nanorods for their surface functionalization, such as Ag, Pt and Au particles [18,19], as well as ZnO core-shell nanostructures, such as ZnO/TiO₂ [20], ZnO/In₂O₃ [21], and SnO₂/ZnO [22]. It is confirmed that one-dimensional heterostructured nanomaterials are the best candidates for high-performance gas sensors, exhibiting high sensitivity, good selectivity, fast response and recovery times, and long-term stability [23,24]. Recently, Li et al. [25] synthesized the hollow SnO₂-ZnO core-shell nanofibers for improving ethanol sensing performance and observed that the response of the sensor increased about 11 times in comparison with SnO₂ sensor. Hwang et al. [26] reported a considerable improvement in gas response to both NO₂ gas and ethanol vapor for ZnO-SnO₂ core-shell nanowires in comparison with bare ZnO nanorods. Choi et al. [27] investigated the effect of ZnO shell thickness in SnO₂-ZnO core-shell nanowires on detection of trace amounts of reducing gases. Also, ZnO/WO₃ core/shell nanowires were synthesized by Park et al. [28] through thermal evaporation followed by sputter-deposition of WO₃ and their sensing properties toward H₂ gas were examined.

Since the sensing mechanism of ZnO nanorods is based on the surface reaction with the exposed gas (adsorption and desorption of the test gas molecules), surface decoration of nanoparticles or doping with an element that has a stronger chemical affinity may cause enhancement of gas sensing performance [29-31]. Usually, doping in nanostructures can create defects and these defects play a role as preferential adsorption sites for adsorption of gas molecules [32]. However, the results of many publications showed that direct doping of multivalent ions like In, Al, Sn and etc. with desired high amounts is a challenging issue [33-36].

Fe doped ZnO nanostructures have fantastic characterization so that up to now, the many groups have been investigated their properties and applications. Fe ions have multivalence state. It was reported that Fe dopant into the ZnO appears in the form of Fe^{2+} and Fe^{3+} which influenced the band gap and electrical property [37,38]. In this work, we have suggested the fabrication of Fe doped ZnO/ZnO shell/core nanorods (NRs) using a simple and low cost hydrothermal method followed by dip. The effect of Fe content on structural, optical, electrical and also gas sensing properties to ethanol were investigated in detail. In addition, we have also done a complementary work to find out the optimal Fe concentration in shell layer.

2. Material and methods

2.1. Sample preparation

The Fe doped-ZnO/ZnO shell/core NRs were prepared on glass substrates by a simple two-step method, as reported elsewhere [23]. Firstly, the glass substrates were ultrasonically cleaned by acetone, ethanol and deionized water to remove contaminants. Then, the clean glass substrates were spin-coated by a sol of 0.05 M zinc acetate dihydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, Merck, 99.0%) and 0.06 M diethanolamine ($\text{C}_4\text{H}_{11}\text{NO}_2$, Merck, 98%) in ethanol. The spin-coating was performed with a speed of 3000 rpm for 30 s and then, the obtained films were dried at 180°C for 10 min. This procedure was repeated for five times and finally, the films were annealed at 450°C for 1 h in air.

In the second step, the hydrothermal method was used to grow up the oriented ZnO NR array on ZnO seeds. The substrates were suspended horizontally in a 0.001 M zinc nitrate and 0.1 M sodium hydroxide aqueous solution under slow constant stirring at 70°C for 90 min. Afterwards, the samples were cleaned by deionized water to remove the residual salts, dried in air and finally annealed at 500°C for 1 h.

The shell layer was formed by encapsulation ZnO NRs by using dip-coating method in a Fe-doped sols including 0.5 M zinc acetate dihydrate, 0.6 M diethanolamine and various concentrations of iron nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck, 98%) ($[\text{Fe}/\text{Zn}] = 0, 0.5, 1.5, 4.5$ and $9 \text{ at.}\%$) dissolved in ethanol. To obtain a transparent and homogeneous solution, each sol was stirred at 60°C for 20 min. Then, the annealed ZnO NR samples were dipped vertically into the solution and withdrawn for 1 min. Subsequently, they were pulled out at a constant speed of 3 cm/min and dried at 180°C for 10 min in air. The ZnO shell/core NRs with uniform layer with desired thickness were obtained by two dipping cycles. Finally, all of the samples were annealed at 450°C for 1 h in air. The sensors were formed by sputtering of Au grid contacts (70 nm) on top of the samples in metal-semiconductor-metal structure.

2.2. Characterizations

The X-ray diffraction (XRD) (X'Pert PRO, Philips) was used for structural investigation. Topography of the samples was investigated by scanning electron microscope (SEM) (VEGA, TESCAN) and atomic force microscope (AFM) (NT-MDT). The SEM samples had been coated by a gold thin film using a desktop sputtering system (Nanostructured Coating Co.-Iran). The optical properties of the prepared samples were measured using an ultraviolet –visible (UV-Vis) spectrophotometer (Jasco v570). A two point probe method was applied for verifying the electrical resistivity of the films. The performance of the sensors to ethanol vapor was measured by using a purpose-built system. The sensor response is defined by the ratio R_a/R_g while R_a and R_g are the sensor electrical resistance in air and gas, respectively.

3. Results and discussion

The AFM micrograph of seed layer as well as SEM images of bare ZnO NRs and 1.5 at.% Fe doped- ZnO/ZnO shell/core NRs are shown in Fig. 1(a-c), respectively. Fig. 1(b) contains ZnO

NRs with diameter of 40~60 nm while the encapsulated nanorods have been thickened to about 60-100 nm (Fig. 1(c)). The length ($\sim 1\mu\text{m}$) and number density ($\sim 3 \times 10^7 \text{ cm}^{-2}$) of the NRs were almost unchanged by encapsulation. So, it indicates that the encapsulation process forms a thin shell layer on the surface of ZnO NRs whereas the length of NRs is nearly intact. These results demonstrate that the encapsulation of ZnO NRs is a well-controllable efficient method for fabrication of doped ZnO NRs with minimal morphological changes. Also, it has been reported that the surface of the ZnO NRs would be partially roughens after encapsulation [39,40] which is an important issue for surface adsorption and desorption of the oxygen atoms.

<Fig. 1>

The XRD patterns of x at.% Fe doped-ZnO/ZnO shell/core NRs ($0 \leq x \leq 9$) are shown in Fig. 2(a). As can be seen, all of the patterns have a main diffraction peak at $\sim 34^\circ$ corresponding to (002) plane of ZnO NRs which indicates a preferential texture in hexagonal wurtzite crystal structure (JCPDS Card No. 80-0074). There are no other diffraction peaks corresponding to FeO, Fe_2O_3 or Fe_3O_4 phases indicating that Fe atoms are doped in the ZnO host lattice without any segregation [41].

<Fig. 2>

The intensity of (002) peak considerably increases with incorporation of Fe atoms (up to 4.5 at.%) in the shell layer. In order to quantitatively evaluate the preferential crystal orientation, the texture coefficient parameter (TC) for the (002) peak of ZnO NRs was calculated and plotted in the inset of Fig. 2(a) [42]:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{(1/n) \sum_n I(hkl)/I_0(hkl)} \quad (1)$$

where $I(hkl)$ is the intensity of the (hkl) plane, $I_0(hkl)$ is the relative intensity of the corresponding plane given in the XRD reference (JCPDS Card No. 80-0074), and n is the total number of diffraction peaks. When the TC value is more than 1, the preferential growth can be assumed. The texture coefficient for (002) peak increases with the increase of Fe concentration up to 4.5 at.% and then decreases slightly. This observation indicates that 4.5 at.% Fe doped ZnO NRs can be taken into account as the optimized value for improving the crystallinity of shell layer. Similar observations have been reported by others [41,43]. For example, Xu et al. [41] showed that the 1 at.% Fe-doped ZnO thin film has the strongest (002) peak while higher concentrations of Fe gradually decline the preferential growth of (002).

The d -spacing value of (002) peak and average grain size, D , were calculated for all of the ZnO NRs (Fig. 2(b)). The decrease of the d -spacing value with increasing Fe dopant content can be attributed to the difference in ionic radius between Zn and Fe ions [40]. It is known that Fe ions can be substituted in the Zn sites in the ZnO lattice in both Fe^{2+} and Fe^{3+} states [37,44,45]. The X-ray patterns show that the (002) peak of Fe doped ZnO NRs shifted toward the higher angles. Thus, according to the ionic radius of Zn and Fe ($Fe^{2+} \sim 0.76$ Å, $Fe^{3+} \sim 0.64$ Å and $Zn^{2+} \sim 0.74$ Å [45]) and also contraction of ZnO lattice (by increasing the Fe content), it can be discerned that the Fe^{+3} ionic state is predominantly substituted instead of Zn^{2+} ions in the ZnO lattice.

The transmittance spectra of the core/shell NRs are shown in figure 3(a). As can be seen, the transmittance in the visible range increase with Fe doped into ZnO shell layer upto 4.5 at.%. Also, it is clear that absorption edge of all NRs samples is sharp and located at wavelengths below 400 nm. This implies the intrinsic absorption edge is originated from direct transition of electrons and then all the films are assigned to be semiconductors with a direct band gap [46]. The transmittance increasing can be described as the enhancement of the crystallinity of shell

layer with Fe doped, as seen in the structural analysis. The optical band gap of samples was obtained by exerting the Tauc relation to optical transmittance spectra. The optical band gap is determined through the plotting a direct line at absorption edge of the curve in $(\alpha h\nu)^p$ versus $h\nu$ plot. The $h\nu$ is the photon energy, A is the constant of the transmittance probability, E_g is the value of band gap, and p is a power constant which takes the value of 2 for direct transition and $\frac{1}{2}$ for indirect transition. The results of fittings showed that all of the Fe doped-ZnO NRs behave like a direct transition semiconductor. The value of the optical band gap of the samples was obtained through extrapolating the linear part of the graph at $(\alpha h\nu)^2 = 0$ (Fig. 3). The band gap of pure ZnO/ZnO shell/core NRs is 3.11 eV which is regularly increased with increasing the concentration of Fe dopant to about 3.28 eV for 9 at.% Fe doped ZnO NRs. The enhancement of the optical band gap of Fe doped ZnO NRs may be explained by Burstein-Moss band filling effect [41]. The ZnO is an n-type semiconductor and the Fermi level (ξ_n) positions inside of the band gap. According to the Burstein-Moss effect, if the Fermi level gets pushed inside of the conduction band, therefore the states below ξ_n in the conduction band are filled and the absorption edge shifts to the higher energy caused to widening the band gap. This is satisfied when Fe ions contribute to coordination number 3+ in the ZnO structure [47].

<Fig. 3>

The electrical resistivity of samples was measured through 2-electrode method and compared as shown in Fig. 4. Also, the inset of Fig. 4 shows that all of the bare and doped ZnO NRs follow from ohmic behavior in the applied DC voltage range of 0-6 V. By comparing the results, it was found that the resistance of devices remarkably reduces with increasing Fe concentration into ZnO shell layer up to 4.5 at.% Fe, and then, it increases a little in 9 at.% Fe doped sample, which confirms the ionic state of Fe dopant (Fe^{3+}) obtained by XRD results.

<Fig. 4>

In other words, ZnO is naturally an n-type semiconductor due to its intrinsic defect states such as zinc interstitials and oxygen vacancies [48]. Besides, ZnO surface tends to intrinsically adsorb the oxygen molecules which act as electron acceptors. The adsorbed oxygen species capture electrons from the conduction band of the ZnO and form chemisorbed O_2^- or O_2^{2-} [49]. This leads to surface electron depletion in the ZnO semiconductor and consequently, decreases of the carrier density. As can be seen in Fig. 4, the resistance of Fe-doped ZnO NRs decreases with the increase of Fe concentration in shell layer. Therefore, one can conclude that much of the multivalent Fe atoms (2+ and 3+) are substituted in ZnO lattice in three valence state (Fe^{3+}). The Fe^{3+} ions substituted into Zn^{2+} lattice sites act as donor dopants and increase the carrier concentration and thereby, electrical conductivity [41]. On the other hand, increasing the concentration of Fe dopant increases the scattering centers [50] and consequently, impedes the mobility of electronic carriers, as what is seen for the sample with 9 at.% Fe dopant.

In the next step, the performance of pure and Fe-doped ZnO/ZnO shell/core NR sensors to ethanol vapor at various temperatures (room temperature to 270°C) was investigated. Fig. 5 shows the response of the samples to 500 ppm ethanol vapor at different operating temperatures. The optimal operating temperature was 230°C for bare ZnO/ZnO sample and 250°C for Fe doped NR sensors. It is clear that the optimal operating temperature depends to the Fe dopant. Fig. 6 shows the response of the samples to different concentrations of ethanol at the optimized temperatures.

<Fig. 5>

<Fig. 6>

For studying the current levels of the sensors, the changes of current versus time to the single ethanol cycle (500 ppm) at their optimal operating temperatures is shown in Fig 7 (a). The current level for the pure ZnO and 4.5% Fe doped sensors are minimum and maximum, respectively. The highest electrical current level of the 4.5% Fe doped sample is due to the increase of charge carriers in this sensor which was previously described. A higher electrical current level is important for making a device that not only operates with simple electrical measuring tools, but also is less sensitive to environmental noises.

For the better comparison of the sensors response, the each current curve of Fig. 7(a) was normalized to its base current (I_0) as the normalized response curve (Fig. 7(b)) [23]. It can be seen that the sample with 0.5% Fe dopant shows the maximum response (18.6) while the sensor with 4.5 at.% Fe encapsulated ZnO nanorods shows the minimum response (2.2).

<Fig. 7>

Mechanism of ethanol sensing by ZnO NRs has been described by many groups [25,51]. In the sensing process and at the optimal operating temperature, the oxygen molecules adsorbed on the surface of ZnO NRs and afterwards, dissociated to atomic oxygen [3]. These species capture the surface electrons from the conduction band of ZnO, chemisorb on the surface and produce different species of oxygen (O^{2-} , O^- , O_2^-). Therefore, an electron depletion layer on the surface of ZnO would be formed. The formation of the depletion layer increases the electrical resistance of the sensing layer. When ZnO NRs are exposed to the ethanol vapor, the reaction between ethanol and ionic oxygen goes on as following:

According to the above chemical reaction, the freed electrons tend to rapidly return back to the conduction band of NRs. Hence, the resistance of the ZnO NRs decreases in the presence of ethanol and sensor current increases.

The performance of ZnO NRs-based gas sensors is dependent to parameters like dopant material and quality of surface depletion layer. Hongsith et al. [52] offered a formula for explaining the ethanol sensing response of a semiconducting sensor which contains the effect of different parameters:

$$S_g = \frac{R_a}{R_g} = \frac{\Gamma_t k_{Eth}(T) [O_{ads}^{ion}]^b [CH_3CH_2OH]^b}{n_0} + 1$$

where Γ_t is a time constant, $k_{Eth}(T)$ reaction rate constant as a function of activation energy and temperature, b is the charge parameter which is 1 and 0.5 for O^- and O^{2-} , respectively. $[O_{ads}]$ and $[CH_3CH_2OH]$ are concentrations of adsorbed oxygen on the surface of metal oxide sensor and ethanol vapor, respectively. Also, n_0 is the concentration of free electrons at the working temperature and air atmosphere which determines the conductivity and base current of the sensor at the operating temperature. However, according to this equation response of the sensor is proportional to the reaction rate.

As seen, there is an optimum operating temperature for each sensor in which response is highest and above that, the response decreases. It results that ZnO NRs sensors should be operated in optimum temperature for enhancement of activation and chemisorption of ethanol species by the oxygen species [53]. As the thermal energy reaches the proper limit to conquer the activation energy barrier of reaction, electron concentration significantly increases and a high response is accomplished [54]. Increasing temperature above the optimum value causes to intensive

desorption of oxygen molecules from the surface of ZnO NRs and consequently reduction of the sensor response due to progressive desorption of oxygen ionic species [53,55].

In accordance with above equation, the increasing of responsivity of 0.5 at.% Fe doped-ZnO/ZnO shell/core NRs can be well-described. Here, surface doping of ZnO with the Fe ions increases the surface reaction rate. This implies that Fe ions injected to the surface of ZnO NRs operate as a catalyst and subsequently, enhance the reaction rate and adsorption of gas species (oxygen and target gas) on the surface of crystal at the optimum temperature. Since sensing quality of metal oxide sensors is highly affected by adsorption and desorption of gas species on the surface, the sensor response increases in 0.5 at.% Fe doped-ZnO/ZnO shell/core NRs. According to space-charge model, adsorption of oxygen on the oxide surface make the depletion layer thicker and this property can improve the sensing features of 0.5 at.% Fe doped-ZnO/ZnO shell/core NRs [41].

The activation energy of the sensors can be calculated by the Arrhenius equation [56].

$$k_{Eth}(T) = A \exp \left(- \frac{E_a}{k_B T} \right)$$

where E_a is activation energy. According to this equation, increase of the sensor temperature amplifies the reaction rate. On the other hand, Fe dopant could increase the activation energy for the Zn oxide nanostructures [57]. Therefore, it is clear that adding of Fe dopant into shell layer leads to increase the optimum temperature from 230°C for pure ZnO/ZnO shell/core NRs to 250°C for Fe doped-ZnO/ZnO shell/core NRs.

On the other hand, further increasing the number of Fe ions in the ZnO shell layer have a destructive effect on the ethanol sensing. This leads to the enhancement of the number of carriers, which can decrease the response of the sensors (especially 4.5% Fe doped-ZnO/ZnO

shell/core NRs) according to the equation (1). Furthermore, large number of scattering atoms for the high concentrations of Fe decreases the surface reaction rate in the shell layer and declines the oxygen capturing sites. This can cause to reduce the Debye length and consequently attenuation of depletion region.

Using Fe dopant for modification of sensing properties of zinc oxide and other semiconductors have been reported by different groups. Kuo et al. [58] investigated the response of ZnO thin films doped with Fe for ethanol sensing and founded the maximum response for 5% doping. Yuliarto et al. [59] measured the response of Fe doped thin film-based sensors towards liquefied petroleum gas and observed the maximum response for the sample with 0.5% Fe. In addition, the effective catalyst role of Fe in improvement of H₂S gas detective properties in sensors fabricated based on the SnO₂ nanostructures has also been reported [60].

Conclusions

In summary, the pure and Fe doped-ZnO/ZnO NRs samples were prepared by a simple two-steps process. The XRD characterization showed that all of the NRs were crystallized in the wurtzite hexagonal crystal structure. According to the SEM images, one dimensional ZnO nanorods were grown in hydrothermal method and appropriately encapsulated with a thin layer of Fe-doped ZnO. With increase in Fe dopant concentration into ZnO shell layer, the band gap increased from 3.11 eV to 3.27 eV. The I-V measurements showed that the electrical resistance of samples decrease with increase Fe concentration can easily. The sensors exhibited a good performance in detecting the ethanol vapor. Addition of Fe-dopant into shell layer increased the responsivity of the sensors compared to pure ZnO sample and was also optimized at dopant concentration amount of 0.5 at%.

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Figure Captions:

Fig. 1. The AFM micrograph of ZnO seed layer (a) and the SEM images of the bare ZnO NRs (b) and 1.5 at.% Fe doped- ZnO/ZnO shell/core NRs (c).

Fig. 2. (a) XRD pattern of pure and Fe-doped ZnO/ZnO shell/core nanorods (Inset: texture coefficient (TC) as a function of the Fe concentration. (b) The d-spacing value and grain size of the samples with various Fe concentration, along with patterns of (002) peaks in inset.

Fig. 3. The transmittance (a) and graph of $(\alpha h\nu)^2$ vs. photon energy (b) for Fe doped–ZnO/ZnO shell/core NRs with different Fe concentrations as well as the value of the optical band gap in inset.

Fig. 4. The electrical resistivity of Fe doped–ZnO/ZnO shell/core NRs (The inset: the I-V curves of samples).

Fig. 5. The response of the bare and doped ZnO NR samples to 500 ppm ethanol vapor at different operating temperatures.

Fig. 6. The response curves of x at.% Fe doped-ZnO/ZnO shell/core NRs ($0 \leq x \leq 9$) to different concentrations of ethanol at the optimal operating temperatures.

Fig. 7. The electrical current (a) and normalized response curves (b) versus time of x at.% Fe doped-ZnO/ZnO shell/core NR sensors ($0 \leq x \leq 9$) to 500 ppm of ethanol vapor at the optimal operating temperatures.

Fig. 1

Fig. 2

Fig. 3

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Fig . 5

Fig. 6

Fig. 7