Influence of Cr dopant on the microstructure and optical properties of ZnO nanorods

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ABSTRACT

One-dimensional (1D) undoped and Cr doped ZnO nanorods with average length of 1 µm and diameter of 80 nm were synthesized using hydrothermal method. The effects of Cr dopant on the structure, surface morphology and optical properties of nanorods were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultra-violet visible (UV-Vis) spectroscopy. The results showed that ZnO is crystallized in wurtzite hexagonal crystal structure. Moreover, it was found that Cr atoms were incorporated in the ZnO lattice and made a regular red-shift on the XRD peaks. Also, with respect to the optical properties it was concluded that doped ZnO nanorods were quite appropriate for photocatalytic applications, because the lower the optical band gap, the higher the light gain by the photocatalyst material. For example, the calculated band gap of ZnO nanorod decreased from 3.12 eV for pure ZnO nanorods to about 2.41eV for 3at.% Cr doped ZnO nanorods, which is quite enough to be activated even at visible (550nm) light for photocatalyst aims.

1. Introduction

ZnO is an important semiconductor with direct band-gap of 3.37 eV and high exciton binding energy of 60 meV [1, 2]. Thus, zinc oxide can be a promising candidate for novel applications such as UV detectors [1], field emission devices [2], high sensitivity gas sensors [3], biosensors [4], dye-sensitized solar cells [5], photoluminescent materials [6], photocatalytic degradation of pollutants [7] and antibacterial purposes [8].

One of the key properties of ZnO is that when it is exposed to light, photoexcited electron-hole pairs will be generated. The holes can be trapped by water or adsorbed –OH groups and consequently produce hydroxyl group (OH^{o}) which is known as a key factor in photocatalytic applications. Therefore, with broadening the light gain to visible range, one can make a photocatalyst material with higher activity. Thus, the ZnO nanostructure with narrower band is usually preferred. For example, it was shown that photocatalytic bactericidal activity of ZnO / MWCNTs thin film can be synergically improved through the formation of Zn–C carbonaceous bonds between ZnO and MWCNTs [12].

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Ohyama [13] reported that aluminum-doped ZnO thin films heat treated in reducing atmosphere show better optical and photocatalytic performance. Nunes [14] found that when the doping concentrations of Al was 1at.%, the electrical and optical properties of the doped ZnO were superior. Here, it is noteworthy that the size and morphology of ZnO are two other important parameters which determine its activity in various applications. In fact, ZnO nanostructures, by providing different shapes and higher surface area, might exhibit some interesting properties which cannot be obtained by its bulk or other structures. In this regard, several reports on the growth of high quality ordered ZnO nanostructures with enhanced physical and chemical properties have been published [9-11].

Nevertheless, according to our studies, very little papers have focused on the effects of dopant concentration on the structural and optical properties of ZnO nanorods, which is the objective of the present study. In this work, to study the synergistic effect of Cr atoms in ZnO nanorods, various contents of Cr nitrate were added in hydrothermal bath for the growth of Cr doped ZnO nanorods. Then, optical and structural properties of the nanorods were studied. Furthermore, the effect of Cr content on the degree of crystallization and band gaps was discussed.

2. Experimental

ZnO thin films (as seed layer) were coated on the glass substrate by sol-gel method. At first, Zinc acetate dehydrate was dissolved in ethanol, and then diethanolamine (DEA) as a stabilizer was dripped into the solution. The complex solution was stirred for 0.5 h at 60 ^{o}C until a transparent and homogenous sol was obtained. After that, the ZnO thin films were coated on the glass substrates by dip coating at a constant dropping speed of 3 cm/min. Each sample was soaked for 2min in the sol. The coated films were dried at 200 ^{o}C for 15min and the coating procedure was carried out twice to obtain a thicker and more uniform film. Finally, the samples were annealed at 500 ^{o}C for 1 hour to produce ZnO thin film as seed layer. In the next stage, hydrothermal bath for the growth of nanorods was carried out in supersaturated aqueous solution of 0.001M Zinc nitrate – 0.1M NaOH solution. To prepare the Cr doped ZnO nanorods, various contents of Cr nitrate (by considering Cr/Zn ratio of 0, 0.125, 0.25, 0.5 and 3at.%) were added to the hydrothermal solution. The previously fabricated seed layers were horizontally suspended in the hydrothermal bath at 70 ^{o}C for 1 hour. Finally, the resultant samples were rinsed with DI water and dried at room temperature.

The crystalline structure of the undoped and Cr-doped ZnO nanorods was determined by X-ray diffraction using PW1800 Philips diffractometer. Surface morphology and microstructure of some samples were depicted by AIS-2100, SERON SEM. A Jasco V530 UV-visible spectrophotometer was used to measure the optical transmittance spectra of the samples in UV-Vis ranges. X-ray fluorescence (XRF) elemental analysis was carried out using an S-360 link-analytical apparatus. The topography of the seed layered sample was studied using atomic force microscopy (AFM) using a Park Scientific model CP-Research (VEECO) at a non-contact mode.

3. Results and Discussion

The two different stages of ZnO nanorods growth are schematically shown in Fig 1a, b. At first, ZnO seed layer (Fig 1a) was coated on the glass substrate by dip-coating method and subsequently, ZnO nanorods were grown on the seed layer in super-saturated hydrothermal bath. surface morphology of the seed layer on the glass substrate is shown in Fig1c, d. SEM and AFM micrographs show the formation of a dense film, with almost no porosity or voids, including the islands on the surface with a grain size ranging between 20-50 nm. The root mean square (RMS) surface roughness of the films was 1.73 nm indicating an almost smooth surface.

As can be seen, the closely-packed Zno nanorods (NRs) were formed with an average diameter of ~ 50 nm and average length of ~1 μm on the seed layer, while by increasing the Cr dopant content to 0.5 and 3at.%, the thickness of ZnO nanorods partially increased to ~ 50 nm. Moreover, SEM image of the bare

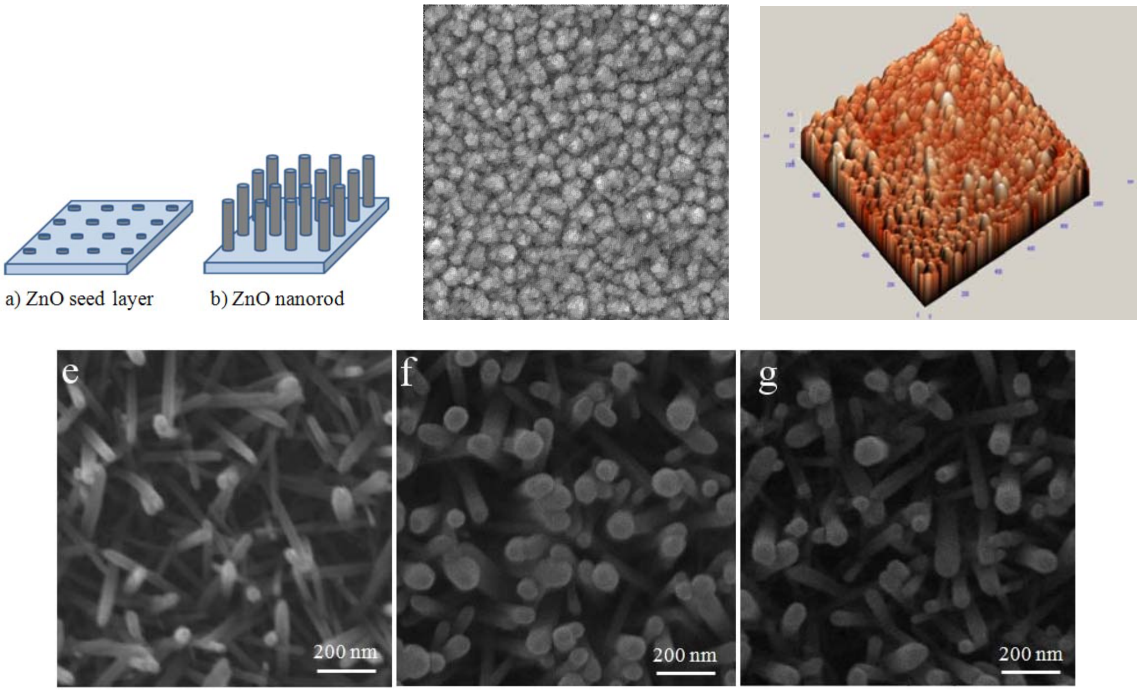

Fig. 1. a, b) Schematic of ZnO seed layer and nanorod growth. c) SEM and d) AFM micrograph of the as-prepared ZnO seed layer. e) the bare, f) 0.5 at.% and g) 3 at.% Cr doped ZnO nanorods

and doped ZnO arrays shows that NRs are nearly aligned along the normal direction of the substrate. Concerning the one-dimensional growth of ZnO nanorods in all cases, Abbasi et al. [15] suggested that nitrate anions facilitate the preferential growth of high energy plane (002) along [0001] direction of ZnO unit cell in an alkaline growth solution.

X-ray diffraction patterns of seed layer, bare ZnO and 3at.% Cr-doped ZnO nanorods are presented in Fig 2. These patterns show that all samples are crystallized in hexagonal wurtzite structure (No. 36-1451- data of wurtzite ZnO powder). As can be seen, the relative intensity of (002) to other crystallized peaks is much bigger for bare and doped ZnO NRs compared with ZnO seed layer. This observation confirms the growth of ZnO nanorods along the preferential orientation which was observed in SEM images.

Moreover, a shift of (002) peak toward higher wavelengths revealed that the ZnO host lattice is contracted by incorporation of Cr atoms into ZnO host lattice. It is known that in compounds, Cr ions can exist in the form of Cr^{2+} as well as Cr^{3+} [16-19]. On the other hand, the ionic radii of Cr^{2+}, Cr^{3+} and Zn^{2+} are 0.087, 0.075 and 0.088 nm, respectively [16]. Therefore, it is rational that by Cr substitution (especially in the form of Cr^{+3}) instead of Zn in ZnO lattice, a lattice distortion would be induced [17]. Therefore, the (002) peak shift toward higher angles with incorporation of Cr dopant (see higher magnification of XRD pattern around (002) peak in Fig 2) means that Cr is incorporated in the lattice with its +3 ionic state. The Cr ionic state is very important in electrical and optical properties (by formation of sub-levels through optical band gap) of ZnO nanostructure. Similar observation has been reported by other researchers and has been attributed to the incorporation of dopant ions into the lattice of the host material [17-20].

The average crystallite size of ZnO seed layer was estimated by t Sherrer's equation o be ~ 20 nm. In order to identify the presence of Cr in the samples, a typical elemental analysis XRF was obtained from 3at.% Cr doped ZnO nanorod sample. The results showed the existence of Cr but the concentration of Cr was about 0.5at.%. The observed difference between the XRF-results and the actual concentration of Cr in Cr:ZnO NRs could be due to the presence of considerable amount of

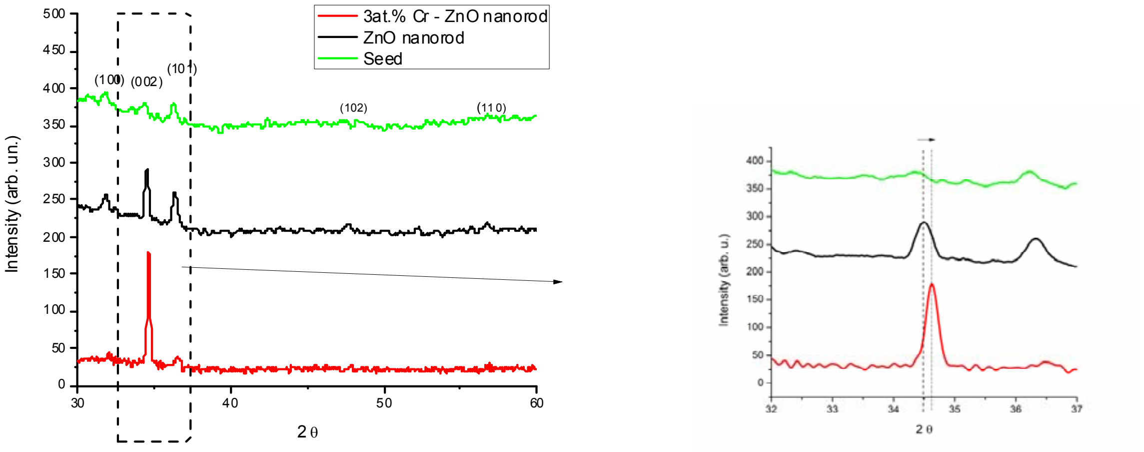

Fig. 2. X-ray diffraction patterns of the ZnO seed layer, bare and 3 at.% Cr-doped ZnO nanorods. The inset revels the higher magnification of XRD pattern around (002) peak

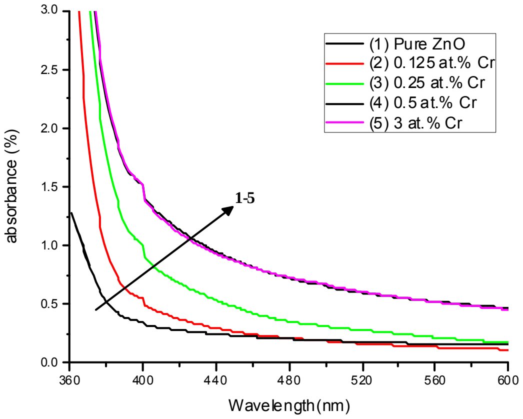

Fig. 3. Optical absorbance spectra of undoped and Cr doped ZnO nanorods showing optical absorption edges

physically adsorbed functional groups on ZnO NRs with high surface area [21].

Fig 3 shows the absorbance spectra of undoped and Cr-doped ZnO nanorods grown on the glass substrate. The samples have high transmittance in the energies lower than their optical band gap. Also, it is shown that absorbance obviously decreases in the visible range with increasing the Cr concentration in ZnO nanorods. It is clear that the undoped ZnO nanorods show an absorption onset at approximately 390 nm which is in good agreement with the intrinsic energy band gap of ZnO (~3.19 eV). With the increase of Cr-doping concentration, the absorption edge of ZnO red shifted. A significant increase of the Cr content was observed; the stronger absorption was assigned in the range of 400-600 nm (visible light region) which indicated a red-shift in the band-gap transition.

The band gap energy (E_g) values for the samples were evaluated by plotting $(\alpha h\nu)^2$ versus hν (see Fig 4), where hν is photon energy and α is the absorption coefficient. Extrapolation of the linear portions of $(\alpha h\nu)^2$ to zero gives the value of E_g for each spectrum.

The estimated E_g values for $Zn_{1-x}Cr_xO$ shifted to lower energies from 3.12 to 2.41 as the Cr content increased. A similar trend of decrease of band edge in ZnO doped has beenreported by other researchers [18, 19]. Yilmaz et al. [17] also observed a regular decrement in optical band-gap of ZnO micro-rods with increasing the concentration of Cr dopant and attributed this phenomenon to the formation of various optically active deep sub-levels through the band-gap. In fact, the Cr^{+3} ions not only make a considerable contraction in ZnO lattice due to different radii with Zn^{+2}, but also induce an optical-sublevel due to the difference of their ionic number [17, 19]. Bhat et al. [23] and Ba-abbad et al. [24] suggested that the shift of absorption toward the red-part of the spectra could be attributed to the sp-d exchange interaction between the band electrons of ZnO and localized d-electrons of the trivalent (here Cr^{+3}) additive element.

4. Conclusions

Cr doped ZnO nanorods were fabricated by simple sequential dip-coating and then hydrothermal growth of nanorods. SEM image

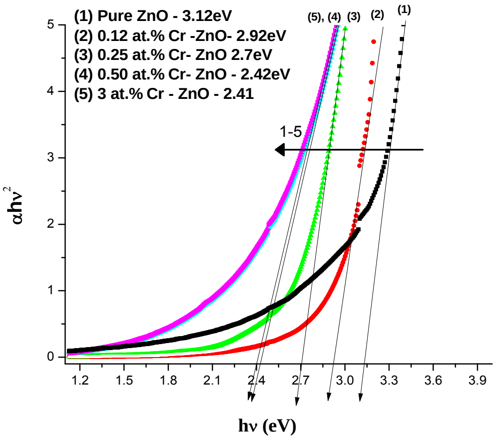

Fig. 4. The calculated Tauc curve of undoped and Cr doped ZnO nanorods

of Cr doped ZnO nanorod arrays shows that ZnO nanorods are aligned toward the normal direction of substrate and RMS surface roughness increased to 20.1 nm. From the X-ray diffraction patterns it could be observed that Cr atoms facilitated the growth of nanorods in preferred orientation (002). The effects of Cr dopant on structural, surface morphology and optical properties of nanorods were also studied. The results showed that optical band gap of 3%at. Cr doped ZnO nanorods decreased to about 2.41eV, quite enough to be activated even at visible (550nm) light for photocatalyst aims.

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