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Tm-doped ZnO nanorods as a TCO for PV applications☆

Hakan Çolak [a,*], Ercan Karaköse [b]

[a] Department of Chemistry, Faculty of Science, Çankırı Karatekin University, 18100, Çankırı, Turkey
[b] Kayseri Vocational College, Erciyes University, 38039, Kayseri, Turkey

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ABSTRACT

In photovoltaic (PV) devices, a transparent conducting oxide (TCO) film is used as a transparent electrode which permits sun rays to reach to the photoactive semiconducting layers and also to collect the photo-generated electrons. Due to their electrical and optical properties zinc oxide (ZnO) based thin films and nanostructures are considered as an abundant and safer option for TCOs. In this study, undoped and thulium (Tm)-doped ZnO nanorods (NRs) were produced on glass substrates via spin coating and hydrothermal methods. The ZnO samples were described by X-ray diffractometry (XRD). Morphological features of the ZnO samples were investigated with scanning electron microscopy (SEM). It is observed that the all ZnO samples have nanorod shape. The average rods diameter is between 75 and 100 nm. Also, the rods length is found to be between 0.96 and 1.62 μm. Electrical properties of the ZnO samples were performed via four probe method. The conductivity increases with measurement temperature and Tm doping. Optical spectra of the ZnO samples were measured in UV–Vis range and the band gap (E_g) is found to be 3.35 eV.

1. Introduction

Most of the global energy needs are provided by using fossil fuels. The fossil fuels are limited. Also they cause environmental pollution and global warming. We have to find new alternative energy sources because of the energy shortages. Examples of renewable energies are wind power, hydroelectric generation, geothermal sources and solar power. Among renewable energies solar power is the most promising because it utilises the nearly inexhaustible energy that we obtain from the sun. Our world receives approximately 1.2×10^{17} W of solar power, while the rate of current worldwide energy consumption is about ten thousand times. The irradiation energy of the sun can be used to produce an electrical current using the photovoltaic (PV) effect by means of PV devices (solar cells).[1]

Transparent conductive oxides (TCOs) are widely used in photovoltaics, because the films have high transmittance in the ultraviolet–visible (UV–Vis) range wavelength and electrical conductivity. Indium thin oxide (ITO) film is one of the most interesting TCO materials. Since the indium sources are restricted and it is expensive, it is necessary to find alternative TCO materials.[2] ZnO has been considered as other TCO materials due to its transparent and great conducting characteristics. Using ZnO instead of ITO is useful because of its typical properties such as non-toxicity, low cost, and abundance in nature. Furthermore, the visible light can pass through the ZnO film because it has a wide energy gap (3.37 eV). To improve the optical transmittance and electrical conductivity of the ZnO some metal atoms such as Al, Ga, In, Sn and Sb are doped into the ZnO crystal lattice.[3] Recently, the use of rare earth metals as doping materials has attracted great interest as a good alternative.[4,5] Band gap of Gd doped Al:ZnO films were investigated, and the lowest resistivity of undoped and Gd doped Al:ZnO were found to be 10.6×10^{-3} and 8.4×10^{-3} Ω cm, respectively.[6] In another work, Nd doped ZnO thin films were synthesized by sol–gel method on glass substrates, and it was found that the absorption peak shifts towards shorter wavelength with the increasing Nd amount.[7] Also, Pr-doped ZnO nanorods were synthesized, and it was determined that the lattice constants increased slightly with increasing Pr amounts.[8] In another report, Sm doped ZnO nanorod arrays were synthesized via vapour phase transport technique, and structural, optical and magnetic properties were investigated.[9] Eu^{3+} doped-ZnO nanorods were synthesized via microwave assisted technique by Korake et al, and their photocatalytic activity was investigated.[10]

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* Corresponding author. Fax: +90 376 218 95 41.
E-mail address: hakancolak@karatekin.edu.tr (H. Çolak).

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In our previous work, Tm_2O_3 doped ZnO powder was synthesized in the different stoichiometric amounts by solid state method at high temperatures. The limit solubility of Tm_2O_3 in the ZnO is found to be 4 mol%. Their average grain sizes were about 1 μm. Also, it was observed that electrical conductivity of the samples increases with increasing temperature and Tm_2O_3 doping concentration.[11] In another work, Tb^{3+} and Tm^{3+} doped ZnO thin films were synthesized by polymeric precursor method, and their electroluminescence properties were investigated.[12] Most of the reports about rare earth metal doped ZnO systems have been focused on magnetic and luminescence properties.[9,13–15] Lately, due to unique properties related to the geometrical shape one-dimensional (1D) nanostructures were investigated for applications in many fields. 1D ZnO nanomaterials (e.g. nanorods, nanowires) are the most promising candidates owing to their important physical properties. As the surface-to-volume ratio in NRs is very high, the surface states have a crucial role in optical and other properties.

In this regard, we synthesized Tm-doped ZnO NRs on glass substrate via spin coating and hydrothermal methods. The fabricated Tm-doped ZnO NRs were characterized using XRD, SEM, four point probe method and UV–Vis spectrophotometry. Tm-doped ZnO-NRs as alternative TCO material were investigated in terms of the suitability for PV applications in terms of their electrical and optical properties.

2. Experimental

Undoped and Tm-doped ZnO-NRs were produced by sol–gel spin coating and hydrothermal methods. Initially, the ZnO seed layers were coated on glass substrates by a sol–gel spin coating method. Zinc acetate dihydrate [$Zn(Ac)_2 \cdot 2H_2O$] was dissolved in 2-methoxyethanol ($C_3H_8O_2$), and monoethanolamine (MEA, C_2H_7NO) was added which served as the stabilizer. The concentration of Zn^{2+} was 0.5 mol/L, and the molar ratio of Zn^{2+}:MEA was 1:1. The resultant solution was stirred at 60 °C for 2 h and then aged for 24 h. The solution was then coated on glass substrates using the spin-coater system at 3000 r/min for 30 s. The deposited films were preheated at 250 °C for 15 min inside an oven. The depositing and preheating treatments were repeated for 5 times. Afterwards, the ZnO seed layers were heated at 450 °C for 12 h. To growth of ZnO NRs on the ZnO seeded substrates, aqueous solution of zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$], hexamethylenetetramine [HMT, $C_6H_{12}N_4$], and thulium (III) nitrate pentahydrate[$Tm(NO_3)_3 \cdot 5H_2O$] were prepared in deionized water (DI H_2O). The concentration of Zn^{2+} was 0.075 mol/L, and the molar ratio of Zn^{2+}: HMT was 1:1. The mixture was taken in a teflon-lined stainless steel autoclave. In the mixture, $[Tm^{3+}]/[Zn^{2+} + Tm^{3+}]$ ratio was varied from 0 to 5 mol%. The growth was carried out at 95 °C for 4 h. After the growth, the substrate was rinsed with DI water and dried in air.

The films were investigated as structural, morphological, electrical and optical by XRD (Bruker AXS D8), SEM (Zeiss, EVO LS 10), four probe dc system and a UV/vis spectrophotometer (Rayleigh UV-2601).

3. Results and discussion

3.1. Structural analysis

The undoped and Tm-doped ZnO-NRs were examined by the XRD analysis. Fig. 1 shows XRD patterns of the undoped and Tm-ZnO-NRs on the glass substrate. All the patterns were indexed as hexagonal structure. The patterns were indexed as wurtzite structure (PDF Card No: 36-1451).[16] It is evident from the XRD results that there are no extra peaks due to thulium metal, thulium/other oxides or any zinc thulium phase, exhibiting that the as-synthesized samples have single phase. The Tm^{3+} ions were understood to have substituted the Zn^{2+} site without changing the hexagonal structure. The undoped and Tm-doped ZnO-NRs have single crystalline (1D) structure owing to have single peak (002). The very strong (002) peak indicates that *c*-axis is the fastest growth direction and the film has rod shape structure. The diffraction patterns exhibit high crystalline quality with very well defined peaks and large intensity.

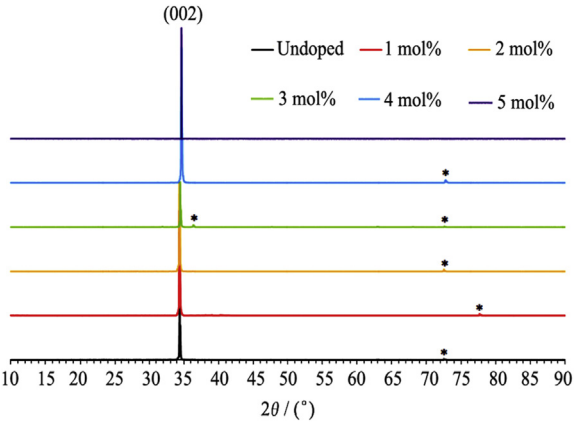

Fig. 1. XRD patterns of the undoped and Tm-doped ZnO-NRs samples.

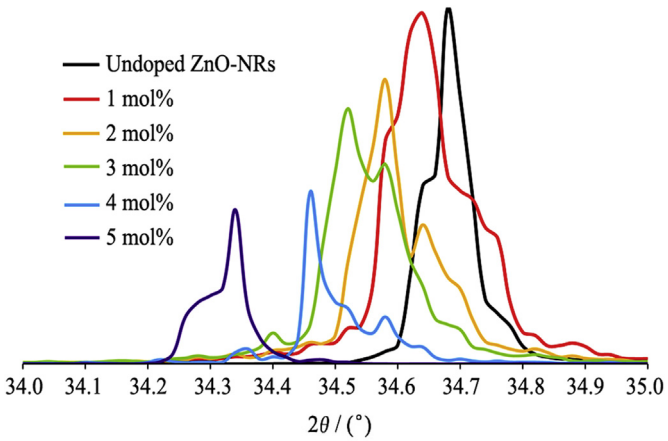

Fig. 2. Shifts in (002) peak position of the undoped and Tm-doped ZnO-NRs samples.

The lattice distortion owing to the defects (interstitial atoms, vacancies) may give rise to the shift in XRD peak place towards higher or lower angle. Fig. 2 shows the enlarged view of the (002) peaks of the patterns. The (002) peaks positions are slightly shifted towards lower angle with increasing Tm doping amount. This indicates that an increase in the lattice constants occur with increasing Tm concentration. Peak shift in XRD peak can be caused by strain or by changes in chemical composition. Change in stoichiometry can produce similar effects, too. The small shifts in the peak positions of the diffraction peaks illustrate the incorporation

Table 1
Unit cell parameters of the undoped and Tm-doped ZnO-NRs samples.

Sample name	*a* (10^{-1} nm)	*c* (10^{-1} nm)
Undoped ZnO	3.2415	5.1673
1 mol% Tm-ZnO	3.2415	5.1764
2 mol% Tm-ZnO	3.2517	5.1851
3 mol% Tm-ZnO	3.2552	5.1938
4 mol% Tm-ZnO	3.2593	5.2026
5 mol% Tm-ZnO	3.2597	5.2032

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