Fayoum University
Faculty of Science
Department of Physics

CHARACTERIZATION OF SOME TM-DOPED ZNO NANOSTRUCTURES SYNTHESIZED VIA CHEMICAL DEPOSITION

By

Adel Mohamed El Sayed Abdel Aal

A thesis submitted in partial fulfillment

Of

The requirements for the degree of

Doctor of Philosophy

In
Physics

(Experimental Solid State Physics)

Department of Physics
Faculty of Science

FAYOUM UNIVERSITY

2011

ABSTRACT

Zinc oxide (ZnO), a member of the II-VI group semiconductors with a direct wide band gap (3.3 eV), a large excitonic binding energy (60 meV) at 300 K and availability of large single crystals, possesses a unique position among materials owing to its superior and diverse properties such as piezoelectricity, chemical stability, biocompatibility, optical transparency in the visible region, high radiation hardness, high voltage current nonlinearity, etc. Also ZnO has a lower threshold voltage for use as a light-emitting diode (LED) and in laser emission and TM-doped ZnO is predicted to display properties of diluted magnetic semiconductors with ferromagnetic Curie temperature well above 300 K. Thus, ZnO as a multifunctional material could be used in a range of industrial applications such as transparent electrodes, solar cells, gas sensors, photodiode, transistors, and surface acoustic wave devices and for use in spintronics applications. Its low cost compared with other materials makes it a good candidate for industrial applications. Recently, nanostructured ZnO has been obtained by using various physical and chemical techniques.

TM-doped ZnO or $Zn_{1-x}TM_xO$ thin films were deposited onto glass substrates by the sol–gel method via a spin-coating technique. The dopant ratio x < 10 %. The used transition metal (TM) is copper (Cu) for the first system, chromium (Cr) for the second system, and for the third system, TM was cadmium (Cd). The choice of these systems arises from that they are less investigated; however, they are expected to have excellent optical, electrical, and magnetic properties and could be used in many research, environmental, industrial, and technological applications.

The prepared $Zn_{1-x}TM_xO$ (where x=0.0, 0.7%, 2.1%, 6.3%, 8.4%, and 9.8%) were analyzed by X-ray diffraction (XRD) and atomic force microscopy (AFM). The effect of doping on transmittance, reflectance, optical band gap, Urbach energies, and optical constants (refractive index, extinction coefficient, dielectric constants, and optical conductivity) were also investigated. Also, we studied the effect of doping on electrical conductivity and magnetic susceptibility.

The XRD pattern of the undoped and TM-doped ZnO thin films [for each of the three systems; $Zn_{1-x}Cu_xO$, $Zn_{1-x}Cr_xO$, and $Zn_{1-x}Cd_xO$] indicated the existence of a ZnO single phase with a hexagonal wurtzite structure and no extra phases involving any TM compounds were observed. Also, the crystallinity of ZnO thin films were gradually deteriorated with increasing of TM dopant ratio from x=0.0 to x =9.8%. Particle size was decreased with increasing TM ratio in each system. $Zn_{1-x}Cr_xO$ thin films showed

preferential orientation along (002) direction, but in both $Zn_{1-x}Cu_xO$ and $Zn_{1-x}Cd_xO$ systems, the XRD patterns did not show preferential orientations.

AFM measurements showed that the surface of the undoped ZnO film to consist of nanorods turned into nanofibers for Cu-doped ZnO thin films, and wrinkled network structure for Cr-doped ZnO thin films, but the surfaces of Cd-doped ZnO thin films consisted of nanoclusters. AFM measurements confirmed the decrease in particle size observed from XRD data due to the incorporation of TM atoms in ZnO lattice. Also, surface roughness increased with increasing TM ratio in each of the three systems.

Optical measurements showed that the optical band gap decreased from 3.3 eV to 3.255 eV for the change of x from x=0.0 to x = 9.8% in case of $Zn_{1-x}Cu_xO$ system and decreased from 3.3 eV to 3.215 eV for the change of x from x=0.0 to x = 9.8% in case of $Zn_{1-x}Cr_xO$ system and decreased from 3.3 eV to 3.182 eV for the change of x from x=0.0 to x = 9.8% in case of $Zn_{1-x}Cd_xO$ system. This observed red shift in E_g resulted from the s-d and p-d exchange interactions giving rise to negative and positive corrections to the conduction and the valance band edges respectively, leading to the band gap narrowing. The E_U values changed inversely with optical band gaps of the films. Also, the effect of TM dopants (Cu, Cr, and Cd) on the refractive index, extinction coefficient, dielectric constants, and optical conductivity of ZnO thin films were investigated and determined.

The measurements of electrical conductivity showed a decrease due to Cu incorporation. However, the electrical conductivities increased due to Cr or Cd incorporation into ZnO lattice. This suggests that Cu atoms incorporated into ZnO act as acceptors in the form of Cu^{1+}, while both Cr and Cd atoms are incorporated into ZnO lattice as donors.

Magnetic susceptibility measurements showed that both $Zn_{1-x}Cu_xO$ and $Zn_{1-x}Cr_xO$ are paramagnetic systems, and the magnetic susceptibility decreased on increasing of the applied magnetic field.