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Influence of copper incorporation on the structural and optical properties of ZnO nanostructured thin films

A.M. El Sayed [a,c,*], G. Said [a], S. Taha [a], A. Ibrahim [b,c], F. Yakuphanoglu [d,e]

[a] Physics Department, Faculty of Science, Fayoum University, Fayoum, 63514, Egypt
[b] Physics Department, Faculty of Science, Tanta University, Tanta 31527, Egypt
[c] Physics Department, Faculty of Science, Northern Border University, Arar 91431, Saudi Arabia
[d] Physics Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[e] Physics Department, Faculty of Science, Firat University, Elazig, Turkey

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ABSTRACT

The copper-doped ZnO thin films were grown on glass substrates using the sol–gel method and the spin coating technique. Cu dopants with ratios less than 10% (in molar ratio) were chosen because they are anticipated to have excellent optical and electrical properties and could be used in many research, environmental, industrial, and technological applications. XRD results indicate that a ZnO single phase with a hexagonal wurtzite structure is formed. The crystallinity of ZnO thin films is gradually deteriorated with increasing the Cu ratio. AFM images of the films indicate that the Cu-doped ZnO films seem to be consisted of nanofibers. The surface roughness of the films is increased with increasing Cu content. The optical band gap is red shifted from 3.3 eV to 3.255 eV with the increase of Cu content from $x = 0\%$ to $x = 9.8\%$. The refractive index, extinction coefficient, and optical conductivity show a decrease with increasing Cu content. The correlation between the structural modifications and the resultant optical properties are reported. The results of the present system are compared with those of similar materials.

* Corresponding author at: Physics Department, Faculty of Science, Fayoum University, Fayoum, 63514, Egypt. Tel.: +96502608368.
E-mail addresses: ams06@fayoum.edu.eg, ad_286@yahoo.com (A.M. El Sayed), .

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1. Introduction

The great interest towards ZnO Nanostructures, in the recent years, is due to their excellent properties. ZnO has a wide and a direct band gap (3.3 eV) and large exciton binding energy of 60 meV. ZnO crystals and, in particular, thin films exhibit second- and third-order non-linear optical behavior, suitable for integrated non-linear optical devices. Also, due to a strong luminescence in the green–white region of the spectrum, ZnO is also a suitable material for phosphor applications [1]. Transparent oxide semiconductors (TOSs) such as doped zinc oxide (ZnO:Al; ZnO:Ga; ZnO:In) are widely used in flat-panel displays, light-emitting diodes, solar cells, and imagers [2]. The invention of the first transparent thin film transistors (TFTs) in 2003, with ZnO as channels, marked the birth of transparent electronics [3]. The large band gap in TOSs is due to the large electronegativity of oxygen in n-TCOs [4]), rendering them highly transparent (80–90%) in the optical portion of the electromagnetic spectrum.

The transition metal Cu (Cu; [Ar] $3d^{10}4s^{1}$) is an attractive dopant for ZnO, because: (i) it has a similar electronic shell structure to Zn, so it has many physical and chemical properties similar to those of Zn [5]; (ii) Cu behaves as an acceptor in ZnO crystals making it a good candidate for creating p-type ZnO [6]. ZnO nanocrystals doped with Li, Na, Cu, Pr and Mg were prepared solid-state reaction method. The un-doped ZnO and Li- and Na-doped ZnO showed well formed nanorods. However, Cu- doped ZnO tended to form cluster [7]. Lee et al. [8] fabricated surface acoustic wave (SAW) devices using both ZnO and ZnO:Cu films prepared by RF magnetron co-sputtering. The electro-mechanical coupling coefficient and insertion loss of ZnO-based SAW devices noticeably improved by Cu-doping. Cu is a prominent luminescence activator in II–VI compounds [9] and it could modify the luminescence of ZnO crystals by creating localized impurity levels. Cu-doped ZnO gas sensor has been reported to detect CO and ethanol [10]. This is attributed to the promoted CO adsorption at the Cu sites [11]. Few reports on the physical properties of sol–gel synthesized Cu-doped ZnO nanostructures, at low Cu dopant concentrations, were found. Peng et al. [10] prepared Cu-doped ZnO nanocrystals (20–30 nm in size) by a sol–gel method. They reported that the introduction of Cu had no influence on the hexagonal structure of ZnO and the gas response of the Cu-doped ZnO nanocrystals is greater than that of ZnO.

Due to its excellent control of the stoichiometry and its relative simplicity, sol–gel spin coating technique was used to prepare ZnO thin films doped with Cu at low dopant concentrations. The effect of incorporating Cu on the structural, morphological, and optical properties of ZnO thin films were studied.

2. Material synthesis and characterizations

In the synthesized Cu-doped ZnO thin films, the Cu dopant ratios were 0%, 0.7%, 2.1%, 6.3%, 8.4%, and 9.8%. These low doping concentrations allow mixing of the chemicals at the atomic level thus reducing the possibility of undetectable impurity phases and to solve the problem of the small thermodynamic solubility of some TM in ZnO. Cu-doped ZnO thin films were deposited onto glass substrates by the sol–gel method via a spin-coating technique (using TC100 spin coater). The used precursors are zinc acetate dehydrate [$Zn(CH3COO)_2{\cdot}2H_2O$ (purity 99.5%), 2-methoxethanol ($C_3H_8O_2$) and ethanol amine (C_2H_7NO, ME). The dopant source of Cu was copper acetate dehydrate [$Cu(CH_3COO)_2{\cdot}2H_2O$ – CARLO ERBA, purity > 99%]. All of these chemicals were used without any further purifications. The choice of acetate coming from the fact that hydrolysis of acetate group give products which are soluble in the solvent medium and get easily decomposed into volatile compounds under heat treatment [12]. The molar ratio of MEA to zinc acetate dehydrate was maintained at 1:1. Copper acetate dehydrate and zinc acetate dehydrate of 0.5 M solutions were mixed together in different volume proportions. The obtained mixtures were stirred at 60 °C for 2 h to yield a clear and homogeneous solution, which was then served as the coating source after cooling down to room temperature and aging for 24 h.

The glass substrates were firstly cleaned by methanol and acetone baths for 10 min using an ultrasonic cleaner and then, the substrates were rinsed with deionized water and dried with nitrogen gas. The coating solution was dropped into a glass substrate, which was rotated at 1000 rpm for 60 s. After the spin coating, the film was dried at 150 °C for 10 min on a hot plate to evaporate the solvent and to