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Some physical investigations on silver-doped ZnO sprayed thin films

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ABSTRACT

The spray chemical route is used to prepare undoped and Ag-doped ZnO thin films using zinc acetate dehydrate isopropyl alcohol and silver nitrate as doping element in starting solution. XRD analysis shows that all films crystallize in a hexagonal würtzite structure with a preferential orientation along (002) direction. Similarly, the variation in peak positions of X-ray diffraction shows that the silver element is well incorporated into ZnO matrix and not remains in the interstitial sites. Surface morphology studies showed that an increase in the concentration doping causes an increase in the grain size and the mean square roughness R_q. Finally, the optical analysis via the transmittance and the reflectance measurements reveals that the bandgap energy E_g decreases from 3.29 to 3.25 eV in terms of Ag content.

1. Introduction

Due to its interesting intrinsic properties, zinc oxide is still the most demanded material in many fields of applications such as transparent electrodes [1], gas sensors [2,3], light emitting diodes (LEDs) [4], laser systems [5], heterojunction solar cells [6,7], photocatalytic process [8,9] etc. To improve the performance of this oxide, doping in ZnO with suitable dopants offers an effective method to adjust their properties, which is crucial for their practical applications. Generally, the doping of semiconductors with noble metals is one of the most effective ways [10]. ZnO/Ag structure presents now an exciting area in research for developing photocatalytic applications as stated by Wang et al. [11] who elaborated Ag doped zinc oxide (ZnO:Ag) films using a pulsed laser deposition method, Karunakaran et al. [12] who fabricated nanocrystalline ZnO and Ag–ZnO (0.1 at%) for bactericidal and photocatalytic activities and Ravishankar et al. [13] who outlined the fact that ZnO:Ag nanoparticles show better photocatalytic activity for the degradation of trypan blue (TrB) compared to pure ZnO.

Ag as an electron sink is proposed to allow electrons transfer from ZnO to Ag through the interface when coupled with ZnO, which benefits the separation of photo-generated electron–hole pairs, and enhancing the photocatalytic activity. However, during the preparation of ZnO thin films doped Ag may encounter the following problems: (1) the silver is chemically unstable and rapidly oxidizes when exposed to air [14,15], (2) the interaction between the noble metals and the semiconductor is complicated because the interaction relates to the carrier concentration, defect level, surface states of the semiconductor, electronic, optical properties, and so forth. Therefore, good understanding of the interaction will facilitate the fundamental and technical applications of such oxides doped with some metallic elements [16].

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From this rapid review, it is noted that this oxide emerged as of a promising active compounds in some sensitivity applications. Indeed, it is reported that Ag–S codoped p-type ZnO films can be obtained by RF magnetron sputtering. This p type may be due to S alloying in ZnO an increase of solid solubility of substitutional Ag acceptor [17]. Recently, Hall-effect measurements confirmed that Ag–N co-doped ZnO films, which were grown on quartz substrates by radio frequency magnetron sputtering deposition, were converted to p-type ZnO under optimum post-annealing conditions. Metastable interstitial nitrogen was suspected to be the principal cause of the instability of this p-type character [18]. On the other hand, noticeably visible-light-responsive Graphene–Ag/ZnO nanocomposites were obtained by a solvothermal technique for the photodegradation of organic dyes. The as-synthesized Graphene–Ag/ZnO nanocomposites showed unprecedented photodecomposition efficiency compared to the Ag-doped ones [19].

To address possible ways to control the structural optical as well as electrical properties of Ag doped ZnO, some works still pay attention to the possible causes of the change in its electrical behavior by using appropriate doping.

The present work aims to reach the synthesis of Ag doped ZnO thin films by a low-cost spray pyrolysis chemical process. Also, to understand the interaction between silver and ZnO, these samples were investigated using X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and UV–vis absorption spectroscopy (UV–vis), This study is of great interest in some applications such as gas sensors, photocatalys dye solar cells.

2. Experimental details

In order to deposit ZnO thin films, the precursor solutions were prepared from zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Merck) and silver nitrate ($AgNO_3$, Aldrich). First, 0.1 M of zinc acetate salt was dissolved in a mixture of isopropyl alcohol and deionized water (in ¾, ¼ proportion) and acetic acid was added to adjust pH to 4.7. The molar ratio in the solution was varied to give a [Ag/Zn] ratio ranging from 1% to 3%. The obtained solution was stirred at room temperature for 30 min to yield a clear and homogeneous solution and then sprayed on glass substrate at 460 °C. This temperature was used to prepare these films according to precedent successful attempts of spray pyrolysis deposition [20,21]. The absorption measurements of the prepared samples were recorded using the LAMBDA 950 UV/Vis/NIR spectrometer from Perkin Elmer and the crystalline properties of undoped and Ag-doped ZnO sprayed thin films were analyzed by the X-ray diffractometer (Phillips (PW3719) X'pert materials research) with a Cu Kα radiation, and a scanning range of 2θ set between 10° and 70°.

It is worth noting that the same deposition conditions were preserved for all samples and the films were cooled to room temperature.

3. Results and discussions

3.1. Structural properties

Fig. 1 shows the XRD patterns of the different samples. These spectra show well-defined peaks of (100), (101), (102), (002) and (103), corresponding to hexagonal würtzite phase according to JCPDS 036-1451card. Similar XRD spectra were achieved by Xue et al. for ZnO prepared by a sol–gel technique [22]. At first glance, these films and especially ZnO film doped with 1 at% Ag are preferentially oriented (002) direction. It means that the doping of small amount of Ag in the ZnO film promotes *c*-axis orientation of the crystallites even though a solvent of low boiling point, isopropanol is used. On the other hand, peak intensity of other planes such as (100), (101), (102) and (110) increases moderately with Ag content and the variation observed at the peak position of X-ray diffraction shows that Ag element may be incorporated into ZnO matrix and does not remain in the interstitial sites at surface as reported by Chai et al. [23]. In addition, for samples prepared using 3% as silver content there are two small peaks corresponding to silver oxide located respectively at 67.93° and 68.25°. A similar finding regarding silver oxide appearance at the same angle positions is previously reported by Bodiul Islam et al. [24].

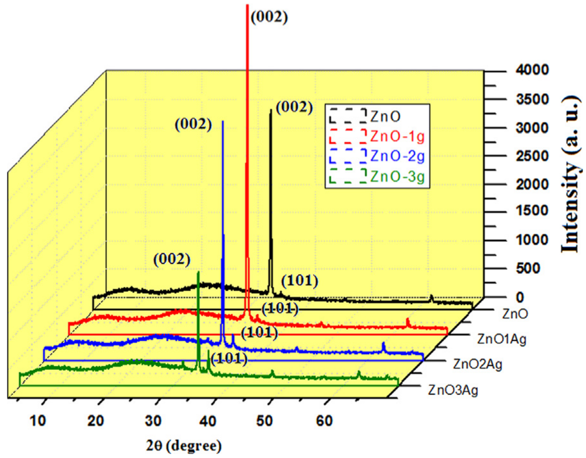

Fig. 1. X-ray patterns of undoped and Ag doped ZnO thin films prepared by spray pyrolysis at 450 °C.

As ZnO crystallizes in the Würtzite structure, the interplanar spacing of given Miller indices *h*, *k* and *l* d_{hkl} values of ZnO:Ag thin films were also calculated by using the Bragg equation [25] as follows:

$$2d_{hkl} \sin \theta = n\lambda \quad (1)$$

where n is the order of diffraction (usually $n=1$) and λ is the X-ray wavelength. In the ZnO hexagonal structure, the plane spacing is related to the lattice constants *a*, *c* and the Miller indices by the following equation [26,27]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (2)$$

Both lattice parameters *a* and *c* for the hexagonal compact phase (HCP) are calculated via (002) and (101) orientations. Table 1 summarizes also calculated values of the interplanar spacing d_{hkl} of ZnO:Ag thin films.

First, it can be seen that d_{hkl} values decreases for film prepared using 1% than increase with Ag content. This phenomenon shows that the Ag element is introduced into the ZnO matrix. On the other hand, the grain size *D* values