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Full Length Article

A critical study of the optical and electrical properties of transparent and conductive Mo-doped ZnO films by adjustment of Mo concentration

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ABSTRACT

Mo-doped zinc oxide (ZnO: Mo) transparent conductive thin films were prepared on the glass substrates using simple chemical spray pyrolysis technique by varying the Mo doping concentration in the range, 0–5 at.% at a constant substrate temperature, 400 °C. The effect of Mo-doping concentration on the physical behavior of ZnO films was investigated. The X-ray Photoelectron Spectroscopy (XPS) analysis confirmed the presence of Zn, O, and Mo in the layers with Mo in +6 state. The X-ray diffraction (XRD) patterns exhibited hexagonal wurtzite crystal structure without any secondary phases. The microstructural analysis revealed the spherical nut-shaped grains over the substrate surface. The optical studies revealed that the films with Mo-doping concentration of 2 at.% showed high optical transmittance and a wide band gap than pure and highly Mo-doped ZnO films. From the optical transmittance versus wavelength data, the refractive index, extinction coefficient, dispersion constants were evaluated. In addition, other optical parameters such as the optical conductivity, dielectric constants, dissipation factor, electron energy loss functions and Haze were also calculated. The FTIR studies revealed the presence of modes related to ZnO. Finally the electrical parameters such as resistivity, charge carrier mobility and density of ZnO: Mo films were also analyzed and presented.

1. Introduction

Transparent conducting oxide (TCO) films have been used for different applications, particularly for optoelectronic devices [1] and for many decades detailed investigation has been carried out on these materials. The conventional TCOs are SnO_2 and InO_2 that possessed low metallic forms and also exhibit low stability when exposed to a hydrogen plasma [2,3], but zinc oxide films showed high stability in presence of hydrogen plasma [4]. Coming to the photovoltaic sector, the most utilized TCO is tin-doped indium oxide (ITO) due to its low resistivity, high transmittance and high work function [5,6]. However, ITO has some disadvantages such as a high energy barrier for injection of holes at the ITO/hole transport layer and scarcity of metal indium. In this scenario, doped ZnO films become promising candidates to replace ITO because they are nontoxic, inexpensive, earth-abundant and exhibit comparable optical and electrical properties to ITO films. Due to the low thermal expansion coefficient, wide energy band gap (3.3 eV) and high exciton binding energy (60 meV) at room temperature [7–11], ZnO can be used as a transparent conductive material in flat panel displays, light emitting diodes and solar cells [12–16]. ZnO films were also used for chemical sensor application because of its high surface sensitivity to gases [17].

Depending on the necessity and application, many researchers extensively studied doping of ZnO films using different transition metals such as Titanium (Ti) [18], Vanadium (V) [19], Chromium (Cr) [20], Manganese (Mn) [21], Iron (Fe) [22], Cobalt (Co) [23], Nickel (Ni) [24], Copper (Cu) [25], Zirconium (Zr) [26], Niobium (Nb) [27], Molybdenum (Mo) [28], Gold (Au) [29] and Halogens such as Fluorine (F) [30] and Chlorine (Cl) [31] also some metalloids such as Boron (B) [32] and Germanium (Ge) [33] and also some pure metals such as Aluminium (Al) [34], Tin (Sn) [35], Gallium (Ga) [36], Indium (In) [37] and Bismuth (Bi) [38] (see Fig. 1). Among all these dopant materials, Mo is particularly interesting due to its larger valency (5+ and 6+) with respect to that of Zn^{2+} ions, which suggests that each Mo atom can contribute 3 or 4 free electrons depending on valency to the ZnO lattice that can alter the electrical conductivity significantly and reduce the impurity ion scattering effect [39,40]. Moreover, its ionic radius (0.046 nm and 0.041 nm for Mo^{5+} and Mo^{6+} respectively) is lower

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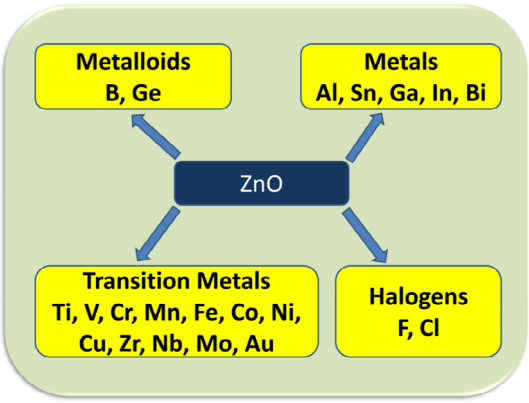

Fig. 1. Various dopants used to dope ZnO in the literature.

than that of Zn^{2+} (0.060 nm) so that Mo substitutes easily Zn ions in the host lattice and occupies less interstitial positions [41].

Several deposition techniques were used by researchers to grow ZnO: Mo thin films such as spray pyrolysis [42–44], RF and DC magnetron sputtering [45,46] and ion beam sputtering [47]. Among these techniques, spray pyrolysis is a simple and low-cost technique to deposit ZnO films as it is easy to dope the layers with appropriate dopants and it does not require vacuum for film deposition. In our laboratory, investigations were already made earlier on doped ZnO films using different dopants like Ga, Mg, Mn, Co, Ni by spray pyrolysis technique [48–53]. The present work is a continuation of this research where Mo is used as the dopant in ZnO layers. Further, a complete optical analysis of ZnO: Mo films are important for the design of heterojunction solar cells because only optical properties give the information to understand the optical transmittance/reflectance, photon loses and band structures. Many researchers studied the optical properties of ZnO: Mo films, however, they analyzed only the transmittance, absorbance and reflectance properties including the determination of optical band gap, refractive index and extinction coefficient values. This analysis was extended further to find the dielectric constants, optical conductivity, dissipation factor, dispersion parameters, optical Haze and electron energy loss functions using optical data. Generally, the chemical potential of doping ions can tune the optical transmittance, which minimizes the structural imperfection and optical losses in the films. Literature survey revealed that there were no reports on the effect of Mo concentration on optical and electrical properties of MZO films deposited by chemical spray pyrolysis technique. A key to achieving better optical and electrical properties lies in a good understanding of the role of Mo concentration in MZO films. Therefore in this paper, we study the effect of doping concentration on compositional, structural, microstructural, optical and electrical properties of Mo-doped ZnO thin films.

2. Experimental and characterization details

2.1. Reagents

Zinc chloride ($ZnCl_2$) is taken as a precursor for zinc and molybdenum chloride $(MoCl_5)_2$ as the precursor for Mo (both chemicals of 99% purity obtained from Sigma Aldrich) to prepare Mo-doped ZnO layers. Methanol was used as the complexing agent and distilled water as the solvent in order to prepare a clear final solution.

2.2. Formation of ZnO: Mo (MZO) thin films

ZnO: Mo films were deposited by chemical spray pyrolysis (see Fig. 2) on Corning 7059 glass substrates by using an aqueous solution of 350 ml containing zinc chloride and molybdenum chloride with few drops of methanol. The substrate temperature was maintained constant at 400 °C, while the Mo-doping concentration was varied in the range, 0–5 at.%, Solution flow rate of 6 ml/min was maintained during the film deposition. Compressed air with a flow rate of 8 l/min was used as the carrier gas. The precursor solution was sprayed on the substrate, which was kept at a distance of 25 cm from the nozzle at an interval of 1 min.

2.3. Characterization of MZO thin films

The elemental composition of the films was studied using VG Microtech ESCA 2000 X-ray photoelectron spectrometer. The structural properties were studied using a Siefert X-ray diffractometer with a Cu K_α radiation source ($\lambda = 1.542$ Å). The surface morphology was analyzed using an FSI Serion scanning electron microscope. The optical properties were studied using Perkin Elmer Lambda – 950 UV–Vis-NIR spectrophotometer in the wavelength range, 300–900 nm. The Fourier transform infrared (FTIR) spectrum of the films was recorded in the wave number range, 500–4000 cm^{-1} using a Thermo Nicolet IR-200 FTIR spectrophotometer. Electrical resistivity (ρ), carrier mobility (μ) and carrier concentration (n) of the films were measured using the Hall effect measurement setup (model: HMS-3000).

3. Results and discussion

The visual appearance of the as-grown layers revealed pale whitish colour, which was pinhole free and strongly adherent to the substrate surface.

3.1. Composition

The XPS spectra were recorded in the binding energy range, 0–1100 eV in order to evaluate the chemical composition and the valence state of Mo ion in ZnO lattice. Fig. 3 shows the wide scan XPS spectrum of Mo-doped ZnO films deposited at a substrate temperature of 400 °C with the molybdenum doping concentration of 2 at.%. The spectrum showed two strong peaks related to $Zn2p_{3/2}$ and $Zn2p_{1/2}$ at 1021.24 eV and 1044.42 eV respectively. The presence of both the peaks at these binding energy values is different from those of elemental Zn, indicating that Zn is present in +2 chemical state in ZnO lattice. The observed binding energy values of Zn were closely related to the reported values in the literature [54]. The peak observed at 530.26 eV is due to the lattice oxygen, corresponding to O 1s, bonded with Zn and Mo atoms. Since the activation energy for diffusion of oxygen is much higher than that required for diffusion of interstitial Zn atoms and Mo^{6+} ions, sufficient oxygen atoms from the atmospheric air can diffuse into ZnO lattice to fill up the new oxygen vacancies formed due to the increase of Zn^{2+} and Mo^{6+} ions during the growth of layers.

Fig. 4 shows the variation of molybdenum peaks intensity in the films with molybdenum content in the precursor solution. $Mo3d_{5/2}$ peak has been observed at the binding energy of 229.1 eV, while $Mo3d_{3/2}$ peak at 232.8 eV. These peak positions mainly depend on the local structure of Mo atoms in the ZnO lattice, which provides information on its chemical state. The observed binding energy values of Mo are different from the elemental binding energy values and also those of Mo-O related compounds. This indicates that molybdenum cations are perfectly substituted in the zinc sites of the wurtzite structure. Further, it is observed that the Mo peak intensity increases with increase of Mo concentration in the precursor solution, which indicates proper doping of ZnO with Mo in the layers.

3.2. Structural properties

The X-ray diffraction patterns of undoped and Mo-doped ZnO films recorded in the 2θ range of 20–70° are shown in Fig. 5. It revealed that all the grown films were polycrystalline in nature, showing multiple