EXPERIMENTAL AND FIRST PRINCIPLES STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF $\text{Zn}_{0.875}\text{Mn}_{0.125}\text{O}$ THIN FILM

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$\text{Zn}_{0.875}\text{Mn}_{0.125}\text{O}$ thin films are fabricated by a simple sol-gel spin-coating technique on glass substrates using zinc acetate dehydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ and manganese acetate tetrahydrate $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ as a starting material and doping source. Isopropanol and monoethanolamine (MEA) were used as solvent and stabilizer, respectively. X-ray diffraction, ultraviolet-visible spectroscopy and photoluminescence spectroscopy are employed to investigate the effect of Mn doping on the structural, electronic and optical properties of ZnO thin films. The obtained results are compared with those using first-principles calculation based on density functional theory (DFT) with local density approximation (LDA) plus Hubbard U (DFT-LDA+U) method. This latter represents the theoretical framework to deal with strongly correlated materials to predicted successfully the electronic properties of such materials.

Keywords: Sol-gel spin-coating technique, Mn-doped ZnO thin film, DFT.

INTRODUCTION

ZnO is a wide band-gap (3.37eV) compound semiconductor that have received considerable attention (Yaakob *et al.*, 2014; Ozgur *et al.*, 2005). The Mn ferromagnetic element is widely used in doping II–IV-based hosts, like Mn–ZnO (Luo *et al.*, 2005; Zhao *et al.*, 2010). Previous studies (Luo *et al.*, 2005; Zhao *et al.*, 2010; Zhao *et al.*, 2012) have found that the Mn–Mn interaction is dominated by antiferromagnetic (AFM) coupling. The doping of ZnO thin films by Mn element presents a feasible means to adjust the band gap. The tuning of the band gap allows DMS to be used as UV detectors and light emitters.

The first-principles and pseudopotentials method based on conventional density functional theory (DFT) cannot efficiently describe the localization of strongly correlated *d* and *f* electrons of transition material (Anisimov *et al.*, 1997; Dudarev *et al.*, 1998). The DFT–LDA+U approach (Yaakob *et al.*, 2014; Anisimov *et al.*, 1997) can significantly improve the calculation including transition metal localization.

Variety of techniques have been used to prepare ZnO thin films. Because of its simplicity, low cost, safety, large area deposition, controllability of compositions and uniformity of thickness, the sol–gel method has attracted much attention (Amari *et al.*, 2018; Mahroug *et al.*, 2017).

The aim of this study is to investigate experimentally and theoretically by using first-principles calculations, the structural, electronic and optical properties of $\text{Zn}_{0.875}\text{Mn}_{0.125}\text{O}$ Thin film.

EXPERIMENTAL AND THEORETICAL DETAILS

Sol-gel spin coating method was used to prepare Mn-doped ZnO thin films on glass substrate. Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and manganese acetate tetrahydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] were used as a starting material and dopant source, respectively, and the isopropanol was added as stabilizer. The molar ratio of the solvent (monoethanolamine; MEA) to metal ions was fixed at 1.0 and the concentration of metal ions was 0.7 M. The Mn dopant concentration was chosen as 12.5 mol%. The subsequent steps were discussed in our previous works (Amari *et al.*, 2018; Mahroug *et al.*, 2017).

An X-ray diffractometer (XRD) (Bruker 8 Advance; $\lambda=1.5406 \text{ \AA}$), UV-vis spectrophotometer (UV-3101 PC-Shimadzu) and spectrofluorimeter (Perkin Elmer LS 50B; excitation source at 325 nm), was used to characterize the structural properties, the optical transmission spectra and the photoluminescence (PL) of the ZnO thin films, respectively.

First-principles calculations of structural, electronic and optical properties of Mn-doped ZnO material ($\text{Zn}_{1-x}\text{Mn}_x\text{O}$ $x=12.5\%$) with wurtzite structure were performed using DFT as implemented in CASTEP code (Clark *et al.*, 2005). The 2.2.2 ZnO supercell containing 32 atoms is used and the substitutional method is adopted (Zhao *et al.*, 2012) to achieve this concentration in which two Zn atoms are substituted by Mn and different geometry configurations for Mn atoms were taken. The exchange-correlation function is treated by the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) (Perdew *et al.*, 1996). Also, the valence-electron configurations for the oxygen, zinc and manganese atoms are employed as $2s^2 2p^4$, $3d^{10} 4s^2$ and $3d^5 4s^2$, respectively. The cut-off kinetic-energy of 450 eV was used. The 7.7.4 k-point grid was adopted over the first Brillouin zone sampling mesh. The optimization convergence for energy change, maximum force, maximum stress, and maximum displacement were set at $5 \times 10^{-6} \text{ eV/atom}$, 0.01 eV/Å, 0.02 GPa, and $5.0 \times 10^{-4} \text{ \AA}$, respectively. Furthermore, the SCF convergence threshold is fixed at $5.0 \times 10^{-7} \text{ eV per atom}$. The semiempirical LDA+U approach (Anisimov *et al.*, 1997) with effective Hubbard U values of 7 eV to treat the transition metal of Zn 3d and Mn 3d electrons was employed.

RESULTS

The total energies of the five different geometry configurations for substitution of Zn by Mn, marked as A: Pm (C_s^1), B: Cm (C_s^2), C: P3m1 (C_{3v}^1), D: P3m1 (C_{3v}^1) and E: Cm (C_s^3), are presented in Table 1.

Table 1. Total energy for different geometry configurations. Energy corresponds to configuration A is chosen as an energy reference

Configuration	E (eV)
A	0
B	-0,978
C	-0,0249
D	-0,0433
E	0,0085

Total energy in configuration A was chosen as an energy reference. It is clear from the figure that the ground state is found to be the configuration B corresponding to symmetry group Cm (C_s^3). So, this configuration will be considered for Mn-doped ZnO material with $x=12,5\%$.

The optimized lattice constant along c-axis is found to be around $5.34\text{\AA}$ which is slightly underestimated by around 2% by our experimental result ($5.23\text{\AA}$) extracted from XRD pattern (figure 2). The (002) diffraction peak is stronger than the other peaks, indicating a preferential growth direction along the c-axis due to its lowest surface free energy among (002) planes.

Figure 2. XRD pattern of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=12.5\%$) thin film

The optical transmission spectra at room temperature of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=12.5\%$) thin films is shown in figure 3. It revealed that the sample is transparent in the visible optical region with an average transmittance about of 62%.

Figure 3. Optical transmission spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=12.5\%$) thin film. Inset presents a plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$)

The absorption coefficient α is related to the optical band gap energy E_g as:

$$\alpha h\nu = \text{constant} (h\nu - E_g) \quad (1)$$

The absorption coefficient α can be calculated by the equation

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \quad (2)$$

where T is the transmittance index and t is the film thickness. The E_g value is therefore determined by extrapolating the linear portion of the plot relating $(\alpha h\nu)^2$ versus $h\nu$ (inset in figure 3).

The obtained value of E_g is 3.196 eV. which is highly underestimated by the theoretical value obtained here (0.91 eV). It is well known that the conventional DFT can underestimate the experimental band gap and despite the incorporation of the semi-empirical LDA+U approach, there is still a significant gap between experience and theory.

CONCLUSION

Structural, electronic and optical properties of Zn_{0.875}Mn_{0.125}O thin films are investigated experimentally and theoretically, within the framework of DFT. The optimized lattice constant is found in a good agreement with the experimental one extracted from XRD pattern. This latter revealed that the preferential growth direction was along the c -axis. The fabricated thin film was transparent in the visible optical region with an average transmittance about of 62%. The deduced experimental band gap was found underestimated by the theoretical one.

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