Optik 125 (2014) 3344–3349

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Structural and vibrational studies of Mo and In-doped ZnO sprayed thin films

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ARTICLE INFO

Article history:
Received 4 July 2013
Accepted 19 December 2013

Keywords:
ZnO
Thin film
Spray
Raman spectroscopy
Vibrational modes

ABSTRACT

This paper deals with the structural and Raman properties of Mo and In doped ZnO sprayed thin films growing onto glass substrates. The structural investigations of these films were made by X-ray diffraction technique. It was found that undoped as well as doped thin films crystallize in the wurtzite structure with crystallites oriented preferentially along (0 0 2) direction perpendicular to substrate plane. The vibrational study revealed a broad identification of the observed vibration modes, and showed that E_2^{high} mode is located at (438 ± 0.8) cm^{-1} for different studied ZnO thin films, thus confirming the wurtzite ZnO structure. Six additional vibration modes were highlighted in ZnO, four local vibration modes (LVMs) related to doping Mo ($\sim$246 and 421 cm^{-1}), In ($\sim$237 and 420 cm^{-1}), Mo_nO_m ($\sim$306 and 354 cm^{-1}), In_nO_m ($\sim$311 and 354 cm^{-1}), and two Raman modes ($\sim$155 and 170 cm^{-1}) activated for the first time to our knowledge.

1. Introduction

During the last two decades, ZnO thin films have attracted great interest, as transparent conductive oxides. This is due to the compromise between the electrical and optical properties of zinc oxide, thermal stability, very high chemical stability, its non-toxicity and its abundance in nature [1]. Further, ZnO belonging to II–VI semiconductor compounds is a wide direct band-gap (3.37 eV at 300K) material with a large excitation binding energy of 60 meV. It is one of the most promising candidates for optoelectronic devices such as light-emitting diodes, laser diodes and UV photo detectors [2,3]. ZnO thin films can be prepared by several techniques such as spray [4], chemical vapor deposition [5], sol–gel and spray pyrolysis [6].

In this paper, Mo and In doped-ZnO films have been prepared by the spray pyrolysis technique. Our interests are focused on the effect of Mo and In doping on the microstructure, and on the vibration modes provided by Raman spectroscopy. A comparison between the two doping elements inside ZnO matrix will be made. To our knowledge, Raman spectroscopy is used, for the first time, to investigate especially Mo-doped ZnO sprayed thin films.

2. Experiments

Mo and In-doped ZnO thin films have been deposited by the spray pyrolysis technique. A solution containing the different constituents of the compound is pulverized mechanically on substrates that are arranged on a carries heated substrate to a temperature 460 °C [7,8]. Due to the temperature, the solvent is removed immediately (volatile components) and leaves only the metal ions, which oxidize in the presence of atmospheric oxygen. The obtained metal oxide is deposit on the glass substrate with excellent adhesion. A series of analytical technologies was employed to characterize undoped, Mo-doped ZnO and In-doped ZnO. Structural analysis was carried out using X-ray diffraction technique (Philips PW 1729 system) by means of Cu k_α monochromatic radiation ($\lambda = 0.15405$ nm). The incorporation of doping elements in the films was also analyzed with a green Raman spectroscopy.

3. Results and discussion

3.1. Structural properties

The crystalline properties of undopped ZnO and In/Mo-doped ZnO sprayed thin films were investigated by the XRD measurements. Fig. 1 shows the XRD patterns of the different samples.

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http://dx.doi.org/10.1016/j.ijleo.2013.12.085
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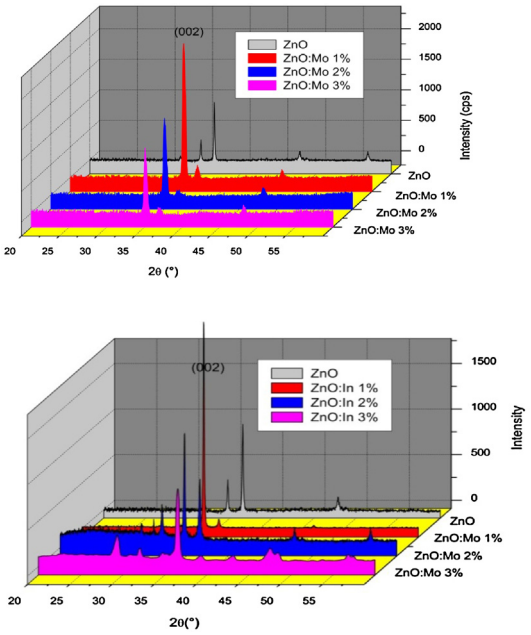

Fig. 1. X-ray diffraction spectra of In/Mo-doped ZnO thin films.

X-ray diffraction spectra show well-defined peaks of (1 0 1), (1 0 2) and (0 0 2), corresponding to hexagonal wurtzite phase according to JCPDS 036-1451 card with the preferential orientation (0 0 2).

As ZnO crystallizes in the wurtzite structure, the interplanar spacing of given Miller indices *h*, *k* and *l*, d_{hkl} values of ZnO:In and ZnO:Mo thin films were also calculated by using Bragg equation [9]:

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

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 relation [10,11]:

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

Both lattice parameters *a* and *c* for the hexagonal compact phase (HCP) are calculated via (0 0 2) and (1 0 1) orientations. Tables 1 and 2 show the calculated values of d_{hkl} and lattice parameters *a* and *c* of In/Mo doped-ZnO thin films.

At first glance, it can be seen that the interplanar spacing d_{hkl} and lattice parameter values are strongly dependent on the In and Mo contents. This phenomenon shows that In and Mo elements are introduced in ZnO matrix and played an important role to improve the properties of such doped films. Finally grains size *D* and microstrain ε are calculated using the following formula [12–14]:

$$D = \frac{k.\lambda}{\beta_{\frac{1}{2}}\cos(\theta)} \quad (3)$$

and

$$\varepsilon = \frac{\beta_{\frac{1}{2}}}{4\tan(\theta)} \quad (4)$$

where $k = 0.90$ is the Scherrer constant, $\beta_{1/2}$ is the width at half maximum.

The calculated values of grains size and microstrain of the different prepared thin films are listed in Table 3. Values of grains size *D* and microstrain for undoped ZnO are, respectively, 140.43 nm and 8.26×10^{-4}.

It can be seen that the microstrain is a function of incorporation level of In and Mo elements. These values can be correlated to grain size *D* values; indeed, when the crystallite size increases, the ratio of the contact surface inter-crystallites on the crystallite surface decreases. Fig. 2 shows the dependence of both *D* and ε to In and Mo concentration. From this structural study, we point out the fact that the decreases in grain size (*D*) as well as the increases of the microstrain calculated values are indeed understood as an important role played by the introduction of In and Mo elements so as to consolidate the structure of ZnO sprayed thin films. This phenomenon is consistent with the effect of In and Mo doping on the interplanar spacing d_{hkl}, lattice parameters *a* and c for the hexagonal compact phase and the *c*-to-*a* ratio values with In/Mo doping.

3.2. Vibrational study

The previous study of X-ray diffraction of ZnO:Mo/In thin films highlights their stability to high doping, and shows the presence, in thin films, of three diffraction lobes (1 0 1), (1 0 2) and (0 0 2). This confirms the hexagonal wurtzite ZnO structure [15,16]. The effect of Mo and In doping on ZnO at the modal responses will be studied by Raman spectroscopy, which is a reliable method for non destructive evaluation and which allows the quantification of vibration modes.

Group theory predicts the presence of optical phonon modes as follows E_2^{low}, E_2^{high}, E_1TO, E_1LO, A_1TO, A_1LO and $2B_1$ silent modes [16]. We recall from the previous work, the standard values of these modes in Table 4. Modal characterization of these thin

Table 1
The different interplanar spacing *dhkl* values of In/Mo-doped ZnO.

	$d_{(100)}$ (Å)	$d_{(002)}$ (Å)	$d_{(101)}$ (Å)	$d_{(102)}$ (Å)
ZnO:In 1%	–	2.5997	2.4748	1.90839
ZnO In 2%	2.78443	2.5768	2.4529	1.89949
ZnO:In 3%	2.79112	2.5768	2.4554	1.90988
ZnO:Mo1%	–	2.56035	2.4347	1.89104
ZnO:Mo 2%	–	2.55343	2.43501	1.88632
ZnO:Mo 3%	–	2.55221	2.42961	1.88581

Table 2
Values of lattice parameter of In/Mo-doped ZnO.

	$c_{(002)}$ (Å)	$a_{(101)}$ (Å)	*c*/*a*
ZnO:In 1%	5.1994	3.2494	1.600
ZnO In 2%	5.1536	3.2205	1.600
ZnO:In 3%	5.1536	3.2249	1.598
ZnO:Mo 1%	5.1207	3.1956	1.602
ZnO:Mo 2%	5.1068	3.1987	1.596
ZnO:Mo 3%	5.1044	3.1900	1.600

Table 3
Values of grain size and microstrain of In/Yb doped ZnO spray thin films.

	D (nm)		*D* (nm)
ZnO:In 1%	22.8351	ZnO:Mo 1%	33.55
ZnO In 2%	84.4513	ZnO:Mo 2%	35.74
ZnO:In 3%	33.8447	ZnO:Mo 3%	37.18
	ε (10^{-4})		ε (10^{-4})
ZnO:In 1%	8.26	ZnO:Mo 1%	34.29
ZnO In 2%	50.37988	ZnO:Mo 2%	32.15
ZnO:In 3%	13.60596	ZnO:Mo 3%	30.90