Substrate temperature effects on the structure and properties of ZnMnO films prepared by pulsed laser deposition

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Abstract. ZnMnO thin films were grown on silicon substrates by pulsed laser deposition (PLD). Pulsed Nd:YAG laser was operated at a wavelength of 1064 nm and 100 mJ. ZnMnO thin films were deposited at the vacuum pressure of 10⁻⁵ Torr and with substrate temperature from room temperature to 600 °C. The effects of substrate temperature on the structural and optical properties of ZnMnO thin films have been investigated by X-ray diffraction (XRD), Raman spectroscopy and UV-vis spectroscopy. From XRD data of the samples, it can be showed that temperature substrate does not change the orientation of ZnMnO thin films. All the films prepared have a hexagonal wurtzite structure, with a dominant (002) peak around 2θ=34.44° and grow mainly along the c-axis orientation. The substrate temperature improved the crystallinity of the deposited films. Uv-vis analysis showed that, the thin films exhibit high transmittance and low absorbance in the visible region. It was found that the energy band to 300 °C is 3.2 eV, whereas for other temperatures the values were lower. Raman reveals the crystal quality of ZnMnO thin films.

1. Introduction

ZnO can be considered as an “old” semiconductor which has been attracted research attention for a long time because of its large area of applications. Zinc oxide is a direct band gap semiconductor (Eg) with 3.37 eV (at room temperature) having hexagonal (wurtzite) structure with lattice parameters a=0.325 nm and c=0.512 nm [1]. Stoichiometric films are insulating whereas nonstoichiometric and oxygen deficient films are very good as transparent semiconducting oxides.

The transition metals (Ni, Mn, and so on) are used as attractive dopants for ZnO because they are isomorphic to Zn, possess variable oxidation states, and have different acceptor properties in a ZnO matrix, thus affecting the electronic surface band structure of ZnO. Mn incorporation in metal oxide systems is interesting because of the band gap variations based on the percentage of Mn ion introduced and the property of the MZO film is essential for wide-ranging applications. Among the oxide semi conducting materials, ZnO is one of the most important oxide material [2]. Beside the generation of novel magnetic properties, the introduction of Mn³⁺ ions can also tune the optical properties viz., band gap (Eg) of ZnO. Generally band-gap is estimated from UV–vis spectrophotometry. But like origin of magnetism, another debatable issue is the nature of variation of Eg with Mn concentration. Thus transition metal-doped ZnO has the potential to be a highly multifunctional material with coexisting magnetic, semiconducting, electromechanical, and optical properties. A large number of reports are available on the different properties of transition metal doped ZnO [3-5]. The first experiments on Mn-doped ZnO were performed by Fukumura et al [6] and room-temperature ferromagnetism for Mn doped ZnO was first reported by Sharma et al. [7].

Some studies have been carried out to realize Mn doped ZnO as a dilute magnetic semiconductors (DMS), however, studies to understand the other properties of Mn doped ZnO are also necessary.
Consequently, the synthesis and the characterization of transition metals doped ZnO-based DMS have become the subject of intense research. On the other hand, the deposition method and parameters are influencing the structural properties of the films and consequently the electrical and optical ones. Therefore, apart from dopant nature and concentration, the deposition method and parameters must be optimized such that the obtained films to possess the desired properties.

Mn doped zinc oxide thin films can be obtained by various deposition techniques including spray pyrolysis technique [8], sol–gel technique [9], chemical vapor deposition (CVD) [10], DC magnetron sputtering [11,12], molecular beam epitaxy (MBE) [13], and pulsed laser deposition [14-17].

Pulsed Laser Deposition (PLD) method has many advantages and technological possibilities. These advantages are: effectiveness and simplicity of the deposition equipment, high deposition rates, wide spectrum of deposition parameters for the control and the optimization of film properties, accurate control of stoichiometry and film thickness, use of background atmosphere of various gases, and high energy and high reactivity of the ablated material. The sum of all these special features enables the growth of oxide thin films at low temperature substrates with perfect crystallinity and good stoichiometry.

In this paper, ZnMnO films were deposited by pulsed laser deposition. The influence of temperature substrate on the structure and optical properties of the deposited films has been investigated.

2. Experimental Details
Mn-doped ZnO thin films were grown by conventional pulsed laser deposition (PLD) using a stainless steel HV deposition chamber and a pulsed NIR laser (Nd:YAG, 1064 nm wavelength, 9 ns pulse duration). The laser was operated at 10 Hz and the laser beam was incident at an angle of 45 with respect to the target surface. The targets were prepared from high-purity powders of ZnO (99.999%), with MnO (99.999%) serving as the doping agent. The pressed targets were sintered at 1000 °C for 12 h in air. The target was fabricated with a nominal composition of 5 wt.%Mn, and was continuously rotated during laser ablation to renew the irradiated surface and to prevent crater formation. The ablated material was collected onto a Si(100) substrate, over a temperature range of RT to 600°C, placed in front of and at 6 cm from the target. Prior to an experiment, the chamber was evacuated to 7×10⁻⁴ Pa. During deposition, oxygen (99.999 %) was flown through the chamber and the background pressure was of 6.13 Pa. The laser fluence was kept at (3.0±0.4) J cm⁻². The target to substrate distance was 6 cm, and the deposition time was kept at 30 min, the average thickness of the film was approximately 200 nm. Structural analysis of the films was carried out in a Bruker D8 advanced diffractometer by X-ray (XRD), using Cu Kα line of 1.5418 Å and scan rate 0.04 2θ/s. The identification of crystalline phases was done using the JCPDS database cards [18]. Optical analysis of the films was carried out in a Jobin Yvon spectrometer.

3. Results and discussions

3.1. XRD analysis
ZnMnO thin films were grown on Si (100) at substrate temperatures from room temperature to 600°C. Characteristic XRD patterns of doped ZnO films are presented in figure 1. The XRD patterns of the studied samples show that the films have a preferential orientation with (002) planes parallel to the substrate. It indicated that the films are well oriented along the c-axis. No characteristic peak of Mn was observed by the means of X-ray diffraction. The absence of Mn XRD peaks indicates that a diffusion of Mn atoms in new formed ZnO lattice takes place.

This indicates that these ZnMnO thin films show a good crystallinity with a wurtzite structure and a c-axis preferred orientation. We can also see the others weak reflection peaks, in the samples grown at substrate temperatures RT, 100°C and 600°C, at diffraction angle 2θ = 31.8°, 2θ = 36.3°, corresponding to (100) and (101) reflection of the hexagonal ZnO respectively (figure1). The presence of these reflections clearly points to the polycrystalline nature of the ZnMnO.
The increasing of the substrate temperature is in favor for the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favorable positions, resulting in the enhancement of the crystallinity and c-axis orientation of film, which can be indicated by increase of (002) peak strength. On the other hand, when substrate temperature is low, the adatoms are rapidly cooled and their diffusion or hopping distance becomes small. Thus, the surface becomes rough and its structure looks like polycrystalline as confirmed by XRD in samples which were grown at RT and 100°C.

The average crystallite size is estimated from Debye-Scherrer equation and the values of lattice parameters $a$ and $c$ for Mn doped ZnO were estimated from the equation (1)

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

where $h$, $k$, and $l$ are the Miller indices and $d_{hkl}$ is the interplanar spacing for the plane (h k l) and the film stress along the c-axis, for a hexagonal crystal structure can be calculated using the biaxial strain model [19] based on the 002 peak position and are shown in table 1.

The value of lattice parameters decreases with the substrate temperature, the average crystallite size is around 24.2 nm and all films are under tensile stress as shown in table 1. The decrease in lattice parameters is caused due to zinc vacancies [20]. Manganese can exist in Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$. The ionic radius of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ are 0.66 Å, 0.58 Å and 0.53 Å respectively. In addition, based on the fact that the ion sizes of Mn are smaller than that of Zn, it is possibly that the Mn ions successfully substitute the Zn sites as increasing growth substrate temperature but there are still interstitially positioned Mn ions in crystal due to smaller ionic radii of Mn ions compared to Zn$^{2+}$ (0.74 Å). Substitution by the smaller manganese atoms decreases the lattice constants due to the intrinsic stress induced in the film [21]. These interstitially positioned ions also may have some contributions to the peak shift of ZnO(0 0 2). We also note that this report have been supported by Dole et al. [22].

**Table 1.** The XRD (002) peak position, lattice constants, grain size and stress calculated at 6.13 Pa and Mn 5 wt%.

| Temp (°C) | (002) Pos. (°) | $a$ (Å) | $c$ (Å) | Grain size (nm) | Stress ($10^9$ Pa) |
|-----------|----------------|---------|---------|-----------------|------------------|
| RT        | 34.425         | 3.188   | 5.206   | 24.656          | 0.029            |
| 100       | 34.491         | 3.182   | 5.196   | 23.106          | 0.461            |
| 200       | 34.490         | 3.182   | 5.197   | 24.465          | 0.454            |
| 300       | 34.540         | 3.178   | 5.189   | 25.997          | 0.781            |
| 400       | 34.550         | 3.177   | 5.188   | 23.696          | 0.846            |
| 600       | 34.596         | 3.173   | 5.181   | 23.112          | 1.150            |
3.2. Raman Analysis
Raman spectrum can sensitively reveal the changes of microstructure of the materials, leading to the analysis of crystal quality. According to the group theory, eight vibrational modes are predicted in the Brillouin zone for wurtzite structure. The A1 and E1 modes are polar and split into transverse optical (TO) and longitudinal optical (LO) phonons, and E2 mode consists of two modes of low and high frequency phonons. On the other hand, the B1 modes are not Raman active. To investigate the influence of substrate temperature on structure and vibrational properties further, Raman studies are performed and the results are shown in Figure 2. The Raman spectra of ZnMnO thin films were analysed in the range 40-900 cm\(^{-1}\), with the substrate temperature varying from room temperature to 600°C. Figure 2 show several peaks at 100 cm\(^{-1}\) and 434 cm\(^{-1}\) are assigned to the two non-polar optical phonons modes, E2 (low) and E2 (high), respectively. The peak located at 570 cm\(^{-1}\) is associated to E1(LO) vibration modes. The peaks at about 520 cm\(^{-1}\) come from the Si(1 0 0) substrates, which can be ignored to be discussed. An additional peak appears at 273 cm\(^{-1}\) and it indicates host lattice defects in the ZnO structure [23].

The E2 phonon mode centered around 434 cm\(^{-1}\) is obviously a good choice in order to understand the stress-induced phenomena in wurtzite ZnMnO. An increase in the E2 phonon frequency is generally ascribed to compressive stress, whereas a decrease is caused by the tensile stress.

The sharpest peak at about 434 cm\(^{-1}\) (E2 (high) mode) is the strongest Raman mode in wurtzite ZnO structure, and the values of the full width at half maximum of E2 (high) mode of these samples are less than 10 cm\(^{-1}\), which indicates that all the ZnMnO films keep a good ZnO wurtzite structure. E2(low) and E2(high) appear with low line width and higher intensity at 300°C.

In our Raman spectra, no Mn related Raman mode is observed. In a word, from the analysis of Raman spectra, we can deduce that Mn ions, at least partially, substitute for Zn ions in ZnO and microscopic structural disorders are introduced. The Raman spectra also exhibit a weak shoulder at about 570 cm\(^{-1}\) (E1(LO)) and has been attributed to the formation of oxygen deficiency, interstitial Zn. The broadening of these bands implies formation of defects electronic states within the band gap [24]. The vibrational modes are not sensitive function of substrate temperature, such behavior was observed and reported before [25].
3.3. UV-vis Analysis
The figure 3 shows the UV–visible diffuse reflectance spectra for ZnMnO, the absorption edge in the UV region depending on film growth temperature. For analysis purposes the diffuse-reflectance, R, of the samples can be related to the Kubelka–Munk function F(R) by the relation $F(R) = \frac{(1 - R)^2}{2R}$ [26]. The energy band gap of the ZnMnO samples was determined from the diffuse-reflectance spectra by plotting the square of the Kubelka–Munk function $(F(R)hv)^2$ versus energy and extrapolating the linear part of the curve to $(F(R)hv)^2 = 0$, as shown in figure 4. The optical band gap ($E_g$) values were determined by the above method to be 2.83, 2.03, 2.89, 3.2, 3.2, and 2.39 eV for the films grown at substrate temperatures RT to 600°C, respectively, indicating that $E_g$ varies irregularly with substrate temperature. The energy gap, $E_g$, is related to the grain size and carrier concentration in films [27]. In addition, quantum size effects may be involved due to nanofeatures on the films [28]. The maximum energy gap $E_g$ for films grown at 300°C may relate to the smallest grain size. Compared with films grown at 600°C, the $E_g$ of films grown at 300°C show a slight increase. This reveals that high substrate temperature will create more defects such as oxygen vacancies. Furthermore, more oxygen vacancies may cause a carrier concentration increase, thus the energy gap $E_g$ slightly increases although $E_g$ must decrease as result of the increase of grain size.

4. Conclusions
The structure of the ZnMnO films clearly varies with substrate temperature. The vibrational modes appear not to be sensitive function of substrate temperature. The increasing of the substrate temperature is in favor for the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favorable positions, resulting in the enhancement of the crystallinity and c-axis orientation of film.

The optical band gap of the films was found to be around 2.03–3.2 eV, which is lower than the theoretical value of 3.37 eV. At 300 °C the band gap is nearest to band gap undoped ZnO.
References

[1] Jagadish C and Pearton S J 2006 Thin Films and Nanonstructures: Processing, properties and applications, (Amsterdam: Elsevier).

[2] Nirmala M and Anukaliani A 2010 Photon Lett. Pol. 2 189

[3] Janisch R, Gopal1 P and Spaldin N A 2005 J. Phys.: Condens. Matter 17 R657–R689

[4] Pradhan A K, Hunter D, Lasley-Hunter B, Dadson J B, Zhang K, and Rakhimov R R 2006 J. Appl. Phys. 99, 08M108

[5] Bai H, He S, Liu G, Cao Q, Zhu D, Chen Y, Yan S, Mei L, 2012 Physica B: Condensed Matter 407 2126 [109]

[6] Fukumura T, Jin Z and Kawasaki M 2001 Appl. Phys. Lett. 78 958

[7] Sharma P, Gupta A, Rao K V, Owens F J, Sharma R, Ahuja R, Guillen J M O, Johansson B, Gehring G A, 2003 Nature Materials 2 673

[8] Singh P, Kaushal A and Kaur D 2009 J. Alloys Compd. 471 11

[9] Xue S W, Zu X T, Zhou W L, Deng H X, Xiang X, Zhang L and Deng H, J. Alloys Compd. 2008 J. Alloys Compd. 471 2126

[10] Waugh M R, Hyett G and Parkin I P 2008 Chem. Vap. Dep. 14 366

[11] Houng B, Hsi C S, Hou B Y and Fu S L 2008 J. Alloys. Compd. 456 64

[12] Devy F C, Barreau N and Kessler J 2008 Thin solid Films 516 7094

[13] Wang D, Zhang J W, Peng Y P, Bi Z, Bian X M, Zhang X A and Hou X 2009 J. Alloys Compd. 478 325

[14] Xiao B, Ye Z Z, Zhang Y Z, Zeng Y J, Zhu L P and Zhao B H 2009 Appl. Surf. Sci. 253 895

[15] Chrisey D B and Huber G K (Eds.) 1994 Pulsed Laser Deposition of Thin Films (John Wiley & Sons, Inc., New York) p. 613

[16] Kotlyarchuk B and Savchuk V 2003 Proc. IEEE “CAOL-2003” 1 149

[17] Kotlyarchuk B and Savchuk V 2003 Phys. Chem. Sol. State 4 434

[18] Jones B S and Smith R Z 1992 Joint Committee on Powder Diffraction Standards, Powder Diffraction File (Philadelphia: ASTM)

[19] Riascos H, Orozco S and J Uzuriaga 2015 Procedia Mat. Sci. 9 523

[20] Khalid M, Ziese M, Setzer A and Esquinazi P 2009 Physical Review B 80 035331

[21] Bhatti K P, Chaudhary S, Pandya D K and Kashyap S C 2005 Solid State Communications 136 384

[22] Dole B N, Mote V D, Huse V R, Purushotham Y, Lande M K, Jadhav K M and Shah S S 2011 Appl. Phys. 11 3 762

[23] Zhaoa Y, Jianga Y and Fang Y 2007 J. Cryst. Growth 307 278

[24] Zeng J N, Low J K, Ren Z M, Liew T and Lu Y F 2002 Appl. Surf. Sci. 197–198 362

[25] Orozco S, Riascos H and Duque S 2016 J. Phys.: Conf. Ser. 687 012036

[26] Kortum G 1969 Reflectance Spectroscopy (New York: Springer)

[27] Lin S S and Huang J L 2004 Surf. Coat. Tech. 185 222

[28] Ozgur U, Ya I, Alivov C, Liu A, Teke M A, Reshchikov S, Dogan V, Avrutin S-J, Cho H and Morkoc 2005 J. Appl. Phys. 98 041301

Acknowledgments

This work was be supported by a grant from the Programa Latino-Americano de Física in 2013 (Brazil). We also acknowledge Dr. Pedro Alejandro Ayala with the XRD measurements.