UV-Vis spectroscopy of Mn-doped ZnO thin films prepared by pulsed laser deposition

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Abstract. Mn-doped zinc oxide (ZnMnO) is of increasing interest to the optoelectronic community for thin film sensors, transistors and solar cells applications. Considerable variability exists in the literature on the growth and doping of ZnMnO films, especially as a function of growth approach, temperature, and oxygen partial pressure. We fabricated ZnMnO thin films on silicon substrates by pulsed laser deposition (PLD). The deposition pressure and the substrate temperature were varied from 2.67 Pa to 26.67 Pa, and from room temperature to 600 °C, respectively. The targets were fabricated with a nominal composition of 1, 5, 10, 15 and 20 wt.% Mn. The influence of the Mn composition, deposition pressure and the substrate temperature on optical properties of the ZnO films was investigated using ultraviolet–visible (UV–Vis) spectrometry. The optical band-gap of the films was evaluated in terms of the Kubelka-Munk function. The results show that the oxygen gas pressure has slightly affected the optical band-gap of the deposited films. Furthermore, the substrate temperature play significant role in the optical properties of the deposited ZnMnO thin films.

1. Introduction

ZnO is an attractive material for short wavelength optoelectronic applications because of its large exciton binding energy (60 meV) and the possibility of tuning the optical band gap (Eg) by doping with some metals to develop an electronic and optoelectronic device. Doping of ZnO nanostructures with different impurities like metals transition (TM) is the primary technique for controlling the properties like bandgap, electrical conductivity and ferromagnetism [1 - 4]. Recently, there has been much attention focused on modifying ZnO by doping with transition metals, these studies demonstrated that the metals induce a change in Eg of ZnO, and that the dopants can control ZnO grain size. It demonstrated the presence of electronic transition between d-orbitals in systems with octahedral geometry manganese (Mn) is very close to the valence band [5, 6]. Unfortunately, up to now the value of the Eg and optimum amount of Mn as dopant is not clear, because the oxidation states are diverse and the doping depends exclusively on the ionic radius and redox potentials that are subject to the oxidation state. The optical and electrical properties of the TM-doped nanostructures are strongly dependent on the fabrication condition.

Many methods were employed in the preparation of Mn-doped ZnO, such as PLD [7 - 9], implanting [10], radio frequency magnetron sputtering [5], sol–gel method [8] and so on. Among the fabrication techniques, the pulsed laser deposition (PLD) has attracted attention because a film stoichiometry is keeping the composition of the multi-component target [11 - 14]. Especially, the PLD is convenient for growth of compound films containing oxygen and it make possible to low temperature growth compare to molecular beam epitaxy (MBE). The
PLD technique has an advantage of controlling a complex composition ratio and less damage during a growth. The effect of deposition properties such as substrate temperature, grow rate, pressure, ambient gas is very important during deposition in PLD process. The main purpose of presented work was to investigate the optical properties of the films. ZnMnO thin films deposited on silicon substrates by using PLD and influence of substrate temperature, gas pressure and Mn-doped composition on the optical properties of the films were investigated by UV–Vis spectroscopy.

2. Experimental details
ZnMnO thin films on silicon substrates were synthetized from Mn doped ZnO target by conventional Pulsed Laser Deposition (PLD) technique. PLD of ZnMnO target was carried out using Q-switched Nd:YAG laser operating at wavelength of 1064 nm, pulse duration of 7 ns, pulse energy of 300 mJ and repetition rate of 10 Hz. Ablation was carried out in vacuum at a residual pressure of 1.33 mPa. In order to study the change of band gap, the films were deposited on Si (100), under different oxygen gas pressure (2.67 to 26.67 Pa), composition (1, 5, 10, 15 and 20 wt. %) and temperature substrate (RT – 600 °C). The laser fluence was kept at 3.0 ± 0.4 J cm². The UV-Vis studies were performed with a Perkin Elmer Lambda 9UV/VIS/NIR spectrometer, covering an extended wavelength range of 190 to 800 nm. The experimental details have been mentioned elsewhere [15].

3. Results and Discussion

3.1. Optical properties
The electronic transition of materials, mainly in semiconductors, occur in uv-visible range, therefore the optical properties depend of the reflectance of incident light of materials and its study is very important to estimating the optical band gap of materials. The UV–Vis reflectance spectra of these three sets of ZnMnO samples in the wavelength range 300–800 nm are shown in figures 1. The absorption band edge of all films is observed at around 300 nm. The strong optical absorption is characteristic of ZnO direct band gap transition and indicating good quality of the deposited films with low reflectance. The band gap energy (Eg) of these films can be determined by using the tauc’s plot according to following relation [16, 17]:

\[(F(R)h\nu)^n = A(h\nu - E_g)\]

Where \(F(R) = (1-R)^2/2R\) is Kubelka–Munk function, \(R\) is the reflectance, \(\nu\) is the frequency, \(A\) is a proportionality constant and \(n = 2\) for direct band gap semiconducting materials. By extrapolating the linear region of these plots to \((F(R)h\nu)^2 = 0\), the direct bandgap values are obtained (inset of Figures 1).

Figure 1a shows the optical reflectance spectra of Mn doped ZnO, Mn fixed at 1, 5, 10, 15 and 20 wt.%, with relative low reflectance in the visible region. Moreover, a change in the reflectance in the visible region is observed by the Mn concentration without any obvious tendency that might be due to the influence of numerous factors such as structural parameters, carrier concentrations and the presence of defects such as oxygen vacancies, which may lead to the Burstein Moss effect [18]. In addition, the reflectance edge, around 300nm, of some of the samples shifts lightly towards the visible region indicating the band gap excitations by visible light.
Figure 1. Reflectance spectra of ZnMnO thin films grown at different conditions. A) varying Mn composition; B) varying the substrate temperature and C) varying the oxygen gas pressure. The insets are the Tauc plots correspondents.

Figure 1b shows the optical reflectance spectra of the 5 wt.% Mn doped ZnO films grown at RT, as a function of oxygen gas pressure (from 2.67 Pa to 26.67 Pa). All of these samples have a sharp absorption edge in the UV region and exhibited strong surface plasmon resonance (SPR) peaks, specially the sample grown at 4.67 Pa and it is clear a shoulder for all samples. This optical behavior is attributed mainly to the sp–d spin exchange interaction between the band electrons and the localized d electrons of Mn$^{2+}$ ions. Moreover, It can be speculated that the appearance of this shoulder (exciton) is generally caused by the change in the surrounding medium (gas pressure), or by the particle agglomeration that optically behave as oblate spheroids [19, 20].

Figure 1c shows the optical reflectance spectra of the 5 wt.% Mn doped ZnO films grown at 6.13 Pa and the substrate temperature ranging from room temperature (RT) to 600 °C. Similar to films grown at different Mn concentration, the reflectance is low for all films. As clearly seen in the figure 1c, an absorption peak is observed at around 333 nm for the samples grown at 300 °C and 400 °C could be attributed to the plasmon resonance absorbance. Additionally, a shoulder at 365 nm is observed for the sample grown at 300 °C, ZnO exciton. Moreover, the presence of SPR peak in the absorption spectra indicates the presence of extra Mn in the deposited films [21, 22].
Figure 2. Values $E_g$ of ZnMnO thin films for A) different Mn concentration; B) varying oxygen gas pressure; C) varying the substrate temperature.

The values of $E_g$ obtained by uv-vis spectroscopy for ZnMnO films at different grown condition are plotted in figure 2. As it can be observed in figure 2a, the values of $E_g$ increase with percentage of Mn up to 10 Pa, and then decrease as the Mn concentration is increased further, it is probably due to charge transfer effect and Mn atoms replaces Zn in the lattice structure partly inducing structure disorder. The band gap energy decreases along with the increase of the gas pressure as shown in figure 2b, the influence of the oxygen pressure on the $E_g$ value indicates that the gas phase plays an important role in ZnMnO synthesis, and this is due to a decrease in carrier concentration [18]. How the gas phase influences the $E_g$ of the semiconductor films is still a matter of discussion [23].

The influence of the substrate temperature on the $E_g$ indicates that the substrate temperature plays an important role in ZnMnO nanostructure and optical properties [24], due to structural changes generated by the interdiffusion process of atoms during the first stages of the growth process. This dependence of $E_g$ upon substrate temperature was reported in our previous work [15]. However, as shown in the figure 2c, the temperature-dependent band gap is slightly fluctuant.

4. Conclusion

The ZnMnO thin films were prepared on Si substrates with different Mn concentrations, oxygen gas pressures and substrate temperatures by pulsed laser deposition. The values of band gap decreased with increasing percentage of Mn over 1 wt%. The band gap decreases along with the increase of the gas pressure, the influence of the gas pressure on the band gap indicates that the gas phase plays an important role in ZnMnO synthesis. AFM analysis has been carried out to characterize the thin films morphologies. Surface morphologies associated with different gas pressures have been investigated, and the results provided evidence that the gas pressures affect the final surface morphology of ZnMnO thin films.

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References

[1] Baruah S and Dutta J 2009 Sci. Technol. Adv. Mater. 10 013001.
[2] Janotti A and de Walle C 2009 Rep. Prog. Phys. 72 126501.
[3] Djurisic A B and Leung Y 2006 Small 2 944
[4] Yi G C, Wang C and Park W I 2005 Semicond. Sci. Technol. 20 S22
[5] Kumar P, Malik H K, Ghosh A, Thangavel R and Asokan K 2013 Appl. Phys. Lett. 102 221903
[6] Hlaingo W M, Saraf L V, Engelhard M H, Shuttanandan V, Bergman L, Huso J and McCluskey M D 2009 J. Appl. Phys. 105 013715
[7] Akin N, Cetin S S, Cakmak M, Memmedli T and Ozcelik S 2013 J. Mater. Sci.: Mater. Electron. 24 5091
[8] Han S, Shen D Z, Zhang J Y, Zhao Y M, Jiang D Y, Ju Z G, Zhao D X and Yao B 2009 J. Alloys Comp. 485 013715
[9] Fortunato E, Raniero L, Silva L, Goncalves A, Pimentel A, Barquinha P, Agus H, Pereira L, Goncalves G, Ferreira I, Elangovan E and Martins R 2008 Sol. Energy Mater. Sol. Cells 92 1605
[10] Liu K, Sakurai M and Aono M 2010 Sensors 10 8604
[11] Black S 2011 Laser Ablation Effects and Applications, 1st Ed. Nova Science Publishers, Inc.
[12] Fischer D, de la Fuente G F and Jansen M 2012 Rev. Sci. Instrum. 83 043901
[13] Eason R (Ed.) 2007 Pulsed Laser Deposition of Thin Films (Wiley, New Jersey,) p. 273
[14] Von Allmen M and Blatter A 2013 Laser-beam interactions with materials: physical principles and applications 2 (Springer Science & Business Media).
[15] Riascos H, Orozco S and Uzuriaga J 2015 Procedia Materials Science 9 523.
[16] Joshi G, Saxena N, Mangal R, Mishra A, Sharma T 2003 Bull Mater Sci. 26 387.
[17] Viezbicke B D, Patel S, Davis B E and Birnie D P 2015 Physica Status Solidi B 252 1700.
[18] Baghdad R, Kharrouri B, Abdiche A, Bousmaha M, Bezzerrouk M A, Zeinert A, Marssi M E and Zellama K 2012 Superlatt. Microstruct. 52 711.
[19] Ren Q J, Filippov S, Chen S L, Devika M, Reddy N K, Tu C W, Chen W M and Buyanova I A 2012 Nanotechnology 23 (42) 425201.
[20] Zeng H, Cai W, Li Y, Hu J and Liu P 2005 J. Phys. Chem. B 109 18260
[21] Ranjgar A, Norouzi R, Zolanvari A and Sadeghi H 2013 Armenian J. Phys. 6 (4) 198
[22] Chen J, Mu R, Ueda A, Wu M, Tung Y -S, Gu Z and Henderson D 1998 J. Vac. Sci. Technol. 16 (A) 1409.
[23] Kim E, Jiang Z –T and No K 2000 Japanese Journal of Applied Physics 39 (8) 4820
[24] Pradhan A, Jhang K, Mohanty S, Dadson J B, Hunter D, Jhang J, Sellmyer D J, Roy U N, Cui Y, Burger A, Mathews S, Joseph B, Sekhar B R, Roul B K 2005 Appl. Phys. Lett. 86 152511.