Raman spectroscopy of ZnMnO thin films grown by pulsed laser deposition

S Orozco¹, H Riascos¹ and S Duque¹
¹ Universidad Tecnológica de Pereira, Pereira, Colombia.
E-mail: sorozco@utp.edu.co

Abstract. ZnMnO thin films were grown by Pulsed Laser Deposition (PLD) technique onto Silicon (100) substrates at different growth conditions. Thin films were deposited varying Mn concentration, substrate temperature and oxygen pressure. ZnMnO samples were analysed by using Raman Spectroscopy that shows a red shift for all vibration modes. Raman spectra revealed that nanostructure of thin films was the same of ZnO bulk, wurzite hexagonal structure. The structural disorder was manifested in the line width and shape variations of $E_2$(high) and $E_2$(low) modes located in 99 and 434 cm$^{-1}$ respectively, which may be due to the incorporation of Mn ions inside the ZnO crystal lattice. Around 570 cm$^{-1}$ was found a peak associated to $E_1$(LO) vibration mode of ZnO. 272 cm$^{-1}$ suggest intrinsic host lattice defects. Additional mode centred at about 520 cm$^{-1}$ can be overlap of Si and Mn modes.

1. Introduction

ZnO is a semiconductor with wurtzite hexagonal structure and belong to space group P6$_3$mc. This material promises applications in optoelectronics, transparent electronics, gas sensors [1], and very interesting material for spintronics [2,3]. ZnO hexagonal lattice is characterized by two interconnecting sublattices of Zn$^{2+}$ and O$^-$, such that each Zn ion is surrounded by tetrahedral of O ions and vice-versa [4]. The irreducible representation of the optical phonons is $\Gamma_{opt} = 2A_1 + 2B_1 + 2E_1 + 2E_2$. In this expression, the $A_1$ and $E_1$ modes are polar, and may split into transverse (TO) and longitudinal (LO) optical phonon, both are active in Raman and infrared spectroscopy. The non-polar $E_2$ modes are only Raman active and the $B_1$ modes are Raman inactive. The Raman spectra can be interpreted to estimate the degree of disorder in a crystal. The structural disorder is manifested in the line shape (line width and asymmetry variation) of the $E_2$ mode [2]. The properties of the grown thin films depend on the deposition process and deposition parameters. In ZnMnO films, formation of defects or introduction of extrinsic doping can cause stress, which can modify the physical properties [5]. In this work, ZnMnO thin films were grown by PLD technique. The optical properties of the grown samples were characterized by Raman spectroscopy; we report some features of Mn-doped ZnO thin films produced by PLD, and we discuss the effects of the oxygen pressure, substrate temperature and Mn concentration on structural and optical properties of ZnMnO films.

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 Nd:YAG laser (1064nm wavelength, 9ns pulse duration). The laser was operated at 10Hz and the laser beam was incident at an angle of 45 degrees with respect to the target surface. The targets were prepared from high-purity powders of ZnO (99.999%), and
MnO (99.999%) serving as the doping agent. The pressed targets were sintered at 1000°C for 12h in air. The targets were fabricated with a nominal composition of 1, 5, 10, 15 and 20wt.% Mn, and were 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 and at 6cm 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 varied between 2.67 and 26.66 Pa. The laser fluence was kept at 3.0±0.4 J/cm². Three sets of ZnMnO samples were prepared by PLD. In the first set, ZnO thin films were deposited at different Mn-doping ranging from 1 to 20wt.% Mn, preserving substrate temperature and oxygen pressure in room temperature and 6.13Pa respectively. In the second set, the substrate temperature was varied from room temperature to 600°C, with 5wt.% of Mn concentration and 6.13Pa of oxygen pressure. The third set was deposited at different oxygen gas pressure in the range 2.67Pa-26.66Pa at room temperature and 5wt.% of Mn content. Optical analysis of the films was carried out in a Jobin–Yvon micro-Raman spectrometer.

3. Results and discussions

The different ZnMnO Raman patterns were analysed in the range 40-900 cm⁻¹. Figures 1, 2 and 3 show the spectra of ZnMnO thin films varying Mn concentration, substrate temperature and oxygen pressure respectively. The spectra in Figure 1 show several peaks at 100 cm⁻¹, 434 cm⁻¹ and 570 cm⁻¹ associated to E₂(low), E₂(high), and E₁(LO) vibration modes respectively. These peaks are typical of ZnO bulk. These spectra are very similar for Figure 2 and 3. The high frequency E₂ mode, E₂(high), involves predominantly the lighter oxygen atoms and ZnO wurzite structure [6]. The line width are assigned to defects, structural damages, residual stress, and impurities of the sample [2]. E₂(low) mode is associated with the non-polar vibration of heavier cations Zn sublattice [6,7]. E₁(LO) Raman line intensity varies with oxidation of excess zinc in the ZnO thin film [8,9]. This mode is caused by defects of O vacancy and Zn interstitial [8]. An additional peak appears at 273 cm⁻¹ and it indicates host lattice defects in the ZnO structure [10]. The peak at 520 cm⁻¹ is associated with overlapping of vibration modes from Si and Mn.

Figure 1. Raman patterns of ZnO thin films deposited by PLD at different Mn-concentration ranging from 1wt.% to 20wt.% of Mn, at room temperature and 6.13Pa.

Figure 2. Raman patterns of ZnMnO thin film deposited by PLD with the substrate temperature varying from room temperature to 600°C. The Mn-doping and oxygen pressure were kept constant, 5wt.% Mn and 6.13Pa, respectively.
3.1. Influence of Mn concentration
The peaks intensity decreases with increasing of Mn content as is shown in Figure 1. For \(E_2(\text{high})\) its line width increases with Mn content increase, while the intensity decreases. However \(E_2(\text{low})\) peak intensity is very weak for all Mn concentration. For 1wt.% Mn, a broad peak appear associated with \(E_1(\text{LO})\); as Mn concentration increases the broadening is higher till is overlap for the Si and Mn modes at 520cm\(^{-1}\). This peak (at 520cm\(^{-1}\)) became more wide and its intensity low with increase Mn concentration. In addition, the peak at 273cm\(^{-1}\) appears with low intensities for 1wt.% and 5wt.% of Mn only.

3.2. Influence of substrate temperature
The variations of substrate temperature are shown in Figure 2. \(E_2(\text{low})\) and \(E_2(\text{high})\) appear with low line width and higher intensity at 300\(^\circ\)C. As the substrate temperature decreases, \(E_2(\text{high})\) is red shift so that the tensile stress increases [11]. The shoulder related with \(E_1(\text{LO})\) has same behaviour that in Figure 1. The peak associated with defects on the lattice appear with very weak intensity at 300\(^\circ\)C. According to these spectra characteristics, the thin film grown at 300\(^\circ\)C has best crystalline quality and optical properties.

3.3. Influence of oxygen pressure
\(E_2(\text{high})\) mode at 9.33Pa is very sharp peak as is shown in Figure 3. For this peak the maximum intensity was observed at 9.33Pa. This behaviour can be understood by two competing processes; the increase of oxygen pressure in the chamber improves the stoichiometry of the films and the crystal quality. On the other hand, the kinetic energy of the reactive particles in the plasma decreases due to high oxygen pressure, which limits surface diffusion of the growing atoms and thus degrades the film quality [12,13]. \(E_2(\text{low})\) is very weak peak for all range of oxygen pressure. \(E_1(\text{LO})\) mode has same behaviour that for Mn concentration and substrate temperature. The peak at 272cm\(^{-1}\) has very weak intensity at 9.33 and 13.33Pa.

![Figure 3](image)

Figure 3. Raman patterns of ZnMnO thin film deposited by PLD, the oxygen gas pressure was varied from 2.67Pa to 26.66Pa. The Mn-doping and substrate temperature were kept constant, 5wt.% and room temperature, respectively.
4. Conclusion
The optical properties have a dependence on Mn-doping concentration, Oxygen gas pressure and substrate temperature. All prepared films present a typical hexagonal wurtzite ZnO structure and a peak own to Mn doped was present. Any extra peaks were found related with other impurities independent of the deposition parameters. It is seen that the crystalline quality of the films are varying with processing conditions (Mn concentration, substrate temperature and Oxygen gas pressure). Defects and residual stress of the samples were found for high Mn concentration, also for high and low substrate temperature and oxygen pressure. The films with better optical properties and less structural disorder have been obtained at relatively low Mn-concentration (1-5wt.% Mn), an intermediate substrate temperature (300–400°C) and relatively intermediate oxygen gas pressure (4.67-9.33Pa).

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