Effects of Deposition Pressure and Target-Substrate Distance on Growth of ZnO by Femtosecond Pulsed Laser Deposition

Joseph A. De Mesa[*], Annaliza M. Amo[*,***], Jessa Jayne C. Miranda[*], Hernanie O. Salazar[**,***], Roland V. Sarmago[**] and Wilson O. Garcia [*]

[*] *Photonics Research Laboratory, National Institute of Physics, University of the Philippines, Diliman, Quezon City*
E-mail: josephabandemesa@gmail.com
[**] *Condensed Matter Physics Laboratory – Superconductor, National Institute of Physics*
[***] *Material Science and Engineering Program, College of Science University of the Philippines, Diliman, Quezon City*

Undoped Zinc oxide (ZnO) was successfully deposited on silicon (100) substrate by femtosecond pulsed laser deposition. A mode-locked femtosecond laser operating at 790 nm wavelength, 100 fs pulse duration and 80 MHz repetition rate was used as an excitation source. The depositions were carried out at vacuum pressures of 10^{-2}-10^{-6} mbar and oxygen background gas pressures of 10^{-2}-10^{-4} mbar. Energy dispersive spectroscopy of samples grown without oxygen background gas shows higher zinc composition on deposited material as compared to oxygen that leads to off stoichiometric ZnO films. Scanning electron microscopy (SEM) images shows that increasing oxygen gas pressure increased the particle size of the deposited ZnO. The material deposited at $2x10^{-4}$ mbar oxygen pressure revealed clustering of nanorods forming a flower-like structure that has an average length of 2700 nm and an average diameter of 450 nm. The X-ray diffraction spectra show c-axis orientation of the deposited ZnO with (002) and (110) reflection.
DOI: 10.2961/jlmn.2016.01.0004
Keywords: pulsed laser deposition, deposition growth, laser ablation, femtosecond techniques, film deposition

1. Introduction

For the past years, there has been great interest in the production of transparent conducting oxide (TCO) and transparent oxide semiconductors for optical applications such as surface acoustic wave (SAW), acoustic-optic, and piezo-optic [1, 2]. Zinc oxide (ZnO) is a novel photonic material with properties similar to Gallium nitride (GaN) such as wide direct band gap (3.3eV), large exciton binding energy (60meV) and high melting temperature of 2248K [2, 3]. The fabrication of ZnO films has been employed by various techniques including thermal evaporation, laser-assisted ablation, chemical vapor deposition, sputtering, sol-gel, molecular beam epitaxy and pulsed laser deposition (PLD) [3, 4]. Among these techniques, PLD has proved to be a suitable method to produce high quality thin films at relatively lower substrate temperature [3, 5].

PLD is a thin film deposition technique that uses a pulsed laser focused onto target to create plasma. The target material is vaporized by the high laser intensities. This ejected materials travels towards a substrate to form a thin film [6]. PLD has been widely used in production of thin films due to its other inherent advantages which include stoichiometric transfer of material, high deposition rate, high film adherence, simple set up and ability to control film thickness [3, 5, 7]. Conventional PLD technique has proven to synthesize high quality ZnO thin films on wide range of parameters.

ZnO thin films can be grown using either a nanosecond (ns) laser or a femtosecond (fs) laser in PLD [7]. In the first case, macroscopic particles (a few micrometers in diameter) are generally present on the surface of the films [7]. The origin of these particles is related to liquid droplets that are generally assumed to be the consequence of thermal effects during laser-matter interaction [7-10]. This problem can be possibly solved by using femtosecond laser deposition [8]. With ultra-short (fs) pulsed laser, energy deposited does not have enough time to move into the bulk, which neglects thermal effects minimizing the molten droplets present in ns-PLD [11, 14, 15]. It was reported by Millon et al [16] that ZnO films can be grown on various substrates by femtosecond pulsed laser deposition which includes Si (100) and glass substrates. They found that smaller crystallite size and smaller residual stresses was obtained for ZnO films grown with femtosecond lasers than by nanosecond laser ablation.

In this experiment, we ablated ZnO ceramic target using ultrashort laser pulses with high repetition rate. High repetition rate (>200 kHz) ultrashort laser pulses can cause heat accumulation effects that can lessen defect-induced damage and avoid collateral damage that causes molten droplets [new reference [16]. Molten particles ejected from the target produces large particulates in the deposited film that are the cause of defects in the film. Thus, using high repetition rate could decrease this effect.

The morphological characteristic of deposited ZnO on silicon (100) grown by fs-PLD technique at different deposition pressure (with and without background gas). The effect of varying the oxygen background gas pressure in the growth of the sample was investigated. Possible potential applications of the fs-PLD grown ZnO film were also reported in this paper.

2. Experimental Details

A sintered ceramic ZnO target was used in the femtosecond pulsed laser deposition. The target was high purity (99.0%) ZnO powder pelletized using a hydraulic pressure set to 8 to 10 tons successively every 5 minutes and annealed at ambient atmosphere for 12 hours. The silicon (100) substrate was cleaned using standard degreasing procedure (TCE, acetone, methanol) sonicated for 5 minutes and oxide strip with 1:50 ml ratio (HF:DI). The Si (100) substrate was loaded to the vacuum chamber and placed opposite to the target at a distance of 1 and 3 cm.

Figure 1 shows the schematic representation of the experimental setup. The fs-PLD was performed using a mode-locked titanium-doped sapphire laser (Spectra-Physics Tsunami laser) operating at its peak output wavelength of 800 nm, 600 mW average output power, pulse repetition rate of 80 MHz and pulse duration of 100 fs. The laser beam was focused using a 57 mm biconvex lens. A rotary pump and diffusion pump was used to reach a base pressure of $8x10^{-6}$ mbar and $4x10^{-5}$ mbar monitored by an ionization gauge. A high purity oxygen gas was introduced to the vacuum system with initial base pressure of $4x10^{-5}$ mbar using a needle valve gas controller to vary the background gas pressures to $2x10^{-4}$, $7x10^{-4}$, $2x10^{-2}$, $4x10^{-2}$ mbar. The deposition experiments were carried out for 180 minutes and without heat treatment.

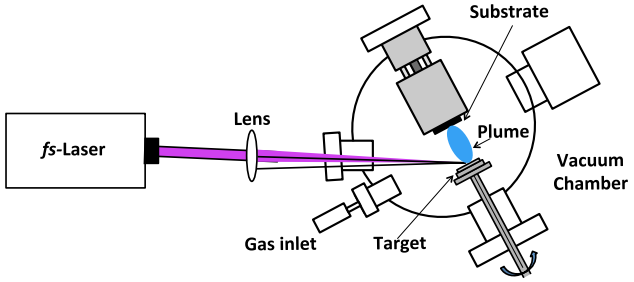

Fig. 1. Schematic representation of the fs-PLD setup.

Scanning election microscopy (SEM) and electron dispersive spectroscopy (EDS) was used to investigate the surface morphology and elemental micro-composition of the ZnO deposited on the silicon substrate at different deposition parameters. The crystal properties of the deposited ZnO were obtained using X-ray diffraction (XRD).

3. Results and Discussion

SEM characterization along with EDS analysis was done on the substrate with deposited materials, to determine surface morphology and elemental composition. Zinc and oxygen are not detected on the samples conducted at 10^{-2} mbar for three different hours. The absence of Zn and O in EDS analysis might indicate that no ZnO particles were deposited on the samples.

The SEM images of ZnO deposited at a vacuum pressure of 10^{-6} mbar and a deposition time of 3 hours are shown on Figure 2. Resputtering of the high-energy particle ejected from the target results to microcracks shown in Figure 2. A random clustering of particle with few hexagonal-like structures that was approximately around 300-500 nm based on the images taken at 1000x magnification SEM micrographs reveal rough to porous surface of the films which is expected for a ZnO film grown at room temperature [18]. The absence of heat treatment (in-situ or post) on the samples caused ejected atoms to have a low time migration after it reached the substrate. Relatively low substrate temperature transfers insufficient energy on the adatoms to migrate on the surface before they settle at the energetically most stable sites. This unable the film to form a texture with lower surface energy that causes uneven surface morphology [19]. The large number of defects shown on Figure 2. is due to the large number of dislocation and strain caused by large lattice mismatch (15.4%) between ZnO and silicon (100) [20].

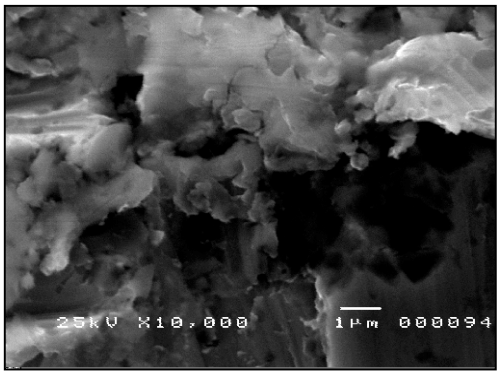

Fig. 2. SEM micrographs of deposited ZnO at vacuum pressure of 10^{-6} mbar, deposition time of 3 hrs, and target to substrate distance of 3 cm.

Figure 3 show the EDS of ZnO thin films of the sample grown at 10^{-6} mbar and deposition time of 3 hrs. The presence of Zn K_α peak at around 0.98, 8.60, and 9.5 keV and O K_α peak at about 0.5 keV could be observed. Three peaks at 0.00, 1.74 and 8.04 keV attributed to silicon substrate were omitted. Zn and O peak was present on different spots taken by EDS on samples with 10^{-6} mbar. Figure 3 showed a similar EDS spectrum reported by A. Dikovska et al. of ZnO grown by pulsed laser deposition at nanosecond regime and L. S Chuah et al. of ZnO grown by dc sputtering [13, 21]. However, EDS spectra show higher zinc composition of deposited material as compared to oxygen. Lack of ambient oxygen on deposition leads to off stoichiometric of ZnO films. It has been reported that the ambient gas mainly provides the oxygen present in the metal oxide and only 1% is attributed from the target material [5]. Absence of oxygen background gas leads to oxygen vacancies.

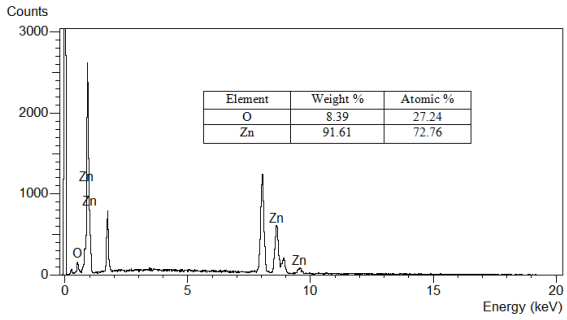

Fig. 3. EDS of ZnO thin film deposited at vaum pressure of 10^{-6} mbar, deposition time of 3 hrs, and target to substrate distance of 3 cm.

In order to compensate the deficiency on the deposition of ZnO particles and the off stoichiometric composition of deposited ZnO, target-to-substrate distance was decreased to 1 cm and an inclusion of high purity oxygen gas was conducted

The SEM images of the samples grown at varying oxygen background gas pressure are shown in Figure 4. A random clustering of particles and microcracks are observed in all SEM images. This random clustering may be attributed to the low kinetic energy of the species arriving on the surface of the substrate that are caused from the multiple collisions between ablated species and oxygen gas molecules. Figure 4 (a) shows the nanorods that are connected at one end forming flower-like structures. The size of each nanorods ranges from 650 to 8000 nm in length and 200 to 700 nm in width. However, these structures are absent in the sample grown at higher oxygen background gas pressure. Thus $2x10^{-4}$ mbar was found to be good oxygen background gas pressure at room temperature for the growth of ZnO nanorods. Stacking of nano-size particle is observed in Figure 4 (b) while small particles overlying large particulates are shown in Figure 4 c&d. These images show that the deposition rate and substrate coverage area increase with oxygen pressure due to the quenching of the energetic species and subsequent reduction in resputtering [22]. It was observed that increasing the oxygen gas pressure increases the particle size. The SEM micrographs also show rough to porous surface of deposited ZnO films at all oxygen pressure. This is in good agreement with the published data on the PLD of ZnO thin films at room temperature [5]. The absence of heat treatment (in-situ or post) on the samples caused low migration of ejected atoms after it reached the substrate because of the insufficient energy of adatoms leading to the uneven surface of the deposited ZnO films. The presence of spheroids in the material contributes to the unevenness of the surface morphology of the deposited material. These deposited spheroids together with the micronsized particle are due to low-energy phase transformations caused by the irradiation of a target material with fs pulses [19].

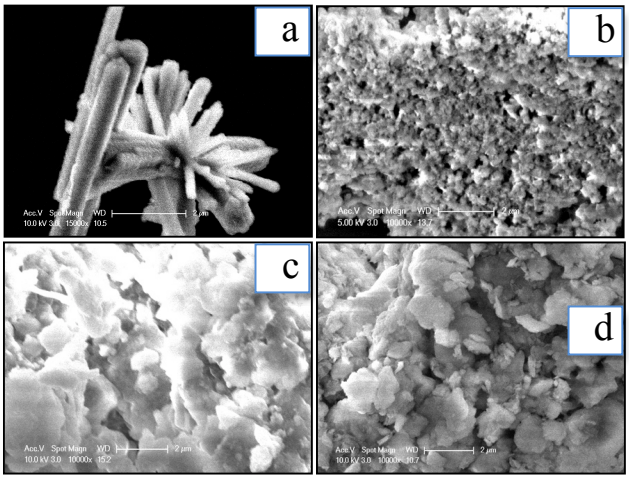

Fig. 4. SEM images with scale bar of 2 μm of samples grown at (a) $2x10^{-4}$ mbar, (b) $7x10^{-4}$ mbar, (c) $2x10^{-2}$ mbar, and (d) $4x10^{-2}$ mbar oxygen background gas pressures

Smoother morphology by ZnO film grown at higher oxygen background gases while the highly porous morphology of sample grown at $7x10^{-4}$ mbar could provide light scattering and subsequently light trapping which is vital for the application of solar cells. The morphology and size of ZnO rods grown at $2x10^{-4}$ mbar can importantly influence the optical properties of the film that could be used in the field of solar technology and electrochemistry [3,18]

The XRD pattern of the samples grown at oxygen background gas pressure of $4x10^{-2}$, $2x10^{-2}$, $7x10^{-4}$, and $2x10^{-4}$ mbar is shown in Figure 5. The XRD spectra for samples obtained in oxygen pressure of $2x10^{-2}$ mbar and $4x10^{-2}$ mbar shows only one intense peak that was attributed to the (004) peak of the silicon substrate. Absence of peaks that can be attributed to ZnO indicates that the deposited particles with the aforementioned parameters grow at random orientation. Based on this data, it can be inferred that lower pressure is preferred for deposition of ZnO films for this laser parameters. The effects of pressure, i.e., presence of oxygen gas species in the deposition affect the growth orientation of the ZnO thin films.

As the oxygen background gas pressure is decreased, new XRD reflection peaks were found and indexed as (002) attributed to ZnO for the sample grown at $7x10^{-4}$ mbar and one as ZnO (110) for the sample grown at $2x10^{-4}$ mbar. This implies that the preferred orientation of the deposited ZnO varies with oxygen gas pressure. The XRD results also indicate that the samples prepared by fs-PLD with the aforementioned parameters show single crystal orientation.

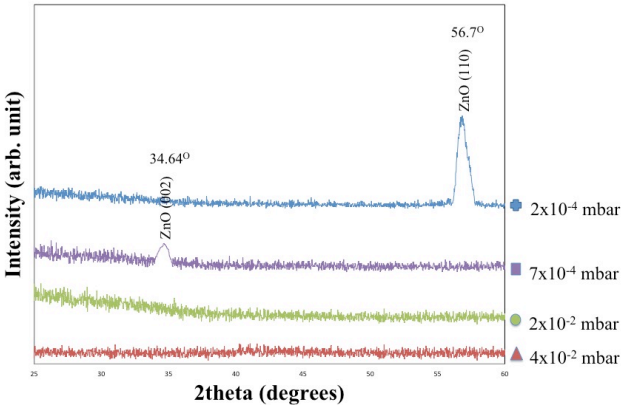

Fig. 5. XRD spectra of the samples grown at 410^{-2}, $2x10^{-2}$, $7x10^{-4}$, and $2x10^{-4}$ mbar background gas pressures.

To assess the quality of the crystallinity of the films deposited, the FWHM of (002) and (110) peaks were measured. The FWHM value obtained for (002) peak is 1.528^{O} while 0.776^{O} is obtained for the FWHM of (110) peak. These FWHM values indicate that the sample grown at $2x10^{-4}$ mbar has a better crystallinity than the sample grown at $7x10^{-4}$ mbar. The ablated species arriving at the silicon substrate for system grown at $2x10^{-4}$ mbar contains a greater energy for the surface migration than the ablated species for system at $7x10^{-4}$ mbar. The amount of kinetic energy loss in the ablated species depends on the background gas pressure (i.e., when the deposition pressure is

high, the collisions between the ablated plume species and gas molecules become more frequent leading to more kinetic energy loss). At higher background gas pressure, the species reaching to the surface of the substrate with low kinetic energy stick where they arrive on the substrate surface, leading to randomly oriented films. Also, low substrate temperature cause the growth of grains along the substrate to be restricted resulting to an inferior crystal quality of the deposited samples [23]. It is reported by many paper that the substrate temperature plays an important role in growing high quality thin films [2, 4, 5]. The large FWHM values and low intensity of the XRD peak attributed to ZnO indicate that the grown film is not highly crystallized. The kinetic energy of the arriving atoms is not enough for the adatoms to migrate on the substrate surface and prevent high crystallization of the film.

4. Conclusions

A mode-locked Ti:sapphire laser with output wavelength of 800 nm and average power of 600 mW was used to ablate a pelletized ZnO target mounted on a rotating target holder and placed inside a vacuum chamber with base pressure of 10^{-2} mbar down to 10^{-6} mbar. SEM and EDS were used to characterize the samples. SEM images showed a random clustering of particles with few hexagonal-like-structures that was approximately around 300-500 nm for the sample deposited in a deposition pressure of ~$8.6x10^{-4}$ mbar. No particles were found for samples deposited for vacuum pressure of 10^{-2} mbar and target-to-substrate distance of 3 cm. EDS analysis showed a greater zinc composition as compared to oxygen for the sample deposited in a vacuum pressure of 10^{-6} mbar and deposition time of 3 hours. Lack of ambient oxygen on deposition leads to off stoichiometric ZnO thin films. Absence of oxygen background gas leads to oxygen vacancies.

ZnO were also successfully grown on silicon (100) substrate by fs-PLD with varying oxygen background gas for target-to-substrate distance of 1 cm. SEM micrographs revealed that increasing the oxygen gas pressure decreases the microcracks and increases particle size. ZnO nanorods were grown at oxygen gas pressure of $2x10^{-4}$ mbar with length of few micrometers and diameter of hundreds of nanometer to few microns. XRD spectra show random orientation of deposited ZnO on silicon (100) substrate.

Acknowledgments

The authors thank Mr. Reynaldo Coria and Ms. Luce Vida Sayson for their assistance in characterizing the samples. We also acknowledge the support provided by the University of the Philippines, Office of the Vice – Chancellor for Research and Development (UPD – OVCRD) and the Department of Science and Technology Grants – in – Aid (DOST – GIA) Program. This work was funded by the UP System Enhanced Creative Work and Research Grant (ECWRG 2015 – 1 – 014).

References

[1] A. Taabouche, A. Bouabellou, F. Kermiche, F. Hanini, S. Menakh, Y. Bouachiba, T. Kerdja, C. Benazzouz, M. Bouafia, S. Amar: Advances in Materials Physics and Chemistry, 3, (2013) 209.

[2] F.K Shan, B.C. Shin, S.W. Jang and Y.S. Yu: Journal of the European Ceramic Society 24, (2004) 1015.

[3] A.E. Djakovska, A. O. Dikovska, M. E. Koleva, G. B. Atanasova, T. R. Stoyanchov, N. N. Nedyalkov, and P. A. Atanasov: Journal of Physics: Conference Series 514, (2014) 012032.

[4] J. Lik Hang Chau, M-C. Yang, T. Nakamura, S. Sato, C-C Yang and C-W Cheng: Optics & Laser Technology 42, (2010) 1337.

[5] B.L Zhu, X.Z. Zhao, F.H. Su, G.H. Li, X.G. Wu, J. Wu and R. Wu: Vacuum 84, **(**2010) 1280.

[6] Mark Stuart Darby, Optics Research Centre, University of Southampton, January 2009.

[7] W. Tang and DC Cameron: Thin Solid Films, 280 (1), (1996) 221.

[8] M. Okoshi, K. Higashikawa and M. Hanabusa: Applied Surface Science 154, (2000) 424.

[9] J. Perriere, E. Millon, W. Seiler, C. Boulmer-Leborgne, V. Craciun, O. Albert, J.C. Loulergue and J. Etchepare: Applied Physics 91, (2002) 690.

[10] M. Gupta, V. Sauer and Y. Tsui: Applied Physics A, 110, (2013) 221.

[11] E. Biserni, A. Scarpellini, R. Brecia, D. Dellasega, A.L. Bassi and P. Bruno: J Nanopart Res 16, (2014) 2461.

[12] S. Christoulakis, M. Suchea, E. Koudoumas, M. Katharakis, N. Katsarakis and G. Kiriakidis: Applied Surface Science 252 , (2006) 5351.

[13] L.S Chuah, Z. Hassan and S.S Tneh: Journal of Optoelectronics and Advanced Materials, 11, (2009) 1637.

[14] S. Ren, Y.F. Bai, J. Chen, S.Z. Deng, N.S. Xu, Q.B. Wu and S. Yang: Materials Letters 61, (2007) 666.

[15] R.K. Gupta, N. Shirdhar and M. Katiyar: Materials Science in Semiconductor Processing 5, (2000) 11

[16] E.Millon,J.PerrièreR.Dfourneau,D.Défourneau,O.Albert, J. Etchepare: Appl. Phys. A **77**, (2003) 73.

[17] S.M. Eaton, H. Zhang and P.R. Herman: 13, (2008) 4708.

[18] B.L. Zhu, X.H. Sun, X.Z. Zhao, F.H. Su, G.H.Li, X.G.Wu, J. Wu, R. Wu and J. Liu: Vacuum 82, (2008) 495.

[19] J.-II Hong, J. Bae, Z.L. Wang and R.L. Synder: Nanotechnology 20, (2009) 085609.

[20] C. Wang, B.L. Cheng, S.Y. Wang, H.B. Lu, Y.L. Zhou, Z.H. Chen and G.Z. Yang: Thin solid films 485, (2005) 82.

[21] A.Og. Dikovska N.N. Nedyalkov and P.A. Atanasov: Materials Science and Engineering B 176, (2011) 1548.

[22] P. R. Willmott: Progress in Surface Science 76, 163 (2004).

[23] T. E. Itina, K. Gouriet, L. Zhigilei, S. Noël, J. Hermann and M. Sentis: Applied Surface Science, Article in Press (2007).

[24] S. Yun. Kim, J. Hyung. Lea, J. J. Kim, and Y.W. Heo: Journal of Nanoscience and Nanotechnology, 14 (2014) 9020.

(Received: May 26, 2015, Accepted: January 4, 2016)