Growth of Zinc Oxide Nanopores by Pulsed Laser Ablation

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Abstract – **ZnO thin films of porous structure with strong c-axis orientation were deposited on *n*-type silicon substrate by pulsed laser ablation of ZnO target in low O_2 pressure (around 0.03 mbar) and at 600^0C substrate temperature. We attribute the formation of nanopores and the crater-like formation to the high kinetic energy of the ablated particles. Photoluminescence spectra show the near band edge emission (UV emission) and the defect related emissions in the visible region (blue-green and yellow emission). Raman spectrum of the nanostructures reveals the highly intense E_1(LO) mode and this mode is associated with the defect states in ZnO.**

Keywords: Pulsed laser deposition, Nanopores, Photoluminescence, Raman spectroscopy.

I. INTRODUCTION

Zinc Oxide (ZnO), an II-VI semiconductor has attracted a great attention in research because of its wide band gap (~ 3.37 eV) and high excitonic binding energy (~ 60 meV) at room temperature. By controlling the morphology and size of the nanostructures they can be used in different applications such as sensors, photo diode, varistors, solar cells, optoelectronic devices etc. ZnO is covering a wide range of photoluminescence spectra because of its various defects and these defect level emission as well as band edge emission makes it suitable for photonic devices from UV range to visible range. Several techniques such as Metal-Organic chemical vapour deposition (MOCVD) [1], chemical vapour deposition (CVD) [2] pulsed laser deposition (PLD) [3] and so on has been used for thin film deposition. 1D nanostructures such as nanorods, nanowires, nanobelts are gaining preference over 2D structures such as nanosheets, nanoflakes [4], nanowalls [1, 5] because of their ability to enhance device performance. They also have potential for applications in energy storage devices, sensors [6] etc. Several deposition methods such as thermal CVD [7], MOCVD [1], self-catalyzed growth [8] have been used for the growth of the nanowall ZnO structures either in presence of catalyst on the surface [7, 9] or on bare substrate [1]. Pulsed laser deposition (PLD) has several advantages over the other deposition techniques. The deposition can be controlled by the simple parameters like laser fluence, pulse duration and repetition rate.

In this paper, we will discuss the growth of ZnO nanopores by PLD technique on silicon substrate without using any catalyst and its orientation, optical properties and the surface morphology.

II. EXPERIMENTAL SECTION

ZnO pellet was prepared by mixing ZnO powder with poly-venyl alcohol (PVA) as a binder. That mixture was pressed under 3 ton and then sintered at 1000^0C for 5 hours. ZnO nanostructure was achieved by ablating a sintered ZnO target by Nd:YAG laser in a vacuum chamber by PLD technique. The Q-switched Nd:YAG laser with 532 nm wavelength (pulse width - 10 ns, repetition rate – 10 Hz) was focused on ZnO target (that is rotated continuously to avoid the drilling at a particular portion on the target) to ablate it and allow the deposition on the clean *n*-type (100) silicon substrate. The substrate was placed 4 cm away from the target and the substrate temperature was fixed at 600^0C. The background (O_2) pressure was maintained at 0.03 mbar during the deposition. The deposition time was 45 minute and the laser fluence was maintained at around 12 J/cm^2.

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III. RESULTS AND DISCUSSIONS

A. *X Ray Diffraction (XRD)*

XRD spectra (Rigaku TTRAXIII with CuK□ radiation) of the nanostructures were taken by using Cu□□□radiation of 1.54 A^0 wavelength. The XRD spectrum of the grown nanostructure taken in the range of ($2\theta = 25^0$ to 65^0) is shown in Figure 1. It shows an intense and sharp peak at 34.4^0 corresponding to (002) plane of ZnO whereas the other peak corresponds to a different plane (103) of ZnO and is very weak. This suggests that the nanostructures are strongly *c*-axis oriented and is single crystalline in nature. The FWHM of the (002) plane are 0.322 A^0 and the calculated lattice parameters from this plane is a = 3.2 A^0 and c = 5.196 A^0. The lattice parameters are well matched with the wurzite hexagonal ZnO lattice parameters. The particle size calculated from the FWHM is 43 nm. XRD spectra of the films reveal the single crystallinity and it is supported by the literature [9]. The ZnO nanostructures reported in the recent literatures [10, 11, 12] reveals that nanowall network structures are highly crystalline and oriented along (002) direction which is in agreement with our work.

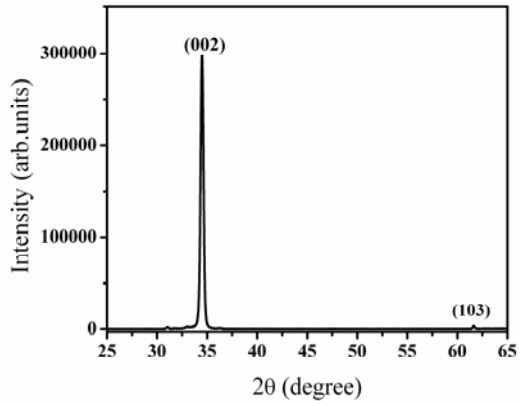

Figure 1: XRD spectrum of ZnO nanopores.

B. *Surface morphology*

Figure 2(a) shows the field-emission electron microscope (FE-SEM) (Sigma, Zeiss, Oberkochen, Germany) images of the grown nanostructures. Figure 2(b) represents the magnified image of Figure 2(a).

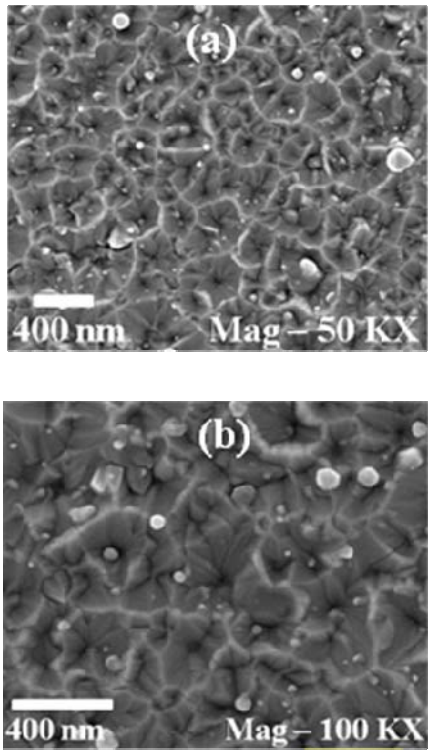

Figure 2(a-b): FE-SEM images of ZnO nanopores.

The FE-SEM images show the porous structures of the ZnO. The boundaries of the pores are connected and it forms like a nanowall structure. From these images, it is clearly observed that the distributions of the nanopores are nearly uniform over the substrate surface. The sizes of the nanopores are calculated from the FE-SEM images and it is nearly 38 nm and the pore size distribution is given in Figure 3.

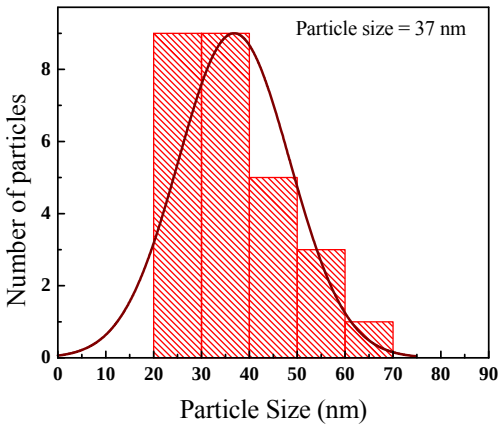

Figure 3: Particle size distribution in ZnO nanopores

The sizes of the nanoparticles are well matched with the size calculated from the XRD spectra. The growth mechanism of the nanowalls can be described in various approaches. In presence of some catalyst, the catalyst works as a nucleation site for the growth of ZnO nanowires and later the bottom of the nanowires are connected to form nanowalls depending on the growth velocity of the planes. In our case, the fluence used is high which may result in high kinetic energy of the incident particles leading to strong impact of the incident particles from the plasma plume to disrupt the initially deposited particles on the substrate giving rise to crater-like structures. Thereafter, the walls of the crater-like structure tends to grow along the *c*-axis. The whitish texture on the crater-like structure is an indication of this in Figure 2. The formation of pores within the crater-like structure thus could be due to the deposition of particles in a random fashion at the initial stage of growth which was later covered by the crater-walls.

C. *Photoluminiscence (PL)*

The PL spectra fitted by Gaussian fitting is shown in Figure 4.

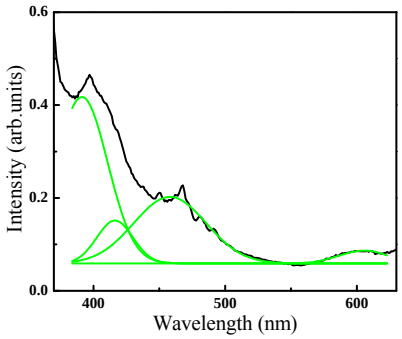

Figure 4: PL spectrum of ZnO nanopores.

PL spectra (ThermoSpectronic, AB2, monochromator xenon flash lamp) were taken by using a xenon flash lamp with 325 nm excitation wavelength. Figure 3 shows the near band edge emission at 395 nm [13], deep level emissions such as violet-blue emissions at 417 nm and 463 nm [14] and yellow emission at 605 nm. All these deep level emissions are attributed to the defects present in the ZnO nanostructures. The blue emission is due to the surface defects and oxygen vacancies [15] and the yellow emission can be attributed to the recombination of oxygen vacancies with oxygen interstitials or other defects.

D. *Micro-Raman spectroscopy:*

The Micro - Raman spectra (Lab Ram HR-800, Jobin Yvon) was recorded by using an Argon ion laser (operating wavelength 488 nm) and is shown in Figure 4. ZnO being a wurzite structure, it belongs to C_{6}^{4} space group and group theory predicts the existence of eight optical phonon modes. Among these modes, two B_1 modes are Raman inactive whereas the others [E_2(low) and E_2(high) modes], [A_1(LO) and A_1(TO) modes] and [E_1(LO) and E_1(TO) modes] are Raman and infrared active. The frequencies of the fundamental optical modes in ZnO are as follows E_2(low) = 101 cm^{-1}, E_2(high) = 437 cm^{-1}, A_1(TO) = 380 cm^{-1}, A_1(LO) = 574 cm^{-1}, E_1(TO) = 407 cm^{-1}, and E_1(LO) = 581 cm^{-1}. From Figure 4, it has been shown that E_2(low) at 99 cm^{-1}, E_2(high) at 437 cm^{-1} and E_1(LO) mode at 582 cm^{-1} are observed for the grown nanostructures. The Raman mode at 277 cm^{-1} can be attributed to the B_1(low) silent mode and at 303 cm^{-1} for silicon. E_2(low) and E_2(high) modes are associated with the vibration of heavy Zn sublattice and oxygen atoms respectively. E_2(high) mode characterize the wurzite structure of ZnO and is well matched with XRD. It is accepted that E_1(LO) mode at 582 cm^{-1} is associated with the defects such as oxygen vacancy, zinc interstitial defects etc.

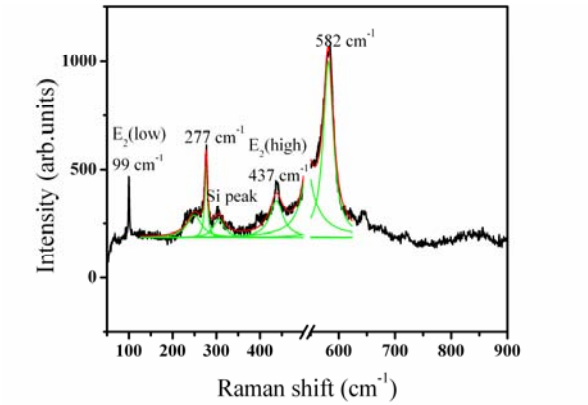

Figure 4: Raman spectrum of ZnO nanopores.

High intense E_1(LO) mode indicates that the nanostructure have many oxygen vacancies or zinc interstitial defect states. Also, PL spectrum shows the evidence of the defect related emissions which is an agreement with Raman spectrum.

CONCLUSIONS

ZnO nanopores were synthesized on silicon substrate by PLD technique without using any catalyst. XRD results reveal that the ZnO nanopores are highly crystalline in nature with strong *c*-axis orientation. The formation of nanopores and the crater-like structure is discussed in the light of strong laser fluence that may result in high kinetic energy of the incident particles leading to strong impact on the particles deposited on the substrate. The Raman spectrum and PL shows that the ZnO nanopores are not free from defects.

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REFERENCES

[1] C. C. Wu, D.S.Wuu, P.R.Lin, T.N.Chen and R.H.Horng: Nanoscale res let 4 (2009) 377-384

[2] S. W. Kim, S. Fujita, H-K. Park, B. Yang, H-K. Kim and D. H. Yoon, "Growth of ZnO nanostructures in a chemical vapour deposition process" J. Cryst. Growth. Vol. 292, pp. 306-310, 2006.

[3] A. B. Hartanto, X. Ning, Y. Nakata, T. Okada, Appl. Phys. A 78 (2004) 299-301.

[4] L.wu (41) Material Research Bulletin

[5] S.W.Kim and H.K.Park: Appl. Phys. Lett 90(2007) 033107

[6] M. Q. Israr, J. R. Sadaf, O. Nur, M. Willander, S. Salman and B. Danielsson, "Chemically fashioned ZnO nanowalls and their potential application for potentiometric cholesterol biosensor" Appl. Phys. Lett. Vol. 98, pp. 253705-1 -253705-3, (2011).

[7] S.D.Lee, H.K.Park and S.W.Kim, J.Korean.Phys.soc 51, 303-307 (2007).

[8] R.C.Wang, C.P.Liu and J.L.Haung Appl.phys.lett 87, 2005, 053103.

[9] X.Wang, Y. Ding, Z. Li, J. Song and Z.L.Wang: J.Phys.Chem.C 113 (2009) 1791-1794.

[10] J. Maeng, G. Jo, M. Choe, W. Park, M-K. Kwon, S-J. Park and T. Lee: Thin Solid Films 518 (2009) 865-869.

[11] L-M. Yu, X-H. Fan, J-H. Shui and L. Cao and W. Yen: Material Letters 68 (2012) 423-425.

[12] T-P. Chen, S-P. Chang, F-Y. Hung, S. J. Chang, Z-S. Hu and K-J. Chen: Sensors 13 (2013) 3941-3950.

[13] R.D.Yang, S. Tripathy, Y.Li andH. J. Sue: Chem.phys.lett 411(2005) 150-154.

[14] L. Wu, Y. Wu and Y. Lu :Materials Research Bulletin 41(2006) 128-133.

[15] Y.H.Yang, Y.Feng and G.W.Yang: Appl.phys.A 102 (2011) 319-323.

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