

Synthesis of Almond-Like ZnO Microcrystals by Chemical Bath Deposition Method at Room Temperature

S. S. Dange ¹, S. N. Dange ², P. S. More ³

Assistant Professor, Department of Physics, The Institute of Science, Fort, Mumbai, Maharashtra, India¹

Assistant Professor, Department of Physics, JaiHind College, Churchgate, Mumbai, Maharashtra, India²

Associate Professor, Department of Physics, The Institute of Science, Fort, Maharashtra, India³

ABSTRACT: Uniform surface morphology of almond-like ZnO microcrystals has been observed in thin film, deposited at room temperature on a glass slide by chemical bath deposition method. The almond-like crystals shows approximate length of 1.5 μm , diameter of 0.5 μm and tip of about 100 nm. This morphology was found in thin film deposited from 0.05M zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution at pH 8. The structural and optical properties of the film was examined and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy-dispersive spectroscopy X-ray diffraction (EDAX) and UV-Vis spectroscopy. XRD pattern shows that the crystals have hexagonal wurtzite structure with preferred (002) growth direction. The deposited film shows UV absorption at 381.3 nm .

KEYWORDS: Zinc oxide, Chemical bath deposition, Annealing, Micro crystals, Morphology.

I. INTRODUCTION

Zinc oxide (ZnO) is a semiconducting material with direct wide bandgap of 3.37 eV and large exciton binding energy of 60meV at room temperature [1]. ZnO shows properties like high electron mobility $\sim 2000 \text{ cm}^2 / \text{V.s}$ at 80 K and high thermal conductivity which makes it a suitable candidate for a wide range of applications such as light emitting diodes [2], solar cells [3], photocatalysis [4] and gas sensors[5]. Nano and microcrystalline ZnO have attracted a great deal of attention because of their size dependent properties and wide range of applications. Various methods have been used to synthesis ZnO nanostructures such as nanowires[6], nanorings[7], nanorods[8], nanobelts[9], nanosheets[10],and nano propeller [11], dumbell like ZnO [12]. Some of these are chemical vapor deposition[13], sol-gel [14], molecular beam epitaxy (MBE) [15], spin coating [16], ion implantation [17], pulsed laser deposition (PLD) [18] and solution phase methods. Chemical bath deposition (CBD) [19] is one of the solution phase method useful for the preparation of ZnO thin film from aqueous solutions. The film thickness, deposition rate and quality of crystallites can be controlled by varying the solution pH, temperature and bath concentration [20]. It is a low cost method and does not require high temperature or pressure. It is also convenient for large area deposition.

In our experiment we have used conventional chemical bath deposition method to synthesis ZnO thin film from 0.05M zinc nitrate and ammonia solution. We have reported a highly uniform almond – like surface morphology of ZnO microcrystals deposited on glass slide without any additives at room temperature.

II. MATERIALS AND METHODS

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonia solution of analytical grade (from SDFCL) were used as received without any further purification. A magnetic stirrer was used to stir the bath solution and glass slide was used as substrate. The glass substrates were cleaned with acetone and then washed with distilled water. The pH of the bath solution was varied by adding ammonia solution dropwise to the continuously stirred 0.05 M zinc nitrate solution. The pH in this

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

process was varied from 7 to 8.5. The glass substrate was kept immersed in the bath solution by a suitable arrangement and the solution was continuously stirred for two hours at room temperature. This solution was then kept idle for 18 hours with the substrate immersed in it. The as deposited substrate was removed from bath solution and washed with distilled water. The quality of the deposited thin film was observed to vary with the change in pH of the bath solution. A milky white and uniform film was obtained at pH 8 which was further annealed at 250°C for two hours. The optical properties of this film was examined and characterized by UV-Vis spectrophotometer (SHIMADZU UV-1800). X-ray diffraction patterns were recorded using an X-ray diffractometer with CuK α radiation ($\lambda = 0.1540$ nm) and the analyses of the surface morphology was performed with a field emission scanning electron microscope (ZIESS Ultra55 FESEM) equipped with EDAX.

III. RESULTS AND DISCUSSION

1. Physical quality of as deposited film

The effect of change in pH of the bath solution at room temperature on as deposited film was studied and is reported in Table 1. The physical quality of the film was seen to vary as the pH value was changed from 7 to 8.5.

pH of 0.05 M zinc nitrate solution	Quality of film
7.0	No film was deposited on the glass substrate . Inhomogeneous bath solution and thick precipitate was formed.
7.5	Milky white and non-uniform thin film was observed.
7.8	Milky white and non-uniform thin film was observed.
8.0	Milky white and uniform thin film was observed. Milky homogeneous bath solution was observed.
8.2	Non-uniform thin film was observed.
8.5	Semi transparent and non-uniform thin film was observed.

Table 1: pH of bath solution and quality of deposited thin film

At pH 7, the bath solution was inhomogeneous and no film was deposited on the glass substrate. At pH 8.5 of the bath solution, a semi transparent film was deposited on the substrate. At pH 7.5, 7.8 and 8.2 of the bath solution, a non-uniform and whitish film was deposited on the substrate. At pH 8.0 of the bath solution, the as deposited film was found to be milky white, opaque and uniform. The physical appearance of this film remained unchanged after annealing and it was further characterized by XRD, SEM, EDAX and UV-Vis measurements.

2. X-Ray Diffraction (XRD)

The XRD pattern of the uniform thin film, given in Fig. 1, shows clear signature of characteristic ZnO without impurities. It is evident from the XRD pattern that the crystals have hexagonal wurtzite structure. The lattice parameters were calculated from :

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

The values of lattice parameters were found to be $a = 3.229$ Å and $c = 5.176$ Å with orientation of the grains along (100), (002), (101), (102), (110) and (103) planes. This is in good agreement with the standard JCPDS data.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

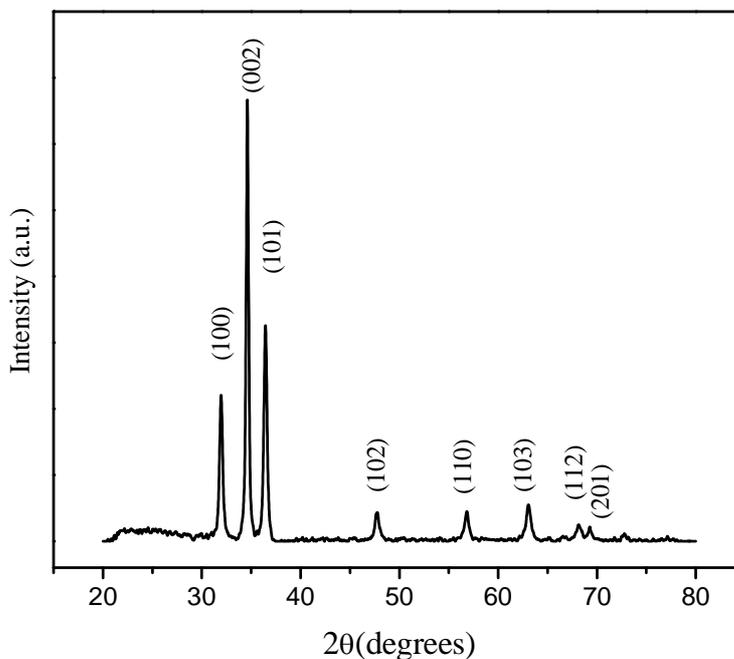


Fig.1 : XRD pattern of ZnO thin film

The comparatively sharp and intense pattern of the peak reflected from the (002) plane shows that the grains have preferred growth orientation along c-axis perpendicular to the substrate. This is also seen from the SEM images given in Fig. 2. A comparison of standard JCPDS data and the deposited thin film is shown in Table 2.

(hkl)	Calculated d_{hkl} (Å)	JCPDS d_{hkl} (Å)
100	2.797	2.814
002	2.588	2.603
101	2.460	2.476
102	1.899	1.911
110	1.614	1.625
103	1.468	1.477
112	1.370	1.378
201	1.350	1.360

Table 2: Comparison of calculated d values of ZnO thin film with JCPDS data

3 SEM & EDAX

Figure 2(a) & 2(b) shows surface morphology of ZnO thin film at two different magnifications. Figure 2(a) shows that the microcrystals are uniformly distributed and their preferred direction of growth is perpendicular to the glass substrate.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

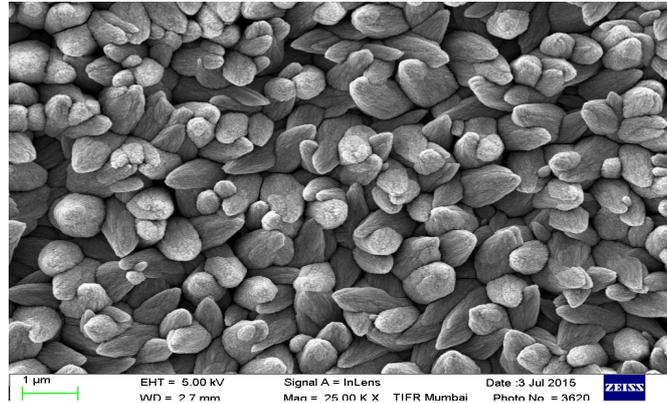


Fig 2(a) : SEM image of ZnO thin film showing uniform surface morphology



Fig. 2(b) : SEM images of ZnO thin film showing almond-like microcrystals

Figure 2(b) shows that the microcrystals have distinct surface morphology which looks similar to the almond structure. These microcrystals are nearly equal in size with approximate length of 1.5 μm, diameter of 0.5 μm and tip 100nm. The surface of each microcrystal shows irregularly developed nanocrystals of size about 50nm.

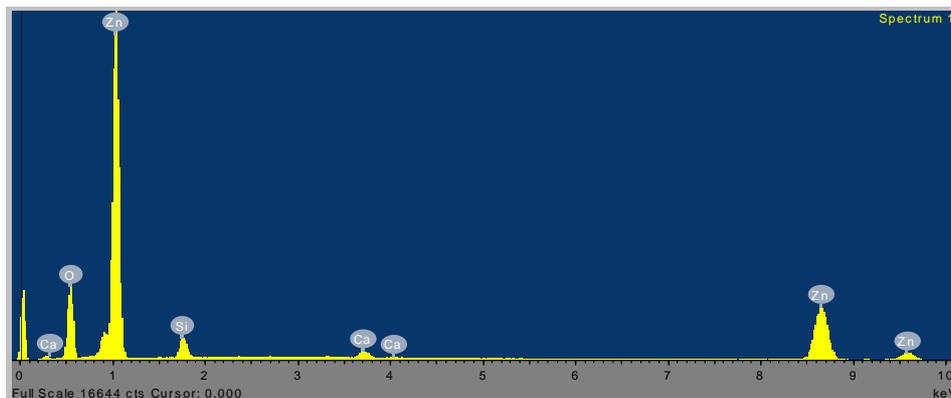


Fig.3: EDAX (All results in atomic%)

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

EDAX spectrum shows there are no impurities in the deposited film. The presence of silicon and calcium is due to glass substrate and alumina crucible used for annealing. The weight percent of Zn and O elements obtained from EDAX is nearly stoichiometric.

4. UV-Vis Absorption Spectrum

Absorption spectroscopy is a powerful technique for exploring the optical properties of the semiconducting materials. Fig. 4. shows the absorption spectrum of ZnO thin film in the wavelength range 250nm to 1100nm. The absorption peak is observed at 381.3 nm and corresponding energy band gap is found to be 3.25 eV.

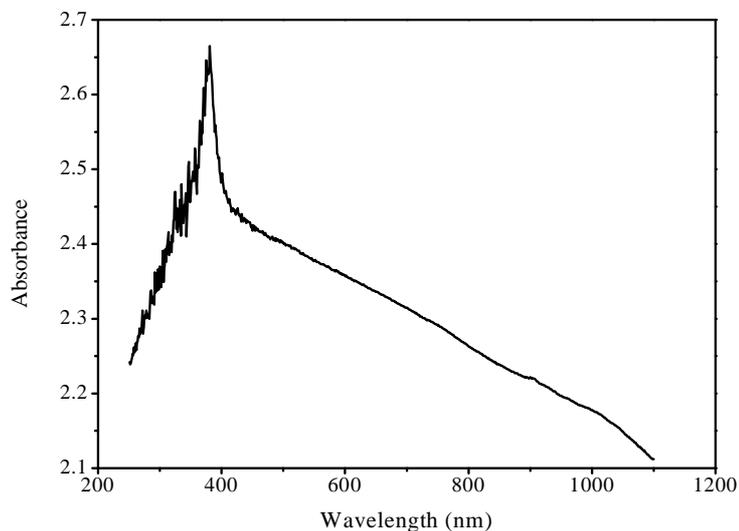


Fig. 3 : UV-vis absorption spectrum of ZnO thin film.

IV. CONCLUSION

ZnO thin films were deposited by chemical bath deposition method from 0.05M zinc nitrate solution at room temperature. The effect of pH on deposition of thin film on glass substrate was observed and studied. Uniform almond-like microcrystals were observed at pH 8 for 0.05 M zinc nitrate solution. The crystals show hexagonal wurtzite structure with lattice constants $a = 3.229 \text{ \AA}$ and $c = 5.176 \text{ \AA}$. Their preferred direction of growth is along c-axis perpendicular to the substrate. The surface of these microcrystals show irregular growth of nanocrystals of size about 50nm. The ZnO microcrystals has UV absorption at 381.3 nm and band gap energy 3.25eV which might be interesting for further applications to microscale optoelectronic devices.

ACKNOWLEDGEMENT

The authors Mrs. S.S.Dange and Dr. P.S. More are thankful to their host institution for support and providing facilities. The authors are thankful to Mrs B. Chalke, Nanomaterials Research laboratory, T.I.F.R., Mumbai for SEM and EDAX measurements.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

REFERENCES

- [1] Ozgur, U.; Alivov, Y. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Dogan, S.; Avrutin, V.; Cho, S. J.; Morkoc, H. A “comprehensive review of ZnO materials and devices.” J. Appl. Phys. 2005, 98, 041301.
- [2] K. Keem, D. Y. Jeong, S. Kim et al., “Fabrication and device characterization of omega-shaped-gate ZnO nanowire field-effect transistors,” Nano Letters, vol. 6, no. 7, pp. 1454–1458, 2006.
- [3] Law M, Greene LE, Johnson JC, Saykally R, Yang P “Nanowire dye-sensitized solar cells.” Nat Mater 2005, 4(6):455-45
- [4] T. J. Kuo, C. N. Lin, C. L. Kuo, and M. H. Huang, “Growth of ultralong ZnO nanowires on silicon substrates by vapor transport and their use as recyclable photocatalysts,” Chemistry of Materials, vol. 19, no. 21, pp. 5143-5147, 2007.
- [5] X. Wang, J. Zhou, J. Song, J. Liu, N. Xu, and Z. L. Wang, “Piezoelectric field effect transistor and nanoforce sensor based on a single ZnO
- [6] Y. C. Kong, D. P. Yu, B. Zhang, W. Fang, and S. Q. Feng, “Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach,” Applied Physics Letters, vol. 78, no. 4, pp. 407–409, 2001.
- [7] X. Y. Kong, Y. Ding, R. Yang, and Z. L. Wang, “Single-crystal nanorings formed by epitaxial self-coiling of polar nanobelts,” Science, vol. 303, no. 5662, pp. 1348–1351, 2004.
- [8] F. P. Albores, F. P. Delgado, W. A. Flores, P. A. Madrid, E. R. Valdovinos, and M. M. Yoshida, “Microstructural study of ZnO nano structures by rietveld analysis,” Journal of Nanomaterials, vol. 2011, Article ID 643126, 11 pages, 2011.
- [9] C. Ronning, P. X. Gao, Y. Ding, Z. L. Wang, and D. Schwen, “Manganese-doped ZnO nanobelts for spintronics,” Applied Physics Letters, vol. 84, no. 5, pp. 783–785, 2004.
- [10] R. C. Wang, C. P. Liu, J. L. Huang, and S. J. Chen, “ZnO symmetric nanosheets integrated with nanowalls,” Applied Physics Letters, vol. 87, no. 5, Article ID 053103, 2005
- [11] S. L. Wang, H. W. Zhu, W. H. Tang, and P. G. Li. “Propeller-Shaped ZnO Nanostructures Obtained by Chemical Vapor Deposition: Photoluminescence and Photocatalytic Properties.” Hindawi Publishing Corporation Journal of Nanomaterials Volume 2012, Article ID 594290.
- [12] Hou Z, Wang Y, Shen L, Guo H, Wang G, Li Y, Zhou S, Zhang Q, Jiang Q “Synthesis of dumbbell-like ZnO microcrystals via a simple solution route.” Nanoscale Res Lett. 2012 Sep 11;7(1):507. doi: 10.1186/1556-276X-7-507.
- [13] An-Jen Cheng, Yonhua Tzeng¹, Yi Zhou, Minseo Park, Tsung-hsueh Wu, Curtis Shannon, Dake Wang and Wonwoo Lee “Thermal chemical vapor deposition growth of zinc oxide nanostructures for dye-sensitized solar cell fabrication” Applied physics letter. 92, 092113 (2008).
- [14] J. Lee a , A. J. Eastal b, U. Pal c , D. Bhattacharyya. “ Evolution of ZnO nanostructures in sol–gel synthesis” J. Lee a , A. J. Eastal b, U. Pal c , D. Bhattacharyya. Current Applied Physics 9 (2009) 792–796
- [15] E Janik, A. Wachnicka, E. Guziewicz, M. Godlewski, S. Kret, W. Zaleszczyk, E. Dynowska, A. Presz, G. Karczewski and T. Wojtowicz. “ZnTe-ZnO core-shell radial heterostructures grown by the combination of molecular beam epitaxy and atomic layer deposition.”
- [16] Vrushali Shelake, M. P. Bhole, D. S. Patil. “Effect of open air annealing on spin coated aluminum doped ZnO nanostructures” Materials Chemistry and Physics. Volume 141, 15 August 2013, Pages 81–88
- [17] Oliveira, R. M. and Vieira, M. S. and Ueda, M. and Tóth, András (2013). “Growth of ZnO nanostructures on Si by means of plasma immersion ion implantation and deposition.” Vacuum, 89, pp. 163-167. ISSN 0042-207X
- [18] D. Valerini, A. P. Caricato, M. Lomascolo, F. Romano, A. Taurino, T. Tunno, M. Martino, “Zinc oxide nanostructures grown by pulsed laser deposition.” Appl. Phys. A. (2008) 93: 729-733, DOI 10.1007/s 00339-008-4703-z
- [19] L. F. Koao, F. B. Degene, H. C. Swart. Materials Science in Semiconductor Processing, Volume 27, November 2014, Pages 33–40.
- [20] Sankpal B. R., Saratale S. D., Lokhande C. D., Ennaoui A, Sol. Energy Mater. Solar Cells, 83 (2004), 447.