EFFECTS OF 6 MeV ELECTRON IRRADIATION ON ZnO NANOPARTICLES SYNTHESIZED BY MICROWAVE METHOD

K.B.Sapnar, V.N Bhoraskar and S.D.Dhole*, Microtron Accelerator laboratory, Department of Physics, University of Pune, Pune, India
L.A. Ghule, K.M. Garadkar,. Nanomaterials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur, India

Abstract

The sizes of zinc-oxide (ZnO) nanoparticles were synthesized by microwave method and were tailored by electron irradiation method. The ZnO nanoparticles having size of ~46 nm synthesised by microwave method were exposed to different fluences of 6 MeV electrons over the range from $1x10^{15}$ to $2.5x10^{15}$ e^{-} /cm^2. The electron irradiated ZnO nanoparticles were characterized by XRD, SEM, UV techniques. The XRD results show that the particle size reduced continuously from 46 nm to 15 nm with the increase in electron fluence and SEM images also confirms the formation of nanoparticles of minimum size of around 14 nm. The band gap of the ZnO nanoparticle also increased from 3.29 to 3.42 eV as the size reduced. The result shows the ZnO particles are broken in to smaller size under electron irradiation and increase in the band gap indicates the formation of defects in ZnO. The electron irradiation method is found to be an efficient method in tailoring the size of ZnO nano particles. The nanosized ZnO particles can suit for the applications such as photovoltaics, photocells and antimicrobial activity.

INTRODUCTION

Zinc oxide (ZnO), a group II–VI compound semiconductor with a wide and direct band gap of 3.37 eV and a large exciton binding energy of 60 meV [1], has been widely used in many applications such as transparent conductive films, resistors, solar cell windows, bulk acoustic wave devices, lasers and diodes [2]. One of the materials that has attracted great interest from a wide range of technological fields associated with nanotechnology is zinc oxide In general metal oxides show enhanced photocatalytic activity with the increase in electronic defects in the crystallites by introducing defects into the crystal lattice of ZnO nanoparticles. Two principal factors cause the properties of nanomaterials to differ significantly from other materials. The increased surface to volume ratio and dominance of quantum effects. These factors can change or enhance chemical reactivity, electronic, optical, thermal, mechanical, magnetic, and electrical/transport characteristics including properties such as ionization potential, electron affinity, capillary forces, melting point, specific heat etc

In order to realize the universal application of nanomaterials, the key is to devise simple and efficient methods for preparing nanomaterials on a large scale at low cost [3]. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution-based synthesis methods, such as chemical precipitation [4], sol–gel, [5] and solvothermal/ hydrothermal reaction Number of other methods such as photochemical, electrochemical and chemical reduction [6], microwave processing [7], gamma irradiation [8], ion irradiation [9] and plasma processing, radiolysis, ultra sound processing also helps in synthesizing nanoparticles.

However, so far no work is reported on the synthesis of ZnO nanoparticles by microwave method and tailors the size of nanoparticles by electron irradiation. Therefore, in the present work 6 MeV electron irradiation process has been used to reduce the size of ZnO nanoparticles synthesized by microwave method.

EXPERIMENTAL

Reagents

Zinc nitrate, Sodium hydroxide and PVA (PVA2000) were used for the synthesis. All solutions were prepared in mili Q water only.

Preparation of Nanoparticles

The nanosized ZnO particles were prepared by microwave-assisted method. Aqueous solution of zinc nitrate (0.01M) and PVA (1 % w/v) was added. The solution thus prepared was set to stir constantly with addition of solution (0.01M) of sodium hydroxide simultaneously for half an hour. After completion of the reaction, white precipitate of zinc hydroxide was produced. The precipitated zinc hydroxide solution was kept for 10 minutes under microwave irradiation with a power output of ~700 W by following on-off cycle. The solution was allowed to cool up to room temperature and then centrifuged in presence of water and acetone to remove all the impurities and allowed to air dry naturally. The powder of ZnO was characterized and used for the irradiation.

Irradiation of Nanoparticles

An electron beam of 6 MeV energy is obtained from the Race track Microtron, Department of Physics University of Pune was used for irradiation of ZnO particles. For irradiation experiment, about 50mg of ZnO particles was placed in a polythene bag, makes sample size ~1cmx1cm.Such fine samples were made and numbered 1to 3. Initially, the number 1 sample was mounted on the Faraday cup, positions at a distance of

*Corresponding author
E-mail: sanjay@physics.unipune.ernet.in

100mm from the beam extraction port of the Microtron. The electron beam position entre Faraday cup was coincide with the sample position. The electron area was large enough to cover the entire sample area. The number of electron falling on the entire sample was extracted by a current integrator connected to the Faraday cup. The electron fluence was increased from sample to sample in the steps of 1.0 x 10^{15} e^- /cm^2, 1.5 x 10^{15} e^-/cm^2 and 2.5x10^{15} e^- /cm^2. To begin, one ZnO sample was fixed on the Faraday cup mounted inside the chamber of the electron irradiation system. After closing the flanges and making electrical connections, the chamber was evacuated to a pressure of ~10^{-6} mbar. The electron beam was incident on the sample by keeping the beam diameter ~15 mm and energy 6 MeV and the sample was irradiated. During the irradiation, the beam current was kept constant at 100 nA and the electron beam was turned off as soon as the coating sample received an electron fluence ~1.5 X 10^{15} e^-/cm^2. The chamber pressure was brought to atmospheric conditions and the electron-irradiated coating was removed from the chamber. Another ZnO sample was then mounted on the Faraday cup and the system was evacuated and the sample irradiated with the fluence of 2.5 X 10^{15} e^- /cm^2.

RESULTS AND DISCUSSION

X-Ray Diffraction

ZnO nanoparticle samples irradiated with 6 MeV energy electrons for the fluence from 1.0 x 10^{15} to 2.5 x 10^{15} e^-/cm^2 were characterized by the X-ray diffraction (XRD) technique. The XRD pattern is shown in Fig. 1. The XRD pattern of the final ZnO nanoparticles was obtained with Cu K_α radiation (λ = 1.5418 Å) on a Bruker axs D8 Advanced diffractometer (CuK_α radiation) at a continuous scan rate of 1-2^0 /min with 0.1^0 resolution. Diffraction peaks were observed at the scattering angles 2 θ 31.52, 34.59, 36.03, 47.94, 56.75, 62.93, 66.407, 67.64, 69.07, and 77.91 θ to the reflections from the planes [1 00], [0 0 2], [1 0 1], [1 0 2], [1 1 0], [1 0 3], [2 0 0], [1 1 2], [2 0 1], and [0 0 4]. The lattice parameters were found to be a = 3.25 Å and c = 5.23 Å, which shows the hexagonal wurtzite structure.

The mean grain size (D) of the particles was determined from the line-broadening in XRD pattern using Scherrer equation

$$D = 0.89\lambda / (\beta \cos \theta)$$

where, λ is the wavelength (Cu Kα), β is the full width at the half-maximum and θ is the diffraction angle. The peak positions and relative intensities were characterized by comparison with Standard data (JCPDS card no 36-1451) for examining the phase structure and purity.

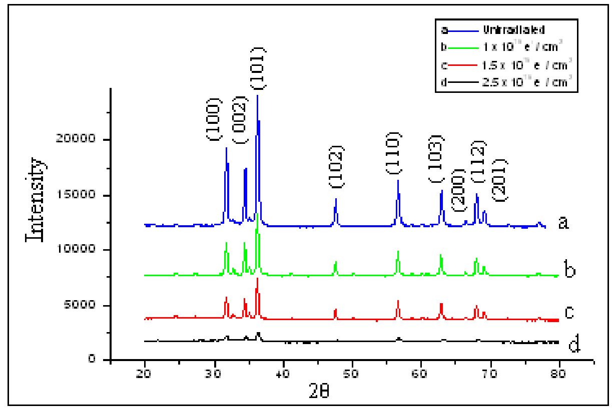

Figure 1: XRD spectra of ZnO nanoparticles irradiated at different 6 MeV electron fluencies.

UV-Visible Spectroscopy

The absorption edge seen to shift towards shorter wavelength for the different fluences of 6 MeV electron irradiation. The peak position is also seen to shift from 370 nm to 362 nm for the virgin to irradiated ZnO at the highest fluence of electron i.e. 2.5 x 10^{15} e^-/cm^2, which is shown in Fig. 2. The absorbance edge, maxima and corresponding band gap are presented in Table 1.The absorption edge around 405 nm, followed by a minimum 380 nm, for typical nanoparticles of ZnO. Consequently, the band gap increases gradually with increasing electron fluence. This could be mainly attributed to quantum size effect as an effect of the strong interaction between the surface oxides of zinc and high energy electrons. This observation strongly suggest that the irradiation significantly affects the particle size and hence the absorption properties. Moreover, the reduction in the intensity of the absorption peak suggests that the irradiation produces sufficient defects.

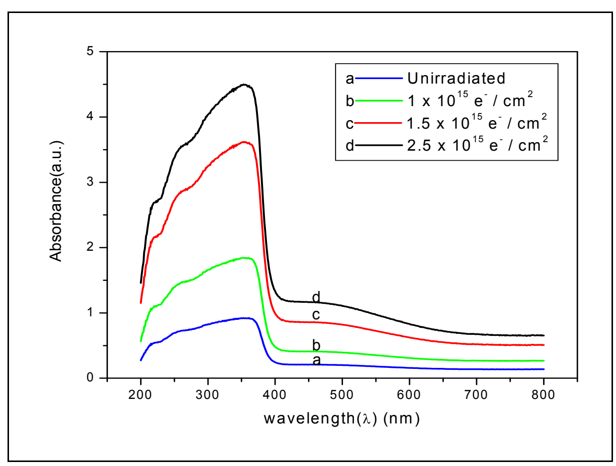

Figure 2: UV-Visible absorbtion spectra for ZnO nanoparticles irradiated at different 6 MeV electron fluences.

Table 1: Peak position, band gap and crystalline size of ZnO nanoparticles at different 6 MeV electron fluencies.

Sample no.	Electron Fluence (e^-/cm^2)	Peak position (λ_{max})(nm)	Bandgap (eV)	Average crystalline size (nm)
1	0.0	375	3.29	46
2	1.0×10^{15}	372	3.33	39
3	1.5×10^{15}	370	3.35	27
4	2.5×10^{15}	362	3.42	15

SEM Analysis:

The SEM micrographs of ZnO nanoparticle samples irradiated with 6 MeV electrons at different fluences from 1.5×10^{15} to 2.5×10^{15} e^-/cm^2 are shown in Fig. 3. From the SEM micrographs, it is observed that there is change in morphology of ZnO nanoparticles with the electron fluence due to defect generation. The average size of the ZnO particles reduced from 46 nm to 14 nm with increase in electron fluences. These results are in good agreement with the results of XRD. SEM micrographs clearly indicating the formation of controlled size and regular shape of the nanoparticles. Therefore, it is possible to control size and shape using the electron irradiation. It clearly indicates that the nanoparticles with aligned orientation and the high degree of crystallinity in the sample.

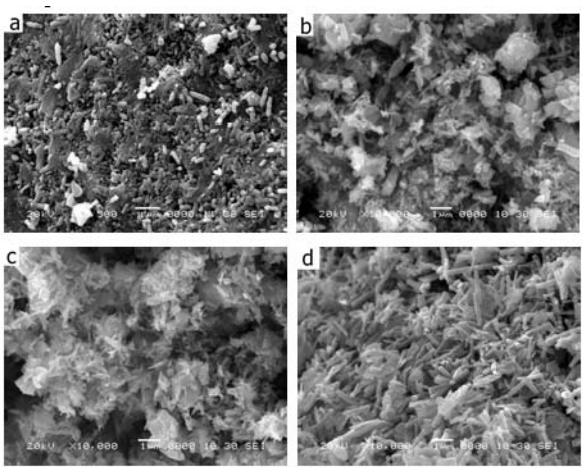

Figure 3: SEM micrographs for ZnO nanoparticles irradiated at different electron fluences (a) virgin (b) 1×10^{15} e^-/cm^2 (c) 1.5×10^{15} e^-/cm^2 and (d) 2.5×10^{15} e^-/cm^2

CONCLUSION:

The microwave technique is simple, rapid, convenient and significant for the synthesis of zinc oxide nanoparticles. XRD results showed that ZnO nanoparticles were composed of hexagonal wurtzite structure with very good crystallinity. Size is varying from 46 nm to 15 nm at different electron fluences from 1×10^{15} e^-/cm^2 to 2.5×10^{15} e^-/cm^2. SEM images confirm the reduction in size of the ZnO nanoparticles from 46 nm to 14 nm. Moreover, UV-visible spectra show the increase in band gap from 3.29 to 3.42 eV of ZnO nanoparticles and blue shift also clearly indicate the decrease in size of ZnO nanoparticles.

REFERENCES

[1] M.Hass, H. Weller and A. Henglein, *J. Phys.Chem.* 92 (1988) 482.

[2] T. L. Yang, D. H. Zhang, J. Ma, H. L. Ma and Y Chen, Thin *Solid Films* 326 (1998) 60.

[3] K. Soulantica, A. Maisonnat, M. C. Fromen, M. J. Casanove, P .Lecante and B. Chaudret, *Angew. Chem. Int. Edn* 40 (2001) 448.

[4] Q.P. Zhong and E.Matijevic, *J. Mater. Chem.* 6 (1996) 443.

[5] A. Chittofrati and E. Matijevic, *Colloids Surf.* 48.

[6] F. Mafune, J. Y. Kohno, Y. Takeda and T. Kondow *J. Phys.Chem.* B 104 (2000) 8333.

[7] M. Treguer, C. de. Cointet, H. Remita, J. Khatouri, M.Mostafavi, J. Amblard, J. Belloni and R. de. Keyzer *J, Phys. Chem.* B 102 (1998) 4310.

[8] A. Henglein and D Meisel, *Langmuir* 14 (1998) 7392.

[9] M. Temgire and S. Joshi, *Radiat. Phys. Chem.* 71 (2004) 1039.