

Variation of Microstrain and Band gap of ZnO nanoparticle Thin Film Prepared by wet Chemical Method.

Anup Kr Kalita¹, Dr.Sanjib Karmakar^{2*}

Research Scholar, Department of Instrumentation & USIC, Gauhati University, Guwahati, India¹

Senior Scientific Officer, Department of Instrumentation & USIC, Gauhati University, Guwahati, India^{2*}

ABSTRACT: The syntheses, structural characteristics and optical properties of ZnO nanoparticle with different size prepared at room temperature (RT) and annealed at 473K and 523K are presented. Utilising Wet Chemical techniques we are able to obtain almost spherical nanoparticles. The structural characterization of synthesized nanoparticles is performed by X-ray diffraction (XRD), UV-vis absorption spectrometry and Transmission Electron Microscopy (TEM). The average particle size of the nanoparticles are calculated by Scherrer's formula and classical Williamson and Hall (WH) method. The WH method also give the microstrain present in the nanoparticles. The microstrain are of the order of 0.0019 and 0.0011 at 473 K and 523 K respectively. The band gap are of 4.33 eV, 4.21eV and 3.69 eV respectively which are greater than that of bulk. This increment suggests that the band gap of prepared nanoparticles are shifted towards the blue region and are dependent on particle size of the nanoparticles.

KEYWORDS: Nanoparticle, XRD, TEM, Microstrain, Band Gap, Scherrer's formula, Wet Chemical method.

I.INTRODUCTION

Studies of ultra fine particles in the size range from a few to several nano meters [1] are increasing worldwide. The nano meter sized particles exhibit structure and properties which are quite different from those of the corresponding bulk materials [2]. Reduction of sizes drastically changes the electronic [2], optical and structural properties of a material. Some emergence phenomenon like quantum size confinement, wave like transport and predominance of interfacial phenomenon has come into play. These nano materials due to their peculiar characteristics and size effectsoften show novel physical properties compared to those of the bulk counterpart. Once the ability of controlling the feature like size and shape is achieved it is possible to enhance the material properties and device function beyond the already established ones. Atomic clusters have the ability to change the properties at large.

II.BACKGROUND

A majority works have been therefore carrying out worldwide in the syntheses of nanostructures for future fabrication of nano devices. ZnO is technologically an important material due to its range of optical and electrical properties; also it is a semiconductor crystal with a large binding energy(60 meV) and wide band gap 3.3eV at room temperature [3]. The ZnO nanoparticles are used in variety of applications such as UV light emitters [4], Solar cell [5], Light emitting diodes, gas sensors [6] and as an additive in many other industrial products. There are different methods for the fabrication of ZnO nanoparticles. Among those the wet chemical method [7],[8],[9] and [10] is the most effective for large scale production. This work reports the syntheses of ZnO nanoparticles with variation of band gap with microstrain and blue shift of the optical band gap.

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III. MATERIALS AND METHODS OF PREPARATION

All materials are purchased from the commercial market with highest purity(99.99%). Zinc Acetate Dihydrate($\text{CH}_3\text{COO}_2\text{Zn}2\text{H}_2\text{O}$) and Sodium Hydroxide(NaOH) as the starting materials, Polyvinyl Alcohol (PVA) as capping agent and double distilled water as dispersing solvent are used to prepare the ZnO thin film. In our previous work [3] we have prepared ZincOxide nanoparticle in powder form using Zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The average particle size obtained by XRD was $\approx 8.5\text{nm}$ using Scherrer formula and the estimated band gap was 3.63eV. In this work we have used Zinc Acetate Dihydrate($\text{CH}_3\text{COO}_2\text{Zn}2\text{H}_2\text{O}$) for synthesissation of Zinc Oxide nanoparticles in thin film. The size of the prepared nanoparticles obtained by XRD are found to be in the range of 21.7nm to 23.8nm using Scherrer formula. Hence Zinc Acetate dihydrate is used to form ZnO nanoparticle in thin film. Therefore 0.1 mole solution of Zinc Acetate Dihydrate($\text{CH}_3\text{COO}_2\text{Zn}2\text{H}_2\text{O}$) is stirred constantly for 1hour at 343K (solution1). 2gm PVA is stirred constantly at 343K (solution2). Now NaOH is slowly added drop by drop into the solution 1 and stirred at room temperature for half an hour and a white solution is obtained (solution3). The final mixture (solution 2 and solution 3) is constantly stirred for 1hr at 343K. Glass substrates are washed with some acid and then with distilled water and allowed to dry. Now the substrate is dipped into the final solution and allowed to dry at room temperature. The experiment is carried out for as deposited and annealed films. The annealing treatment for one hour is applied in order to improve the film crystallinity as well as to clean the surface from probable absorbed impurities [11].

IV. CHARACTERISATION METHODS:

XRD is widely used to determine the particle size of nanoparticle. In order to identify the phase and to know the structure of ZnO nanoparticles X-ray Diffractometer (X' Pert Pro) is employed with generator setting of 30mA and 40kV with $\text{CuK}\alpha 1 (\lambda = 1.54056 \text{ \AA})$ radiation. The XRD is calibrated with a standard silicon sample. The broadening of peaks are also corrected with Warren rule [12] that arises due to instrumental effect. Continuous scanning is applied in the range from $25-90^\circ (2\theta)$ at a scanning rate of 1sec/ step and step size is $0.02^\circ 2\theta$. The HRTEM (TEM, Jeol JEM 2100 200kV) images of the ZnO nanoparticle at annealed temperature are taken. The size and morphology of the ZnO nanoparticle were investigated by these images.

The optical absorption spectra of ZnO are recorded by a UV-Vis spectrometer (HITACHI model U-3210).

V.RESULTS AND DISCUSSION:

V.A XRD STUDY

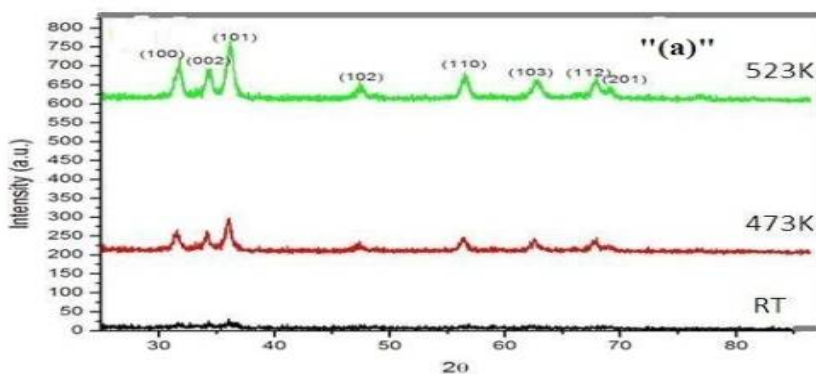


Fig.a

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Fig.a shows the diffraction patterns of the thin films at temperature (RT) and different annealed temperatures of 473 K and 523 K. The diffraction peaks of nanoparticles corresponds to (100), (002), (101), (102), (110), (103), (112), (201) planes are almost matched with standard ZnO powder (ICDD No. 80-0074). The standard ZnO powder is crystallized in a hexagonal system with $a=3.2535$ (3), $c=5.2151$ (5) and space group is P63mc (186). We have found the lattice parameters 'a' 3.206(3), 3.432(3) and 'c' 5.243(2), 5.2751(2) for nanoparticles prepared at 473 K and 523 K respectively. This small changes observed in the length of the lattice axes of the prepared nanoparticles is due to shifts of the diffraction peaks. No diffraction peaks from other species could be observed which indicates that all the precursor have been completely decomposed and no other crystal products have been retained after the decomposition process. The sharp peaks indicate that the products are well crystallized. X-ray peak intensities are weak and broad compared to bulk sample of ZnO, suggesting the small crystalline size. The distance between lattice planes (d values) are calculated using Bragg's equation given by $\lambda= 2d\sin\theta$. It is observed that both peak shift and broadening are present in the peaks of the prepared nanoparticles. The observed shifts in the peaks of the nanoparticles are because of the development of defects in the nanoparticles at higher calcinations temperature. At higher calcinations temperature peaks become more and more intense with reduced broadening, which indicate the increase in grain size with increasing temperature [13]. During slow heating and subsequent cooling the crystal grows and results in the increase in particle size [14].

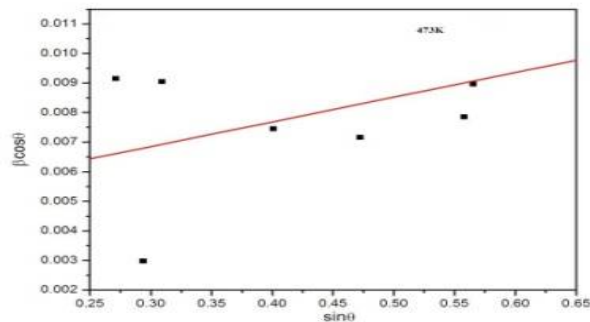


Fig.b

Fig.b shows the W-H plot at 473K. It shows the microstrain developed at 473K.

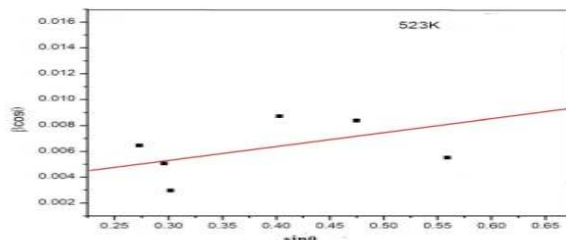


Fig.c

Fig.c shows the W-H plot at 523K. It gives the microstrain developed at 523K. During deformation, the d- spacing for a given (hkl) plane will change (i.e. peak shift) and the associated lattice strain can be calculated. Diffraction peak broaden either because of inhomogenous microstrain induced by dislocation- like defects (strain broadening) or because

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of shrinkage of coherent scattering volume (size broadening). The observed broadening peak is likely the combined result of both effects. Strain broadening and size broadening can be separated by WH plotting which are shown in Fig. b and Fig. c. ZnO nanostructures may have a number of defects such as oxygen vacancies, lattice disorders, etc. As a result of annealing these defects are removed and the lattice contracts. Also lattice relaxation due to dangling bonds should be taken into account. The dangling bonds of ZnO surface interact with oxygen ions from the atmosphere and due to electrostatic attraction, leading to a lattice that is slightly contracted [15-16]. The particle sizes are determined for the preferred planes (hkl) using Debye Scherrer's formula [17]. The average particle sizes are found to be 21.7nm and 23.8nm in the direction perpendicular to (101) and (102) planes. The particle size obtained from WH plotting are 24.7nm and 32.2nm at annealed temperatures 473 K and 523 K respectively. Scherrer's method gives average particle size of all crystallites present in the sample in a direction perpendicular to a particular (hkl) planes. But the WH method gives the average particle size in all directions of all individual particles. As the Scherrer's method and WH method give almost equal average particle size, this is possible only if the shape of the particles are cubical or spherical.

XRD line broadening arises due to small grain size and strain. Grain size causes the radiation to be diffracted individually [18-19]. In the present work Williamson- Hall technique is applied to find out the particle size and microstrain using the following equation:

$$\beta \cos\theta = m \sin\theta + \lambda/D \dots\dots\dots(1)$$

where m' is the microstrain, D is the particle size and β is the full width at half maximum of the peak measured in radian, 2θ is the diffraction angle and λ is the wavelength of X-ray. The slope of the graph between $\beta \cos\theta$ and $\sin\theta$ gives the microstrain and the intercept on y axis gives λ/D . Fig. b, Fig. c shows the Williamson-Hall plot of the ZnO thin film annealed at 473K and 523K respectively. This plot shows grain size 24.7nm and 32.2nm as substrate temperature increases. But the strain value decreases from 0.0019 to 0.0011. Thus as annealed temperature increases microstrain decreases.

V.B TEM STUDY

The shape of nanoparticles under study are found to be cubic in nature as shown in the TEM micrograph of the ZnO nanoparticles annealed at 523k.

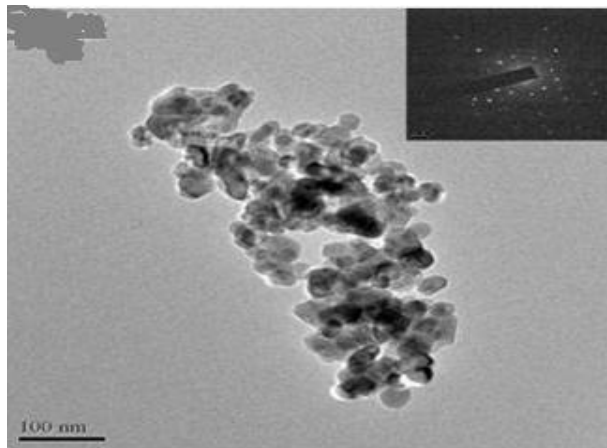


Fig. d TEM image of ZnO nanoparticle

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. In Fig.d the particles are found to be uniform and the average size is found to be of the order of 25nm which almost matches with XRD result (23.8nm). The well crystallinity is observed in lattice planes (100), (101) and (102) and the selected area diffraction pattern (SAED) is shown in inset of Fig.d.

V.C UV-VIS CHARACTERISATION

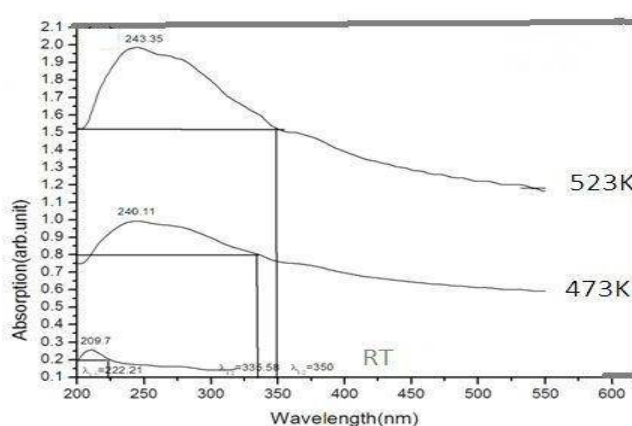


Fig. e

Fig.e gives the optical absorption spectra of ZnO prepared at room temperature and annealed at 473K and 523K respectively. Optical absorption spectra at different annealed temperature are recorded by a pattern of prepared ZnO nanoparticle. The size of nanoparticles play an important role in changing the entire properties of nanomaterials. Thus size evolution of semiconducting nanoparticles become very essential to explore the properties of the material. UV-vis spectroscopy is carried out to study further the optical property of the nano sample from the thin film ZnO. Fig.e shows the UV absorption spectra of ZnO nanoparticles as a function of wavelength in the range from 200 to 600nm at RT and at different annealed temperatures 473K and 523K. By observing the absorption position of the spectra, a blue shift can be observed. This blue shift is due to quantum confinement effect. According to quantum confinement theory, the electrons in the conduction band and holes in the valence band are confined spatially by the potential barrier of the surface. Because of the confinement of electrons and holes, the optical transition energy from the valence top to the conduction bottom increases and the absorption maximum shifts to the shorter wavelength region. The stronger exciton effect is an important character of quantum confinement in nano semiconductors, in which the electrons, holes and excitons have limited space to move and their motion is possible for definite values of energies. Thus their energy spectrum is quantized. The continuum of states in conduction and valence bands are broken into discrete states with an energy spacing relative to band edges which is approximately inversely proportional to the square of the particle size and reduced mass. The highest occupied valence band and the lowest unoccupied conduction band are shifted to more negative and positive values respectively which results the increase in band gap, than the bulk value. Thus there will be a blue shift in the absorption spectra with reduction in crystallite size. Annealed ZnO nanoparticles show stronger UV-Vis absorbance than the as-grown ZnO nanoparticles. The direct band gap of ZnO is estimated from the graph of $h\nu$ versus $(\alpha h\nu)^2$ through the absorption coefficient α which is related to the band gap E_g as $(\alpha h\nu)^2 = k(h\nu - E_g)$, where $h\nu$ is the incident light energy and k is constant. The extrapolation of the straight line in Fig.f to $(\alpha h\nu)^2 = 0$ gives the value of the band gap E_g . The optical band gap are found to be size dependent and the band gap decreases as the particle size increases.

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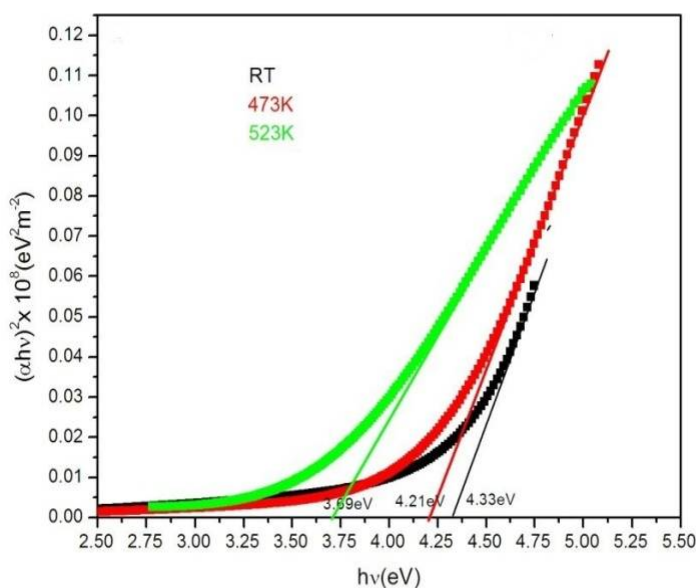


Fig.f

Fig.f gives the Optical Band Gap of ZnO nanoparticle at RT, 473K and 523K. The optical band gap are found to be 4.33eV, 4.21eV and 3.69eV at temperature RT, 473K and 523K respectively.

VI.CONCLUSION

ZnO nanoparticles have been prepared using wet chemical syntheses method and were characterized by XRD, SAED, TEM, UV-Visible absorption spectroscopy. XRD and TEM confirm the nanostructure for the prepared ZnO nanoparticles. SAED pattern consists of bright uniform rings which reveals that the as prepared samples are polycrystalline in nature. The significant sharp absorption of UV radiation by ZnO nanoparticles indicates the monodispersed nature of the nanoparticle distribution. The band gap as well as microstrain increases as the particle size decreases. The prepared ZnO nanoparticles exhibit sharp UV band corresponding to near band gap excitonic emission and broad green emission due to oxygen vacancy at room temperature. These ZnO nanoparticles can be used in different applications like sensors, active medium for lasers etc.

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BIOGRAPHY



Corresponding Author Dr. Sanjib Karmakar is the Corresponding Author of this paper. He has done MSc. in Physics from Gauhati University. He is doing research in the field of transition metals from many years. Presently he is working as Senior Scientific Officer in the Department of Instrumentation & USIC, Gauhati University, Assam, India.



My name is Anup Kr Kalita. I have passed MSc from Gauhati University. Presently I am pursuing PhD in the Department of Instrumentation & USIC, Gauhati University under the Supervision of Dr. Sanjib Karmakar, Senior Scientific Officer Department of Instrumentation & USIC, Gauhati University, Assam, India.