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X Ray Line Profile Analysis of Undoped ZnO thin Films Prepared by Successive IONIC Layer Adsorption and Reaction Method

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Abstract—*Nanostructured Zinc oxide thin films have been synthesized onto suitably cleaned glass substrates by Successive Ionic Layer Adsorption and Reaction (SILAR) Method. The structural properties of the grown thin film were studied using X-Ray Diffraction. The X-ray diffraction results revealed that the sample was crystalline with a hexagonal wurtzite phase. Lattice constant is determined using Nelson Riley plots. From X-ray broadening, crystallite sizes, lattice strain, stress and energy density were studied by using Williamson–Hall method and Modified Williamson Hall method.*

Keywords*: X-ray analysis; Nanocrystals; Williamson–Hall plot; Nelson-Riley plot; Size–strain plot.*

1. INTRODUCTION

With great ability to manipulate structure of the materials on the level of individual atoms and molecules, the nanotechnology is a promising highly interdisciplinary field. The unique optical and electrical properties of ZnO nanomaterial such as wide band gap of 3.37 eV, large exciton binding energy of 60 meV and high electron mobility at room temperature make it suitable for new application and devices. Due to its unique characteristics this material has got wide applications in electronic and optoelectronic devices such as ultraviolet light-emitters, piezoelectric transducers and solar cells [1-4]. Moreover ZnO nanoparticles are used as photocatalyst [5], catalyst [6], antibacterial treatment [7] and UV absorption.

So far, various preparation methods have been used to deposit the ZnO films. Recently much attention of researchers has been attracted to fabrication the semiconductor thin layer by chemical method. Along with this chemical bath deposition (CBD) technique is the most promising method of thin films deposition .The chemical bath deposition method is generally economical, simpler, doesn't require high temperature and pressure and convenient for large-area deposition. Main feature of this method is that for the deposition of thin films there can be used a solution with different chemical compounds.

The crystallite size and lattice strain are the two main properties which could be extracted from the X-ray peak width analysis. Due to the formation of polycrystalline aggregates [8], the crystallite size of the particle is not the same as the particle size. The crystal imperfections could be measured from the distributions of lattice constants. The basis of strain also includes contact or sinter stress, grain boundary, triple junction, stacking faults and coherency stress [9]. The size and strain effects the peak broadening of X-ray analysis. W-H analysis is an integral breadth method. Size-induced and strain-induced broadenings are known by considering the peak width as a function of 2θ [10]. Nelson Riley plot has been used by many research groups for calculating the lattice constant of a cubic as well as hexagonal system [11-13]. Crystallite size, lattice strain and stress have been calculated using Williamson Hall method, Modified Williamson Hall method and Uniform Deformation Energy Density Model [14, 15].

In our work, we have synthesized good quality of ZnO samples using SILAR technique in a controlled manner. Structural characterization of chemically synthesized ZnO films has been undertaken.

2. EXPERIMENT

ZnO thin films have been deposited using SILAR (Successive Ionic Layer Adsorption and Reaction) technique, which is based on the alternate dipping of substrate in the solution and distilled water. For deposition of the film, commercial quality glass microscope slides of dimension 16 mm x 26 mm x 1 mm are used which was cleaned with mild detergent, chromic acid and distilled water. Zinc Acetate dehydrate $Zn(CH_3COO)_2.2H_2O$, triethanolamine (TEA) and ammonia solution [NH_4OH] and distilled water were used for sample

preparation. The cleaned glass substrate was immersed in the zinc complex (at room temperature) for a known standardized time (20 sec) followed by immersion in hot distilled water (near boiling point) for the same time. This cycle was repeated fifty times in order to increase the overall film thickness. The Zinc complex was prepared by adding 1 ml of TEA in 80 ml zinc acetate solution (0.25 M) with continuous stirring. Followed by this, ammonia (25%) was added drop-wise to make the pH value of the solution 11. The final solution was transparent. The equation of the reaction is shown below:

$Zn(CH_3COO)_2.2H_2O + TEA \rightarrow [Zn(TEA)]^{2+} + 2CH_3COO^-$

$[Zn(TEA)]^{2+} \rightarrow Zn^{2+} + TEA$

On dipping the substrate coated with the zinc complexes in the anionic hot processes to form ZnO in the respective baths can be described as follows.

$2NH_4OH \rightarrow 2NH^{4+} + 2OH^-$

$[Zn(TEA)]^{2+} + 2OH^- \rightarrow ZnO + TEA + H_2O$

The film deposited on glass substrate was later heated at100 ^oC temperature for 1 hour. Post deposition heating of the film expelled the water molecules resulting in the ZnO. The structural parameters of the prepared ZnO samples were determined using X-Ray Diffraction technique. The XRD patterns were recorded with Pan analytical XPRT PRO using a CuK_α radiation source.

3. ANALYSIS & RESULTS

The annealed ZnO thin films, Film-1 and Film-2, were analyzed for their structural properties by recording X-ray diffraction pattern. Fig. 1 shows the XRD pattern of ZnO films which were deposited on glass. According to this figure, the films are polycrystalline and the diffraction peaks of ZnO exhibited hexagonal plane (crystals have hexagonal structure) with preferred orientation of the grains along (100), (002), (101), (102) and (110). All evident peaks could be indexed as the ZnO wurtzite structure (JCPDS Data Card No: 36-1451). Diffraction pattern corresponding to impurities are found to be absent. This proves that pure ZnO nanoparticles were as synthesized. The sharp and strong diffraction peaks confirmed the high crystalline quality of the annealed samples. The lattice parameters have been calculated using the relation

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

A comparison of XRD data for standard hexagonal ZnO with the XRD data of the prepared film is shown in table 1.

3.1 Lattice constant

Lattice parameters '*a*' and '*c*' of the hexagonal phase for ZnO were calculated according to the next expressions [16]

$$a = \frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \left(\frac{a}{c}\right)^2 l^2} \quad (2)$$

$$c = \frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3}\left(\frac{c}{a}\right)^2 \left(h^2 + hk + k^2\right) + l^2} \quad (3)$$

where λ is X-ray wavelength.

The corrected values of lattice constants are estimated from the Nelson-Riley plots. The Nelson–Riley curve is a plot between the calculated '*a* 'and '*c'* for different planes and error function [17]

$$f(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \quad (4)$$

and extrapolation to $\theta=90^0$. A typical Nelson–Riley plot for synthesized samples are shown in Fig.2 and the lattice constants *'a'* and '*c'* of the Film-1 are found to be 3.256Å and 5.217 Å respectively whereas those for Film-2 are 3.249 Å and 5.210 Å .These values are different from the bulk values 3.250 Å and 5.207 Å (Jcpds36-1451) which clearly shows that the particles are under strain. The presence of strains contributes towards broadening of the diffraction peak.

3.2 Crystallite Size

The crystallite size of the prepared ZnO-NCs (nanocrystals) is estimated from the Scherrer's formula

$$D = \frac{k\lambda}{\beta_D \cos\theta} \quad (5)$$

where the constant κ is taken as 0.9, λ is the wavelength of the wavelength of X-rays used (λ = 1.5406 Å). β_D is the full width at half maximum of the diffraction peaks. The result is shown in Table2.

3.3 Williamson Hall method

In X-Ray Diffraction, peak broadening arises from two sources: instrumental contributions and sample Contributions. The Bragg peak breadth is a combination of both instrument and sample dependent defects. The instrument corrected broadening β_D is calculated from the relation

$$D = \frac{k\lambda}{\beta_D \mathrm{Cos}\theta} \text{ or } \beta_D = \frac{k\lambda}{D\mathrm{Cos}\theta} \quad (6)$$

Crystal imperfections and distortion of strain induced peak broadening are related by

$$\varepsilon = \frac{\beta_S}{4\tan\theta} \text{ or } \beta_S = 4\varepsilon\tan\theta \quad (7)$$

Depending on different θ positions, the separation of size and strain broadening analysis is done using Williamson and Hall. According to Williamson and Hall

$$\beta = \beta_s + \beta_D \quad (8)$$

Substituting eq. (6) and (7) in the above equation we get,

$$\beta = \frac{\kappa\lambda}{D\cos\theta} + 4\varepsilon\tan\theta \text{ or}$$

$$\beta\cos\theta = \frac{\kappa\lambda}{D} + 4\varepsilon\sin\theta \quad (9)$$

Equation (9) represents the uniform deformation model (UDM), where the strain is assumed to be uniform in all crystallographic directions. A diffraction pattern from the line broadening of a standard material such as silicon is taken to determine the instrumental broadening.

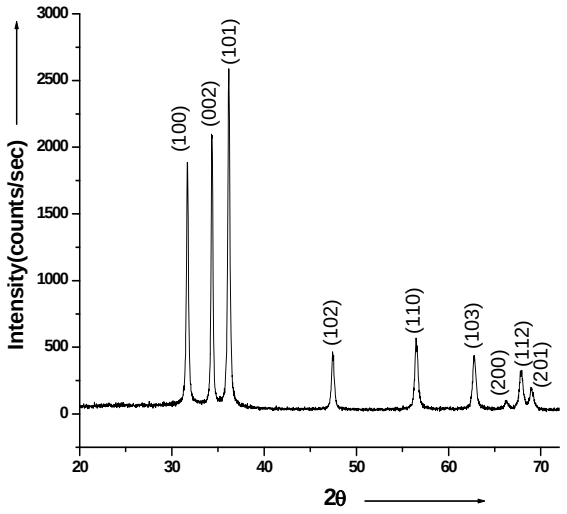
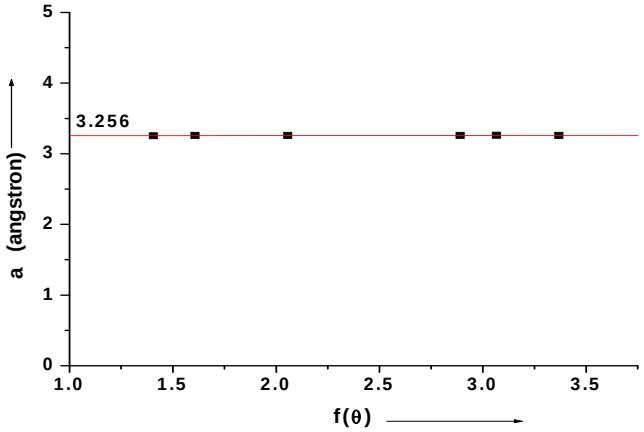


Fig. 1: XRD Patterns of ZnO thin films



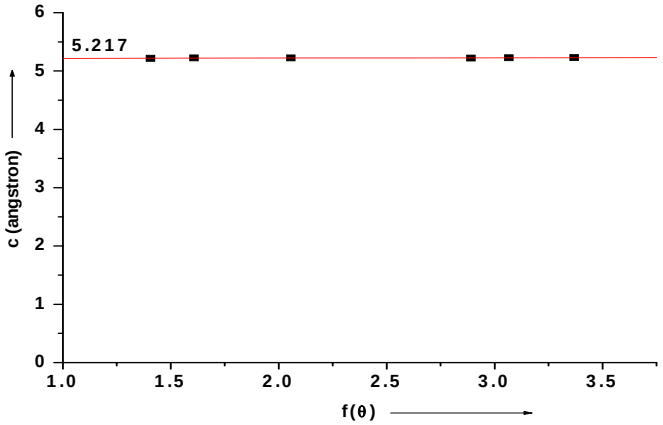


Fig. 2: Nelson–Riley plots of ZnO nanocrystals

Table 1: comparison of XRD of prepared ZnO films with standard data

ZnO (Hexagonal)		Sample						Planes (*hkl*)
		As-grown film						
θ2 (deg)	d (Å)	2θ (deg)	d (Å)	a (Å)	a (Å) corrected	c (Å)	c (Å) corrected	
31.76	2.8147	31.68	2.8221	3.260		5.230		100
34.41	2.6036	34.35	2.6093	3.262		5.227		002
36.25	2.4761	36.18	2.4807	3.259	3.266	5.221	5.217	101
47.53	1.9113	47.46	1.9141	3.258		5.225		102
56.59	1.6251	56.51	1.6274	3.260		5.223		110
62.85	1.4774	62.79	1.4789	3.254		5.216		103

The instrumental broadening corrected FWHM (β) of each reflection is calculated using the following equation [20]

$\beta^2 = (\beta^2)_{measured} - (\beta^2)_{instrumental}$ (10)

A graph is drawn with βcosθ along Y–axis and 4 sinθ along X–axis (Fig. [3]). From the graph, strain and crystallite size are calculated from the slope and y intercept of the fitted line respectively and the values are tabulated in table 2.

In case of isotropic line broadening, another method called 'size–strain plot' (SSP) can be used for estimation of size–strain parameters. In this approximation method, the 'crystallite size' profile is described by a Lorentzian function and the 'strain profile' is described by Gaussian function [18]. Then one can write

$$\left(\frac{d\beta\cos\theta}{\lambda}\right)^2 = \frac{1}{D}\left(\frac{d^2\beta\cos\theta}{\lambda}\right) + \left(\frac{\varepsilon}{2}\right)^2 \quad (11)$$

The term $\left(\frac{d\beta\cos\theta}{\lambda}\right)^2$ is plotted against $\left(\frac{d^2\beta\cos\theta}{\lambda}\right)$ for different peak orientations of ZnO nanocrystals as shown in Fig. 5. The crystallite size is determined from the slope of the linearly fitted data and the value of strain is obtained from y-intercept. The mean apparent size is $D_{app} = \frac{\lambda}{slope}$ and the true size of the crystallite is obtained from $D = kD_{app}$, where K = 3/4 for spherical particle. The mean apparent strain is $\varepsilon_{app} = 2\left(\sqrt{y\,\text{int}\,ercept}\right)$ and the root mean square strain is obtained from $\varepsilon = \frac{\varepsilon_{app}}{2\pi\sqrt{2}}$ [19]. The estimated values of D and ε are shown in table 2.

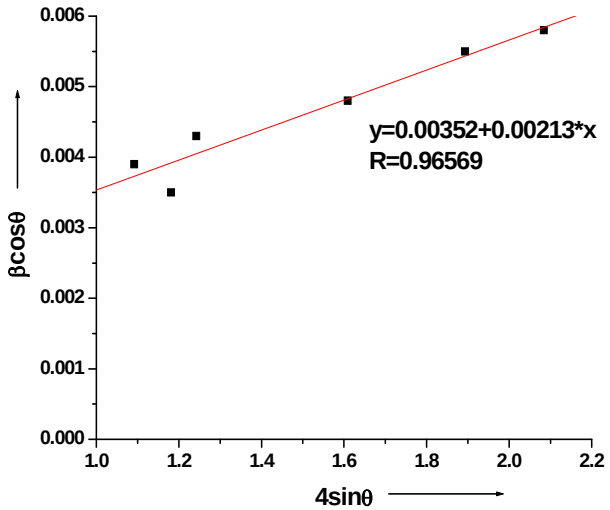


Fig. 3: W–H plots of ZnO NCs

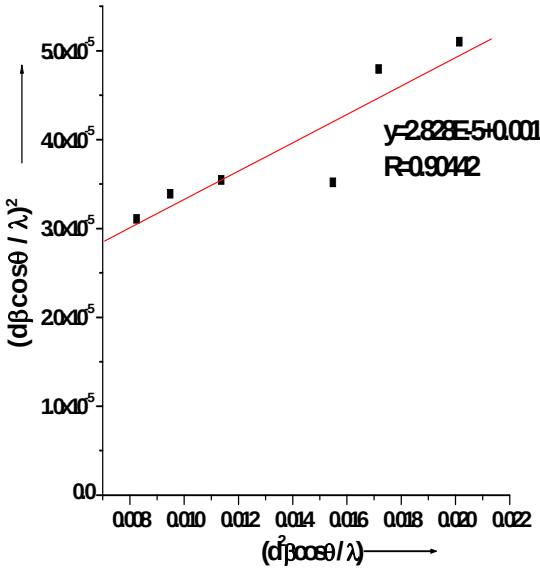


Fig. 4: Size-Strain plot for ZnO NCs

Table 2: Geometric parameters of ZnO films prepared

Sample prepare	Scherrer Method	Williamson-Hall Method								
		UDM		USDM			UDEDM			
	D (nm)	D (nm)	strain ε x10^{-3}	D (nm)	Strain ε x10^{-3}	Stress σ(MPa)	D (nm)	Strain ε x10^{-3}	Stress σ(MPa)	u KJ/m^3
ZnO	32.27	41.12	2.13	42.0	1.91	242.98	41.78	2.018	257.33	260.7

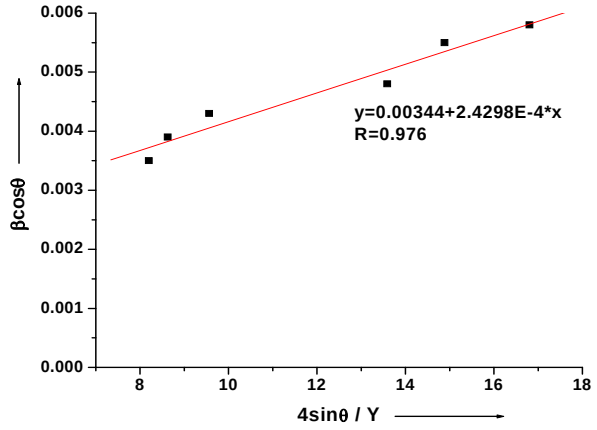


Fig. 6: Modified form of W-H analysis (USDM)

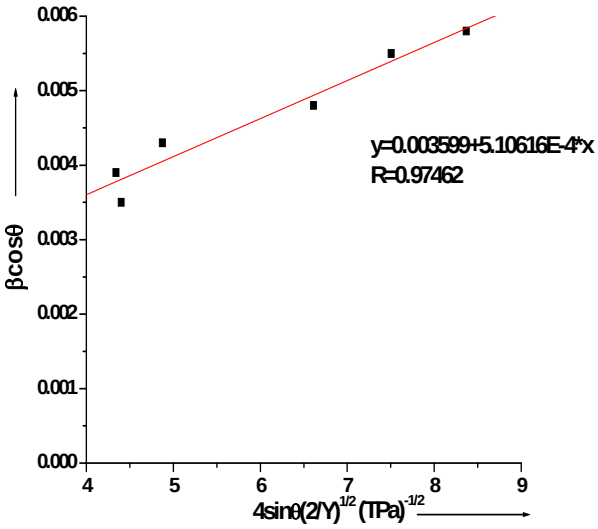


Fig. 7: Modified form of W-Hanalysis(UDEDM)

3.4 Modified Williamson- Hall method

From Uniform Stress Deformation Model (USDM), strain is calculated from Hooke's law maintaining linear proportionality between stress and strain given by $\sigma = Y\varepsilon$ where σ is the stress, ε is the strain and Y is the Young's

modulus. Applying Hooke's law approximation to eq. (9), we get

$$\beta \mathrm{Cos}\,\theta = \frac{\kappa\lambda}{D} + \frac{4\sigma}{Y}\mathrm{Sin}\,\theta \tag{12}$$

For a hexagonal crystal, Young's modulus is given by the following relation [12, 13]:

$$Y = \frac{\left[h^2 + \frac{(h+2k)^2}{3} + \frac{(al)^2}{c}\right]^2}{S_{11}\left[h^2 + \frac{(h+2k)^2}{3}\right]^2 + S_{33}\left(\frac{al}{c}\right)^4 + (2S_{13}+S_{44})\left[h^2 + \frac{(h+2k)^2}{3}\left(\frac{al}{c}\right)^2\right]} \tag{13}$$

Where $S_{11,}$ $S_{13,}$ S_{33} and S_{44} are the elastic compliances of ZnO with values of $7.858\text{x}10^{-12,}$ $-2.206\text{x}10^{-12}$, $6.940\text{x}10^{-12}$ and $23.57\text{x}10^{-12}$ m^2 N^{-1} respectively [20]. Young's modulus, *Y*, for hexagonal ZnO was calculated as ≈127 GPa. A graph is plotted between 4 sinθ/Y along X–axis and βcosθ along Y–axis (Figure6). The stress is calculated from the slope of the graph and crystallite size from the Y- intercept and the values are tabulated in Table 2. The energy density of a crystal was calculated from a model called Uniform Deformation Energy Density Model (UDEDM). According to Hooke's law, the energy density u (energy per unit volume) is $u = \frac{\varepsilon^2 Y}{2}$

Therefore, Equation (9) can be modified to the form

$$\beta\cos\theta = \frac{k\lambda}{D} + 4\sin\theta\left(\frac{2u}{Y}\right)^{\frac{1}{2}} \tag{14}$$

A graph is plotted between $4\sin\theta\left(\frac{2}{Y}\right)^{\frac{1}{2}}$ along X -axis and βcosθ along Y -axis (Figure7). From the slope of the graph, energy density u is calculated and the crystallite size D is calculated from the Y- intercept (Table2)

4. CONCLUSION

The ZnO nano crystal line thin films with hexagonal structure have been synthesized by SILAR co method. The line broadening of ZnO nanoparticles due to the small crystallite size and strain was analysed by Scherrer's formula. The size and strain contributions to line broadening were analyzed by W-H method and three modified forms of W-H method namely uniform deformation, uniform deformation stress, and uniform deformation energy density models. These models are highly preferable to define the crystal perfection.

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