MICROSTRUCTURAL STUDY OF AS GROWN AND 650 ^{o}C ANNEALED ZnO NANORODS: X-RAY PEAK PROFILE ANALYSIS

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Zinc oxide nanorods were synthesized by hydrothermal method at 95°C. The X-ray diffraction analysis revealed that nanorods are crystalline in nature having wurtzite phase, Transmission Electron Microscopy result indicate that the grain size of the sample is about 102 nm. We have studied the development of crystallite size by using X-ray peak profile analysis. Lattice strain and crystallite size were calculated by Scherer's formula and various models of Williamson-Hall analysis. Uniform deformation model, uniform deformation stress model and uniform deformation energy density model with Williamson-Hall method were used to calculate all other physical parameters such as stress, strain and energy density values. The results showed that the estimated crystallite size from Williamson-Hall analysis by using uniform deformation model is highly inter-correlated with the particle size estimated from TEM analysis. In this paper, the X-ray diffraction and TEM results show not so much of deviation between crystallite size and particle size.

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Keywords: ZnONanorods, Hydrothermal synthesis, Crystal structure, W-H analysis, TEM

1. Introduction

The family of nanoparticles is one of the most promising families of science, today. Metal oxide like Zinc Oxide (ZnO) in nanostructure is one of the prominent materials which have intensively studied, due to unique structure and size dependent electrical, optical, mechanical properties with scientifically interest in polymorphism depending on synthesis condition [1, 2]. ZnO is carrying a wurtzite crystal structure, at room temperature it has 3.37 eV energy gap (which is similar to GaN 3.39 eV) along with 60 meV of high exciton binding energy which indicates its high radiation emission for efficient optoelectronic device and gass sensing applications [3-5]. Due to its unique structural properties, ZnO is the largest family of semiconductor's nanostructures among all semiconductor materials [6, 7]. Every perfect crystal would prolong in all direction, it is not possible to synthesis a perfect crystals because of their finite size. The broadening of diffraction peak indicates the deviation from perfect crystallinity. (1) Crystallite size and (2) lattice strain are the two basic microstructural properties extracted from X-ray Peak Profile Analysis (XPPA). Presence of

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polycrystalline aggregation is the basic reason for the difference of crystallite size from actual particle size. Measure of coherently diffraction domains size is known as crystallite size [8]. Scanning electron microscopy (SEM), light (laser) scattering experiment, Brunauer Emmett Teller (BET) and tunneling electron microscopy (TEM) are widely used techniques for the measurement of particle size. Lattice constants are not uniformly distributed due to the imperfection of crystal therefore lattice strain (compressive or tensile) is present between planes, which are measured by distribution lattice constants. In nanostructure materials, lattice distortion is one of the major sources for microstrains caused by sinter stresses, dis-location, triple junctions of grain boundaries, stacking fault, twin boundaries, etc. In general, XPPA is the average method to determine the lattice distortion for microstrains[9]. Enhancement in crystallite size during the mechanically alloying process induces a large amount of strains due to the enriched dynamic recrystallization [10].

The simplest power full tool to estimate the crystallite size and lattice strain is XPPA. Bragg peak effects variously by the change in crystallite size and lattice strain. Due to these effects the change in full width half maximum and shift of 2θ peak position accordingly. Although peak width corresponds to crystallite size varies as 1/Cos θ and lattice strain varies as tan θ [11]. W-H analysis is a simplified integral breadth method where, both size induced and strain induced broadening are deconvoluted by considering the peak width as a function of 2θ. Although X-ray profile analysis is an average method, they still hold an unavoidable position for grain size determination, apart from TEM micrographs.

In this work, mean particle size of ZnOnanorods (ZnO NR's) obtained from direct TEM and from XPPA are evaluated comparatively. The lattice strain due to lattice distortion was estimated by using W-H analysis, namely uniform deformation model (UDM) of as-grown and annealed ZnO sample at 650 ^{o}C. Stress-strain relation and the strain 'ε' as a function of energy density 'μ' was estimated by using Uniform deformation model (UDM), uniform deformation stress model (UDSM) and uniform deformation energy density model (UDEDM). In UDM, the isotropic nature of the crystal is considered, whereas UDSM and UDEDM assume that the crystals are of an anisotropic nature. The strain associated with the anisotropic nature of the hexagonal crystal is compared and plotted with the strain resulting from the inter-planar spacing. We report such investigation on ZnO NR's and suggested that only W-H analysis viz UDM is only reliable model for the estimation of crystallite size as compared to other.

2. Results and Discussion

2.1. XRD Analysis

Fig. 1 shows the diffraction pattern of as grown and 650 ˚C annealedZnO NR's, it is reported that all the detectable peaks are indexed the wurtzite hexagonal structure and 650 ˚C annealed sample does not shows any change in phase or any impurity, its just increases the intensity. Sharp as well as narrow peak's intensity is confirming of high quality with good crystalline in nature and fine grain size of ZnO NR's. There is not detecting any extra diffraction peak of Zn(OH)2, Zinc or any other ZnO phases, indicating the high crystallinity of ZnO NR's. Distance between adjacent planes d (calculated from Bragg's equation $\lambda = 2d \sin\theta$, where λ is the wavelength of Cu $K_{\alpha 1}$

radiation, θ is the diffraction angle), lattice constants ($a = b = \frac{\lambda}{\sqrt{3}\,\mathrm{Sin}\theta}$ and $c = \frac{\lambda}{\mathrm{Sin}\theta}$), packing fraction (c/a), bond length L (calculated by using equation $L = \sqrt{\left(\frac{a^3}{3} + \left(\frac{1}{2} - u\right)^2 c^2\right)}$ where 'u' is a positional parameter as estimated $u = \frac{a^2}{3c^2} + 0.25$) and unit cell volume V (calculated by $V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c$) are named as wurtzite lattice constants [12], and illustrated in Table 1.

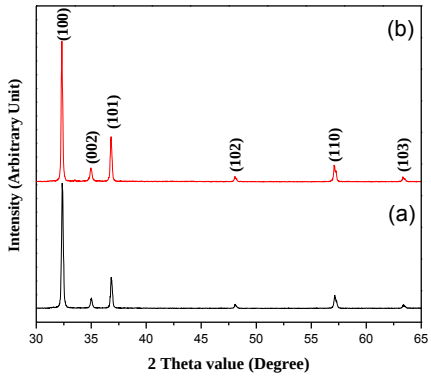

Fig. 1.X-ray diffraction pattern of (a) as grown and (b) 650 ˚CannealedZnO NR's

Table 1.The structural parameter of as grown ZnO NR's and calcinated at 650 °C

Sample Name	Lattice Parameter (nm)		Packing factor	Volume	Position parameter	Bond length
	A	C	c/a	$(nm)^3$	u	L (Å)
ZnO	0.3200	0.5133	1.6040	0.0455	0.3796	1.2144
ZnO-650 °C	0.3203	0.5141	1.6051	0.0457	0.3794	1.2166

2.2. Crystallite size and strain

2.2.1. Scherer Method

XRD can be utilized to evaluate peak broadening with the crystallite size, stress and lattice strain [13]. Using the Scherer formula ($D = \frac{K\lambda}{\beta_t \cos\theta}$ where D is the crystallite size, k is a constant equal to 0.94, λ is the wavelength of Cu $K_{\alpha 1}$ equal to 1.54056 Å, β_t is a peak width at half maximum and θ is the angle of diffraction) of XPPA method was used to determine the particle size of ZnO NR's. The corrected instrumental broadening, β_t corresponding to each ZnO NR's diffraction peak using the relation[14]

$$\beta_t = \left[\beta^2_{\text{measured}} - \beta^2_{\text{instrumental}}\right]^{\frac{1}{2}} \quad (1)$$

$$D = \frac{K\lambda}{\beta_t \cos\theta} \Rightarrow \cos\theta = \frac{K\lambda}{D}\left(\frac{1}{\beta_t}\right) \quad (2)$$

After that $\frac{1}{\beta_t}$ was taken on x-axis and $\cos\theta$ on y-axis to draw the plot for preferred orientation peak ZnO NR's with hexagonal phase appear between$2\theta = 30^{\circ}$ and 65°. By fitting a data, the slope of the fitted line provided the crystallite size D as shown in Figure 2 and listed in Table 2. The sample of 650 ˚C annealed ZnO NR's revealed the crystallite size of 110 nm and that of the as grown ZnO NR's was 90 nm.

Table 2. Geometric parameters for as grown and 650 ˚C annealed ZnO NR's

Sample Name	Scherer Method	W-H Method									TEM Method
		UDM		UDSM			UDEDM				
	D (nm)	D (nm)	Ɛ 1E-04	D (nm)	σ (M Pa)	Ɛ 1E-04	D (nm)	u (KJ/m3)	σ (M Pa)	Ɛ 1E-04	D (nm)
As grown ZnO	90	86	2.31	86	284	1.48	90	148	168	1.24	--
650 C Annealed ZnO	110	116	1.13	112	464	2.39	109	124	155	1.13	102

2.2.2. Williamson-Hall Analysis

The strain-induced in nanostructure due to dislocation along with imperfection of crystal was calculated by Wilson equation

$$\beta_s = 4\varepsilon \tan\theta \quad (3)$$

Where Ɛ is the induced-strain, it is clearly seen from Eq. (2) and (3) that broadening of Bragg peak is the additive effect due to crystallite size and microstrain. Assuming the independently effect of size and strain contribute the Bragg peak broadening and both have a Cauchy like profile, simply the observed broadening $\beta_{hkl}$is the sum of Eq. (2) and (3).

$$\beta_{hkl} = \beta_t + \beta_s \quad (4)$$

$$\beta_{hkl} = \left(\frac{K\lambda}{D\cos\theta}\right) + (4\varepsilon \tan\theta) \quad (5)$$

Simplify Eq. (5)

$$\beta_{hkl}\cos\theta = \left(\frac{K\lambda}{D}\right) + (4\varepsilon \sin\theta) \quad (6)$$

Above equation is called W-H equation. A plot of $4\sin\theta$ along x-axis verses $\beta_{hkl}\cos\theta$ along y-axis was drawn for as grown and 650 ˚C annealed ZnO NR's as shown in Figure 3. UDM based on the assumption that strain is uniformly distributed in all direction of crystal[14-17]; the

isotropic nature of crystal is considered where all properties of material are independent of the direction along which they were measured. The UDM analysis of as grown and 650 ˚C annealed ZnO NR's are shown in Figure 3. After linear fit of the data, y-intercepts and slope of the linear fit provided crystallite size D and microstrainε respectively and illustrated in Table 2. From the table it is clear that the strain induced with as grown and 650 ˚C annealed ZnO NR's indicates the annealing effect on ZnO nanoparticles does not produce any significant changes on strain.

Considering uniform deformation stress and uniform deformation energy density model, the anisotropic nature of Young's modulus of the crystal is more realistic. Only UDSM were taking into account; keeping the linear proportionality between stress and strain then generalized Hook's law referred to the strain as given $\sigma = \varepsilon E_{hkl}$, where σ is called stress of the crystal and E_{hkl} is called Young's modulus in the direction perpendicular to the planes (hkl). Here keeping the elasticity of modulus as proportionality constant, stress is directly proportional to strain and this is valid for significantly small microstrain. Assume that as grown and 650 ˚C annealed ZnO NR's having very small strain then applying Hook's law approximation on Eq. (6), written as

$$\beta_{hkl}\cos\theta = \left(\frac{K\lambda}{D}\right) + \left(\frac{4\sigma\sin\theta}{E_{hkl}}\right) \tag{7}$$

A plot of $\frac{4\sin\theta}{E_{hkl}}$ along x-axis verses $\beta_{hkl}\cos\theta$ along y-axis was drawn for as grown and 650 ˚C annealed ZnO NR's as shown in Fig. 4. After linear fitting, the slope and vertical intersection of the fitted line provides the uniform deformation stress σ and crystallite size D respectively. Anisotropic microstrain ε can be estimated by $\frac{\sigma}{E_{hkl}}$, if E_{hkl} of hexagonal ZnO NR's is known[14, 15]. Young's modulus of hexagonal crystal phase is related to their elastic compliances S_{ij}[18, 19]

$$E_{hkl} = \frac{\left[h^2+\frac{(h+2k)^2}{3}+\left(\frac{al}{c}\right)^2\right]^2}{S_{11}\left(h^2+\frac{(h+2k)^2}{3}\right)^2 + S_{33}\left(\frac{al}{c}\right)^4 + (2S_{13}+S_{44})\left(h^2+\frac{(h+2k)^2}{3}\right)\left(\frac{al}{c}\right)^2} \tag{8}$$

Here $S_{11}, S_{13}, S_{33}, S_{44}$ are the elastic compliance of hexagonal ZnO NR's and their values are $7.858 \times 10^{-12}, -2.206 \times 10^{-12}, 6.940 \times 10^{-12}, 2.357 \times 10^{-11}$ respectively[16].

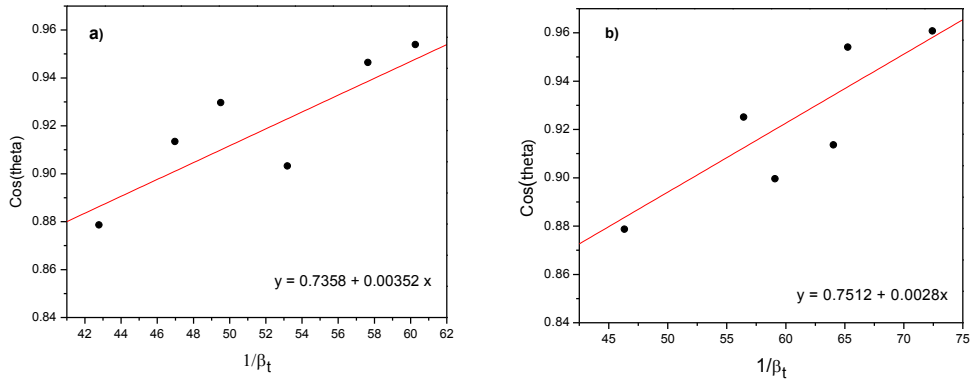

Fig. 2. Scherer plots of (a) as grown and (b) 650 ˚C annealed ZnO NR's. Slope of the linear fit provided the crystallite size D.

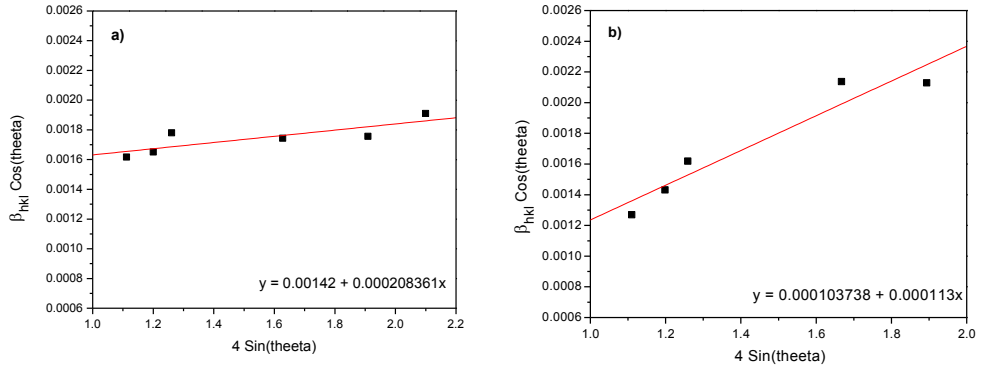

Fig 3. W-H analysis of (a) as grown and (b) 650 ˚C annealed ZnO NR's assuming UDM. Y-intercept and slope of the linear fit provided crystallite size D and microstrain respectively.

There is another model named uniform deformation energy density model, UDEDM; density of deformation energy 'u' is assumed to be the cause of microstrain. In Eq. (6), we assumed to have homogenous and isotropic nature of the crystal; however in many cases the homogeneity and isotropy assumption is not justified. Considering the strain energy density 'u', proportionality constants associated with the stress-strain relation is no longer independent. According to Hook's law for elastic system, the density of energy 'u' (energy per unit) can be calculated by $u = \left(\frac{\varepsilon^2 E_{hkl}}{2}\right)$, then Eq. (7) rewritten as

$$\beta_{hkl}\cos\theta = \left(\frac{K\lambda}{D}\right) + \left(4\sin\theta\left(\frac{2u}{E_{hkl}}\right)^{\frac{1}{2}}\right) \tag{9}$$

A plot of $4\sin\theta\left(\frac{2u}{E_{hkl}}\right)^{\frac{1}{2}}$ along x-axis verses $\beta_{hkl}\cos\theta$ along y-axis was drawn for as grown and 650 ˚C annealed ZnO NR's as displayed in Figure 5. After linear fitting, the slope and vertical intersection of the fitted line provides the anisotropic energy density 'u' and crystallite size D respectively. If E_{hkl} is known then we can calculate microstrain from $\frac{\sigma}{E_{hkl}}$. From Eq. (7) & (9), the energy density is correlated with UDSM whereas deformation stress is correlated with UDEDM, based on different approaches the assumption of uniform deformation stress representing in Eq. (7) whereas uniform deformation energy as per Eq. (9). Although crystal of anisotropic nature is considered in both models. The deformation stress and deformation energy are correlated as $u = \frac{\sigma^2}{E_{hkl}}$. Noted that both Eq. (7) & (9) are taking into account in the anisotropic nature of elastic constant, they are essentially different[20]. In Eq. (3) assumed that the deformation stress 'σ' having the constant value in all crystallographic direction allowing u to be anisotropic, where as in Eq. (9) assumed the deformation energy 'u' has the same value in the all crystallographic direction treating the σ to be anisotropic.

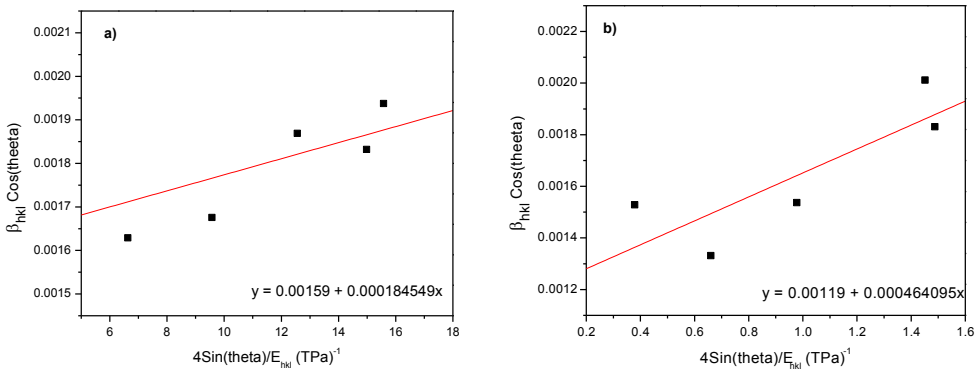

Fig. 4. Modified W-H analysis of (a) as grown and (b) 650 ˚C annealed ZnO NR's assuming UDSM. Vertical intersection and slope of the linear fit provided crystallite size D and uniform deformation stress σ respectively

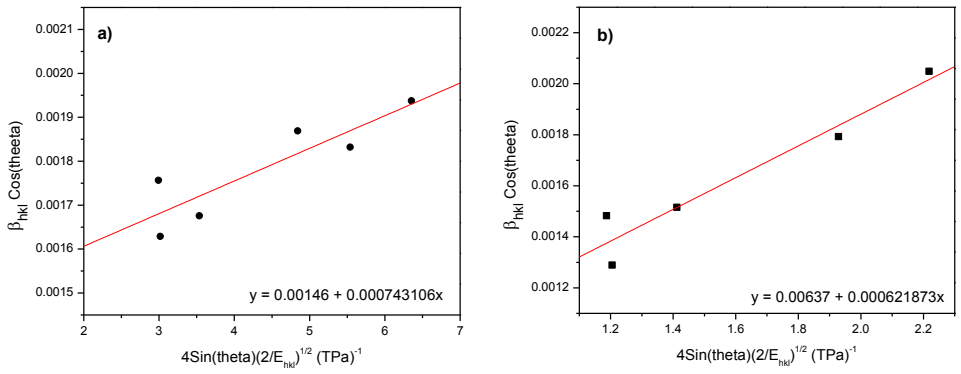

Fig 5. Modified W-H analysis of (a) as grown and (b) 650 ˚C annealed ZnO NR's assuming UDEDM. Vertical intersection and slope of the linear fit provided crystallite size D and anisotropic energy density 'u' respectively.

2.3. TEM Analysis

For size and shape analysis, TEM is considered as the simplest tool because measurements can be estimated through real image[13, 21]. In TEM, electron beams was focused by electromagnetic lines which was transmitted through a thin sample of ZnO NR's. TEM image with selected area electron diffraction (SAED) pattern of 650 annealed ZnO NR's as shown in Figure 6. It is clearly noted that the micrograph of 650 ˚C annealed ZnO is in good agreement of hexagonal wurtzite structure having crystalline in nature. The particle size of 650 ˚C annealed ZnO NR's estimated as listed in Table 2. Wide size distribution of ZnO with no other impurities is confirmed by a doted pattern in SAED. The results obtained from XRD are in close agreement with TEM measurements.

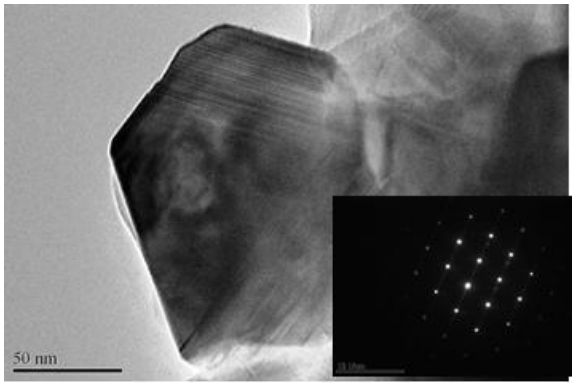

Fig. 6. TEM micrograph and SAED pattern (insert on the right side) of 650 annealed ZnO NR's

Geometrical parameters of as grown and 650 ˚C annealed ZnO NR's (such as crystallite size, stress, strain, energy deformation) estimated from Scherer formula, W-H analysis with different modified models and TEM results are summarized in Table 2. Using Eq. (8), the Young Modulus $E_{hkl}$of as grown and 650 ˚C annealed ZnO NR's was estimated. It is approximately 127 GPa having good agreement with the bulk ZnO[22, 23]. By relating the value of average crystallite size of as grown and 650 ˚C annealed ZnO NR's, estimated from Scherer formula, UDM, UDSM and UDEDM are less or more similar, implying that the inclusion of strain in various forms has a very small effect on the average crystallite size ZnO NR's. All though, the average crystallite size estimated from W-H analysis and Scherer formula (see table 2) displayed a greater variation due to the difference in averaging the particle size distribution. The strain value from each model was estimated by taking Young's Modulus E_{hkl} to be 127 GPa[24]. Various form W-H analysis such as UDM, UDSM, UDEDM, the average crystallite size and the strain values obtained by using UDM is found to be very accurate, comparable, and reasonable, as their entire preferred high intensity points laying very close to the linear fit as compared to other models.

3. Materials and Methods

Zinc acetate di-hydrate, hexamethylenetetramine (HMT) and deionized water were used as reagents. Silicon (Si) substrates were cleaned with acetone, isopropyl alcohol and deionized water with ultrasonic cleaner for 30 minutes, then dipped for 10 minutes into hydrofluoric acid to remove the oxide layer. After that gold (Au) films were thermally evaporated on Si substrate which isapproximately 20 nm thicknesses. Zinc acetate di-hydrate and HMT were mixed into 30 ml deionized water separately of 1:1 atomic ratios and were magnetically stirred at room temperature for 30 minutes, after that these two solution were mixed and make vigorous stirring at 60 ˚C for 1 hour. This solution mixture was transferred into Teflon-lined autoclaves with Silicon substrate (Au coated) and heated at 95 ˚C for 3 hour. Moreover,ZnO NR's on Si substrate were collected and dried at 100 ˚C for 10 minutes. Then, sample was annealed at 650 ˚C in tube furnace in the presence of argon gas environment for 3 hours.

4. Conclusion

ZnO NR's were synthesis by hydrothermal method and characterized by XRD and TEM. Crystallite size and lattice strain are responsible for line broadening and were analyzed by Scherer formula and modified models of W-H method. Modified W-H plots have been worked out and accepted to determine the crystallite size and strain induced broadening due to imperfection of crystal. Lattice strain estimated from UDSM, UDEDM differs from Scherer formula due the assumption of hexagonal anisotropic crystalline nature. TEM micrograph of 650 ˚C annealed ZnO NR's reveals the crystalline nature and particle size is found to be 102 nm. SAED patterns of TEM micrograph is confirmed the wide size distribution of ZnO NR's. In this paper we suggested that out of these three modified models of W-H analysis, the uniform deformation modelsis more reliabled in determining the stress, strain and crystallite size because all the data points are very close to the linear fit in the graph as shown in figure 3.Moreover, these modified forms of W-H analysis are highly preferable defining crystal imperfection. Crystal size and average crystallite size estimated from TEM and W-H analysisviz UDM is in good agreement.

Acknowledgments

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