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Peak Profile Analysis of X-ray Diffraction Pattern of Zinc Oxide Nanostructure

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X-ray diffraction is an important tool to analyze the crystal structure of any crystalline material. By appropriate analysis of X-ray diffraction peaks, the crystallite size and microstrain can be determined. Other parameters such as growth anisotropy, crystallinity, dislocation density and specific surface area can also be determined. We studied here the X-ray diffraction pattern of ZnO nanorods. The crystallite size and strain were calculated for all diffraction peaks of the pattern. The average value of the crystallite size was 47.7 nm. The strain was found to be different for different crystallographic planes. Using the standard formula, the lattice parameters of the wurtzite structure were calculated and found to be equal to $a = b = 3.2467$ Å and $c = 5.2004$ Å. The prepared sample has a very large average specific surface area of 2.26×10^5 cm^2g^{-1}. The intensities of various diffraction peaks are different indicating that the growth of the crystal is anisotropic.

Keywords: Crystalline, Grain, Strain, Anisotropy.

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1. INTRODUCTION

Zinc oxide (ZnO) is an II-VI semiconductor being investigated widely due to its multifunctional properties like optical transparency, high band gap, electrical conductivity, room temperature ferromagnetism [1-5]. It has a very wide direct band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV at room temperature [6]. These properties altogether make ZnO a potential material for transparent conducting electrodes, spintronic memory, UV lasers and LEDs, quantum dot displays and nanoelectronics devices [7]. It has a wurtzite unit cell structure. However, due to lack of center of inversion, there are uncompensated charges along its *c*-axis, i.e., (002) direction [8]. As a result, the crystal is usually polarized and hence exhibits the piezoelectric effect. Thus, the structural study of such a wurtzite structure is very important. ZnO nanostructures can be fabricated by a variety of methods like sol-gel, hydrothermal, chemical vapor deposition, sputtering and laser ablation method [9-12]. However, chemical synthesis or sol-gel method offers a cost-effective approach to synthesizing ZnO nanostructures of high yield. In our earlier reports, we synthesized varieties of ZnO nanostructures like nanorods, nanotubes, nanobelts, nanopencils and nanoparticles by sol-gel method, and their optical properties were investigated in detail [13-20]. In this paper, we report on a detailed crystallographic study of ZnO nanorods synthesized by wet chemical method.

2. MATERIALS AND METHOD

All chemicals used in this synthesis were of analytical grade (MERK, 99.99 % purity) and were used without further purification. In brief, zinc nitrate hexahydrate (14.87 g) was dissolved in deionized water to prepare 0.5 M concentration solution. 4 g of sodium hydroxide was dissolved in de-ionized water for preparing 1 M solution. These two solutions were mixed and stirred in a magnetic stirrer for 2 h. The precipitate was filtered and washed with deionized water. The precipitate was then annealed at 400 °C. The X-ray diffraction (XRD) data were recorded in a RIGAKU powder X-ray diffractometer using CuKα radiation over an angular range $30° < 2\theta < 60°$.

3. RESULTS AND DISCUSSION

A typical XRD pattern of the synthesized ZnO nanorods is shown in Fig. 1. Sharp diffraction peaks were observed, which is an indication of the formation of well crystalline material. Our calculation suggests that the unit cell is wurtzite with the space group P63mc. The peaks appearing at 31.78°, 34.41°, 36.32°, 47.61° and 56.63° correspond to (100), (002), (101), (102) and (110), respectively.

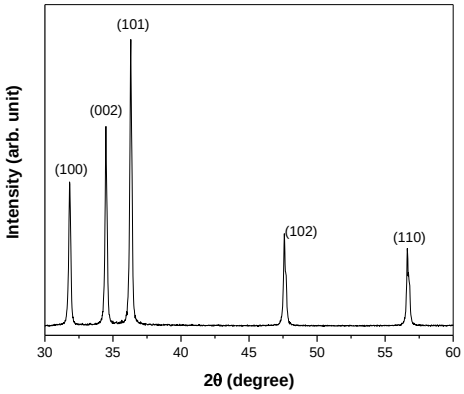

Fig. 1 – Typical XRD pattern of ZnO (reproduced from [21])

These peaks are consistent with the JCPDS card no. 36-1451. Shifts of the diffraction peaks are very small and quite consistent with that of JCPDS data (Table 1). It was further observed that intensities of different

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diffraction peaks are different. This indicates that the growth rate differs in different directions. The higher the growth rate, the smaller the surface area of the plane, and hence the lower the intensity [21]. This growth anisotropy is characterized by a parameter known as the degree of orientation defined by [22]

$$O_{hkl} = \frac{I_{hkl}}{\sum I_{hkl}}.$$

The degree of orientation for various diffraction planes of ZnO is shown in Table 1. The data agree well with the JCPDS data (Fig. 2). However, the value of O_{hkl} for the (002) plane is quite higher than the value reported in JCPDS. This is due to the variation in growth conditions leading to a higher multiplicity factor for the (002) plane. The interplaner spacings (d_{hkl}) for different observed (hkl) planes were calculated from the Bragg's equation [22]

$$2d\sin\theta = n\lambda.$$

The calculated and reported d values are shown in Table 1. A small difference was observed due to the existence of strain in crystals. The crystallite size and strain were calculated using Scherrer's formula [19-22]

$$R = \frac{0.89\lambda}{\beta\cos\theta},\ \varepsilon = \frac{\beta}{4\tan\theta}.$$

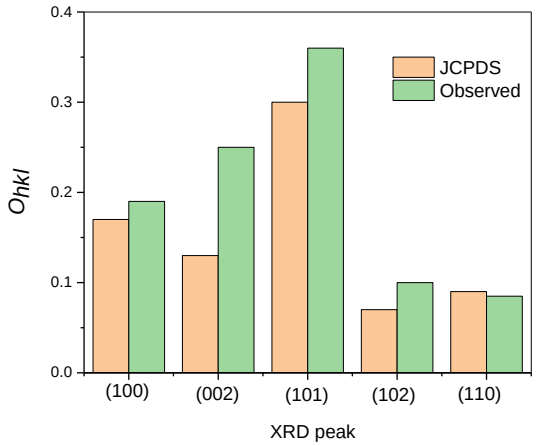

Fig. 2 – Comparison of the observed degree of orientation of various (hkl) planes with that from JCPDS

Here, λ is the wavelength of X-ray used, β_{hkl} is the full width at half maximum (FWHM) corresponding to the glancing angle θ, and K is a constant with a value of 0.89. We calculated both the crystallite size and strain for all the diffraction peaks. For the calculation we fitted the diffraction peak with Gaussian function (Fig. 3). The variation of the FWHM of various diffraction peaks is also shown in Fig. 3.

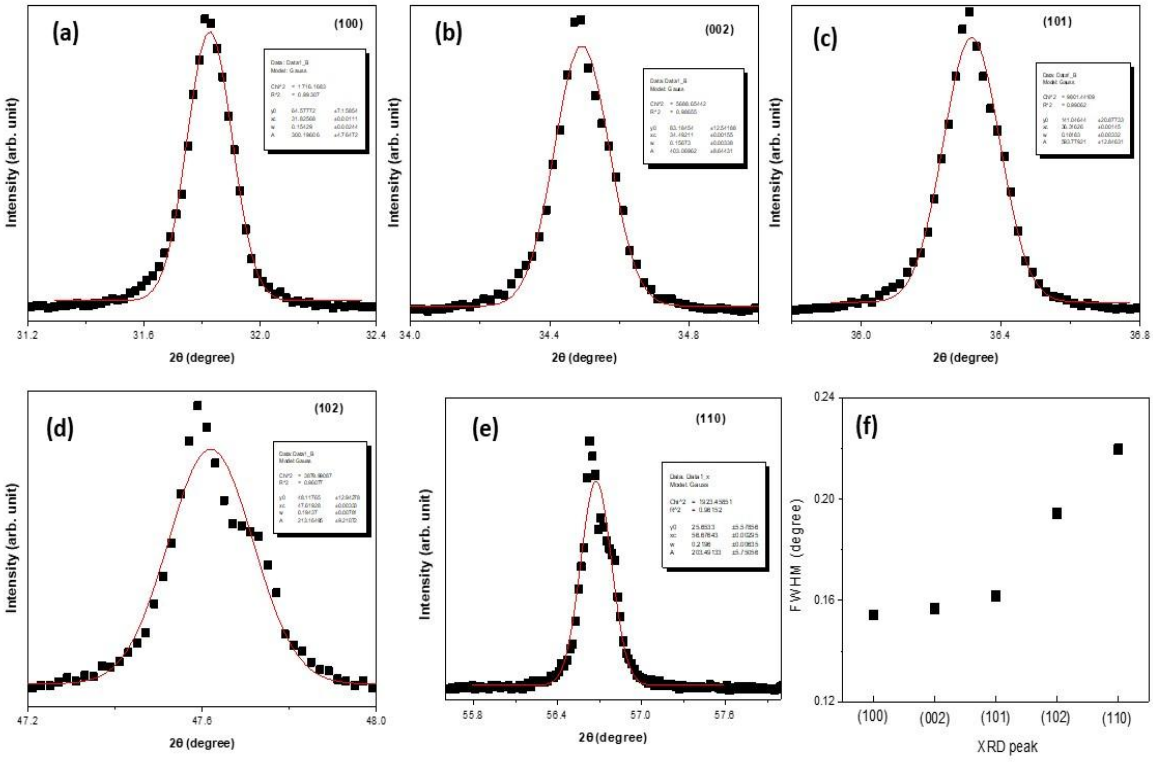

Fig. 3 – Gaussian fitting of the observed diffraction peaks (a-e), calculated values of the FWHM for various diffraction peaks (f)

The value of the crystallite size calculated from different diffraction peaks is shown in Table 2. The average crystallite size was found to be 47.67 nm. The variation of strain over different lattice planes is shown in Fig. 4. The strain is highest for the (100) plane and lowest for the (110) plane. This is due to the difference in the number of atoms per unit area of the planes.

The dislocation density (Δ), representing dislocation line lengths per unit volume in the crystal, was calculated from the crystallite size using the relation [22]

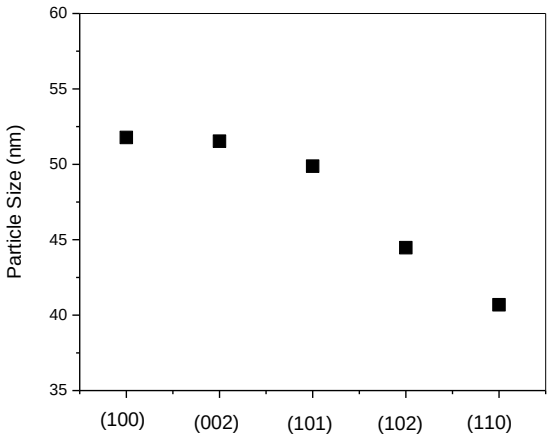

Fig. 4 – Crystallite size calculated from various diffraction peaks

$$\Delta = \frac{1}{R^2}.$$

The dislocation density for different crystallographic planes is shown in Table 2. A significant change in the dislocation density was observed for different planes. It is due to the growth anisotropy of the crystal.

The degree of crystallinity was calculated from the formula [22]

$$X_{hkl} = \left(\frac{0.24}{\beta_{hkl}}\right)^2.$$

A higher value of crystallinity is desired, representing the formation of coarse grains. The values of X_{hkl} for various planes are shown in Table 2. It remains almost constant for (100), (002) and (101) peaks and decreases largely for (102) and (100) peaks. This is because the last two planes have a higher growth rate. So, these planes will be small in size in the crystals. Hence, the grain size will also be smaller compared to the first three planes.

Specific surface area is an important parameter representing the available surface area per unit mass of the material. It is defined as [22]

$$S = \frac{6 \cdot 10^7}{R\rho}, cm^2 / g.$$

The average specific surface area of the material calculated from the XRD pattern was found to be $2.26 \cdot 10^5$ $cm^2 g^{-1}$.

The following equation was implemented to evaluate the lattice parameters [22]:

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

The lattice parameters of the wurtzite crystal were found to be $a = 3.2467$ Å and $c = 5.2004$ Å, which is close to the standard reported value. The bond length of Zn–O can be calculated from the following equations [22]:

$$L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2}, \; u = \left[\frac{1}{3}\left(\frac{a}{c}\right)^2 + 0.25\right].$$

The Zn–O bond length was calculated to be 1.9757 Å. The volume of the wurtzite lattice is expressed as [22]

$$V = \frac{\sqrt{3}}{2}\left(a^2 c\right) = 0.866\left(a^2 c\right).$$

The lattice volume was calculated to be equal to $V = 47.47336$ Å^3. The data are in good agreement with the standard reported data.

All the calculated parameters for different diffraction peaks are summarized in Table 2.

Table 1 – Comparison of the observed XRD data with JCPDS data (Card No. 361451)

(*hkl*) planes	2θ (degree)		Intensity (arb. unit)		O_{hkl}		d_{hkl} (Å)	
	JCPDS	Observed	JCPDS	Observed	JCPDS	Observed	JCPDS	Observed
(100)	31.770	31.825	57	52	0.17	0.19	2.8143	2.8117
(002)	34.422	34.492	44	69	0.13	0.25	2.6033	2.6002
(101)	36.253	36.316	100	100	0.30	0.36	2.4759	2.4737
(102)	47.539	47.619	23	29	0.07	0.10	1.9111	1.9096
(110)	56.603	56.670	32	23	0.09	0.085	1.6247	1.6242

Table 2 – Summary of various crystal parameters calculated from the XRD peaks

(*hkl*)	Crystallite size (nm)	Strain ($\times 10^{-3}$)	Sp. surface area $cm^2/g \times 10^5$	Dislocation density $\times 10^{-4}$ (nm^{-2})	X_{hkl}	*a* (Å)	*c* (Å)	*c*/*a*	Lattice volume (Å^3)	Bond length (Å)
(100)	51.78297	2.4162	2.06686	3.7293	2.3108					
(002)	51.5355	2.2452	2.07678	3.765187	2.2573					
(101)	49.8806	2.20689	2.14547	4.01917	2.0933	3.2467	5.2004	1.60176	47.47336	1.9757
(102)	44.4707	1.91085	2.4067	5.05651	1.5425					
(110)	40.6923	1.7762	2.6302	6.0391	1.1954					

4. CONCLUSIONS

In conclusion, the XRD pattern of ZnO nanostructures has been analyzed in detail to determine the crystallite size for different crystallographic directions. The calculated values of the lattice parameters match well with those reported by others. The growth anisotropy and crystallinity are also analyzed. The material has a large specific surface, which will be useful for use in chemical and gas sensor devices. The dislocation density is found to be very small, indicating the formation of a good-quality crystalline material. The lattice volume and Zn–O bond length are also calculated and agree well with the reported data. The results will be very useful in understanding the crystallographic properties of ZnO nanostructures.

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Аналіз профілю піків рентгенівської дифракційної картини наноструктури оксиду цинку

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Рентгенівська дифракція є важливим інструментом для аналізу кристалічної структури будь-якого кристалічного матеріалу. За допомогою відповідного аналізу піків рентгенівської дифракції можна визначити розмір кристалітів та мікронапруження. Також можуть бути визначені інші параметри, такі як анізотропія росту, кристалічність, густина дислокацій та питома площа поверхні. У роботі вивчалася рентгенівська дифракційна картина наностижнів ZnO. Розмір кристалітів і деформацію розраховували для всіх піків дифракційної картини. Середнє значення розміру кристалітів становило 47,7 нм. Для різних кристалографічних площин деформація була різною. Використовуючи стандартну формулу, були розраховані параметри решітки структури вюрциту, які виявились рівними $a = b = 3{,}2467$ Å та $c = 5{,}2004$ Å. Підготовлений зразок має дуже велику середню питому площу поверхні $2{,}26\times10^5$ см^{2}г$^{-1}$. Інтенсивність різних дифракційних піків різна, що свідчить про анізотропний ріст кристала.

Ключові слова: Кристалічний, Зерно, Деформація, Анізотропія.