

CURRENT DEPENDENCE GROWTH OF ZN NANOSTRUCTURES BY ELECTRODEPOSITION SYSTEM

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ABSTRACT

Zinc nanostructure with a hexagonal structure (101) is deposited through electrochemical deposition (ECD) using a current density of 2, 3 and 4 Adm^{-2} . The intensity of the emissions changes with respect to the current density. X-ray diffraction (XRD) measurements show that the peaks of these grown samples refer to the Zn with a hexagonal structure and a preferable orientation of (101). Refractive index, optical dielectric constant, and bulk modulus are investigated in the Zn nanostructure. The obtained results are in good agreement with the experimental and theoretical ones.

Key Words: *Nanostructure of Zn; Emission of Spectra, Electrochemical Deposition; Refractive Index; Bulk Modulus.*

INTRODUCTION

A variety of approaches have been employed for producing Zn nanostructures, such as chemical vapor deposition, thermal evaporation, and pulsed laser deposition (Park *et al.*, 2002; Kong *et al.*, 2003; Zuniga *et al.*, 2007; Al-Heuseen, 2010; Katayama and Izaki, 2000; Pauporte and Lincot, 2000; Gao *et al.*, 2006). Zinc oxide (ZnO) semiconductors have a promising future. In the development of Zn-based optical devices, the search for effective low-cost techniques has led to a chemical-related method called Electrochemical Deposition (ECD) (Gu and Fahidy, 1999; Chen *et al.*, 2006). Therefore, the high-efficiency detection of ultraviolet emissions is possible using Zn-based optical devices (Pauporte and Lincot, 2000). ECD differs from other methods as follows: the thickness and surface morphology can be controlled by growth parameters; the deposition rate is relatively high; the experimental setup is low cost; the processing temperature is low; and the ease of impurity doping is evident (Yiwen *et al.*, 2007; Vanheusden *et al.*, 1996; Reshchikov and Morkoc, 2005). The surface condition of the substrate effect on the formation of ZnO was studied by Yiwen Tang *et al.*, (2007) using three-electrode electrochemical cells. This work reports the influence of the current density on the structural and optical properties of Zn nanostructures grown on stainless steel panel (302B) using the ECD technique. Structural and optical properties of the samples were measured using Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) were investigated theoretically using specific models of the Zn nanostructure. The effects of the current density on both structural and optical properties were discussed.

MATERIALS AND METHODS

The Zn nanostructure was deposited by ECD technique through AR grade Zinc sulfate [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Merck India- 0.28 M] aqueous solutions at room temperature. Using a simple Zn as the anode and the stainless steel panel (302B) as the cathode. The distance between the electrodes was about 5 cm. Electrodeposition was carried out by changing the current density between 2, 3 and 4 Adm^{-2} . The pH was measured by digital meter (systronics), and the deposition was recorded for every 30 seconds up to 30 minutes. All the products of Zn film were characterized using XRD, PANalytical X'Pert PRO diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54\text{\AA}$) at the X-ray scan rate was 1min^{-1} for 2θ ranging from 10° to 90° and FESEM model JEOL- JSM 6701F.

RESULTS AND DISCUSSION

Morphology of Zn films

The FESEM images of the Zn nanostructure deposited on stainless steel panel using different current densities of the film deposited by ECD are shown in (Figure 1). The surface morphology of the Zn sample deposited at 2 Adm^{-2} shows a particle-like structures grew onto the surface, these particles superimposed on each other's Figure1 (a). Moreover, they are in a different direction with their tips and are deposited to be set up with no uniform shape. When the current density applied on the cell is increased to 3 Adm^{-2} , the Zn^{+2} separates from the zinc sulphate under the influence of the applied electric field to the cell. It moves to the cathode faster than the previous sample and will melt in water. The latter will then bond with oxygen to make ZnO particles, which are arranged as in a uniform and compact manner. Increasing the current density to 4 mAdm^{-2} Zn^{+2} will separates faster, leading to more Zn^{+2} ions than oxygen. With the shapes of the hexagonal destroyed, Zn particles with irregular shapes and a much less compact structure [Figure 1(c)] than the previous two samples emerge, thereby affecting the optical properties of the films.

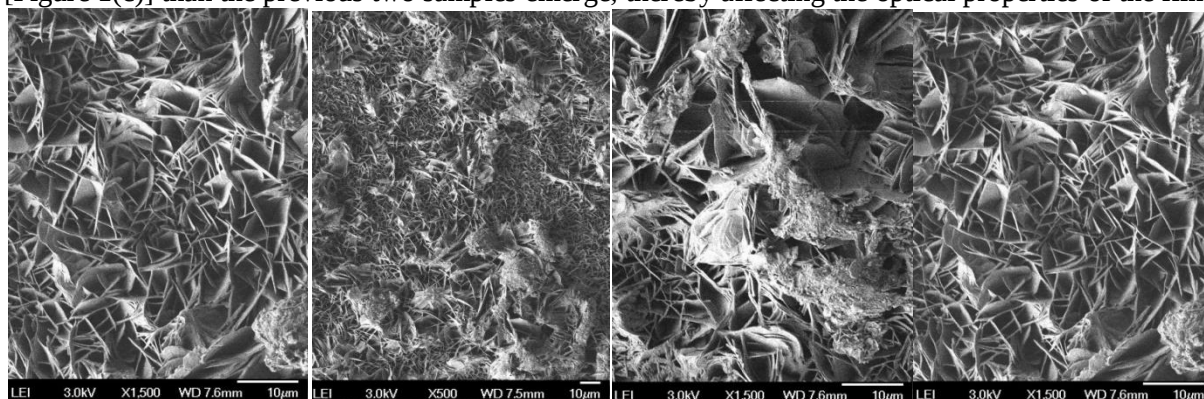


Figure 1: FESEM micrographs (at magnification $\times 2,000$) of samples SRRCF01, SRRCF11, SRRCN01 and SRRCN11 of Zn films using different current densities: (a) 1 (b) 2, (c) 3 and (d) 4 Adm^{-2}

Optical properties of Zn nanostructure

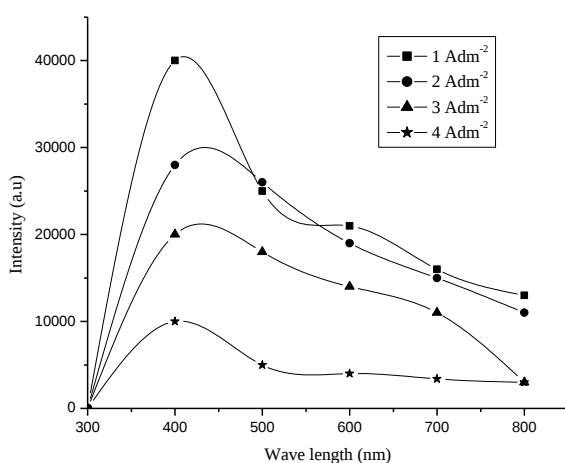


Figure 2

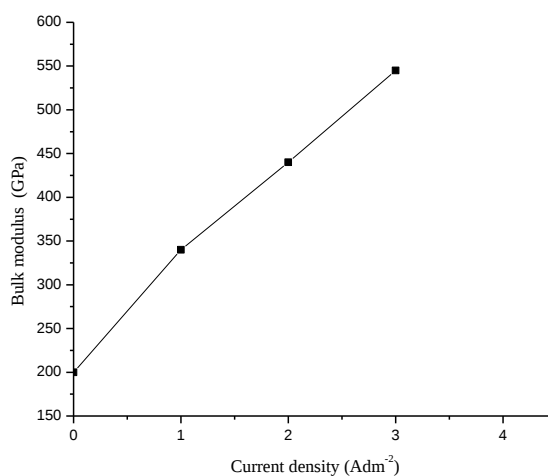


Figure 4

Figure 2: spectra of Zn films using different current densities: 1, 2, 3 and 4 Adm^{-2}
Figure 4: Fitted variation of bulk moduli for Zn as a function of current densities

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The spectra of the Zn nanostructure deposited on Steel panel at room temperature are shown in Figure 2. All samples grown using ECD have a two-peak spectra. The sample grown at 3 Adm^{-2} shows the highest intensity emission, whereas the other, which is grown at 4 Adm^{-2} shows the lowest intensity emission. The peak wavelengths for the near-band-edge emission are 355, 360, and 358 nm for the samples deposited at 2, 3, and 4 Adm^{-2} , respectively. These peaks are generated by the recombination of the excitations through an excitation–excitation collision process (Vanheusden *et al.*, 1996). The spectra were observed to be slightly shifted in the samples deposited with 2 and 4 Adm^{-2} compared with the sample of 3 Adm^{-2} , this phenomenon indicates that the compressive stress takes place in these two samples. The appearance of the shifted emission may be correlated with the development of highly anisotropic structures in the morphology. Based on available literature, many defects related to the spectra have been reported (Reshchikov and Morkoc, 2005). The reason for the presence of this peak may be related to the excitation that is bound to structural defects, strain-induced structural defects, incorporation of impurity-induced disorder, or surface defects during growth process.

The narrow peak at 358 nm with a high intensity of near-band-edge emission as well as the decrease in the peak of emission observed in Figure 2 resulted from high crystallization. This finding indicates that the Zn grown at 3 Adm^{-2} has the best crystallization. As for the emission that is related to sub-band transition, the peak wavelengths are about 512, 530, and 510 nm for the samples deposited at 2, 3 and 4 Adm^{-2} , respectively. This band may be related to the defects in the samples, including vacancies, interstitials, and antisites. Therefore, the difference in the intensity of the peak indicates that the level of defects in the samples is responsible for the recombination. The sample deposited at 3 Adm^{-2} shows that the lowest intensity suggests the lowest level of defects, whereas the sample deposited at 4 Adm^{-2} shows that the highest intensity suggests the highest level of defect. These results are consistent with the FESEM images in Figure 1. A broad emission from the Zn nanostructure stronger can be observed in the Zn samples grown at a current density of 2 and 4 Adm^{-2} . This finding is related to the high quantity of the surface vacancies and defects of the Zn, such as VZn.

An oxygen vacancy has three possible charge states: neutral oxygen vacancy (VO^0), singly ionized oxygen vacancy (VO^+), and doubly ionized oxygen vacancy (VO^{++}). The oxygen singly ionized state is unstable, and the transition involving it can be seen as emission in spectra. Therefore, oxygen vacancies are either in the neutral or doubly charged state. The sample deposited at 2 Adm^{-2} as confirms that the element ratio of Zn:O indicates that this sample is O-rich. Therefore, the main point of defects should be the Zn vacancy (VZn) defects. Figure 1 shows that the element ratio of Zn:O changes with the other two samples by increasing the current density, indicating that the Zn ion transfer becomes faster and that the rate of Zn atoms compound with oxygen in obtaining pure ZnO increases with the current density of 3 Adm^{-2} . As the current density increases, Zn atoms also increase as a result of the fast-moving Zn ions. Zn atoms are diffused to remain at the interstitial sites and act as shallow donors. This ratio indicates that the green luminescence in the samples is deposited at 4 Adm^{-2} because of the oxygen vacancies.

Based on this discussion, reducing the defects by choosing an appropriate current density is possible, leading to a reduction of emission. The refractive index n is a very important physical parameter related to the microscopic atomic interactions. From a theoretical viewpoint, there are two different approaches to this subject: the relation between the refractive index and the density, and the local polarizability of these entities (Balzaretti and Jornada, 1996). As a result, many attempts have been made to relate the refractive index to the energy gap E_g through simple relationships (Ravindra *et al.*, 1979; Herve and Vandamme, 1995; Ghosh *et al.*, 1984; Penn, 1962; Van, 1969; Samara, 1983). The various relations between n and E_g are reviewed in the current paper. Ravindra *et al.*, (1979) presented a linear form of n as a function of E_g .

$$n = \alpha + \beta E_g \quad [1]$$

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Where $\alpha = 4.048$ and $\beta = -0.62 \text{ eV}^{-1}$. Herve and Vandamme (1995) proposed an empirical relation as follows:

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \quad [2]$$

Where $A = 13.6$ and $B = 3.4 \text{ eV}$. As regards Ghosh *et al.*, (1984) found an empirical relationship based on the band structure and quantum dielectric considerations of Penn (1962) and Van (1969):

$$n^2 - 1 = \frac{A}{(E_g + B)^2} \quad [3]$$

Where $A = 8.2E_g + 134$, $B = 0.225E_g + 2.25$ and $(E_g + B)$ refers to an appropriate average energy gap of the material. The calculated refractive indices of the end-point compounds are listed in Table 1.

Table 1: Calculated refractive indices of Zn films under different current densities using Ravindra *et al.*, (1979), Herve and Vandamme (1995), and Ghosh *et al.*, (1984) models

Current density (Adm^{-2})	n				ϵ_∞		
0	2.064a	2.290b	2.329c	2.008d	4.260a	5.244b	5.424c
1	1.902a	2.220b	2.278c		3.617a	4.928b	5.189c
2	1.915a	2.225b	2.282c		3.667a	4.950b	5.207c
3	1.890a	2.215b	2.275c		3.572a	4.906b	5.175c
4	1.885a	2.210b	2.270c		3.577a	4.915b	5.205c
5	1.882a	2.205b	2.265c		3.582a	4.922b	5.185c

^a[Ravindra *et al.*, 1979], ^b[Hervé and Vandamme, 1995]. ^c[Ghosh *et al.*, 1984] and ^d[Penn, 1962]

This relationship is verified by the calculation of the optical dielectric constant ϵ_∞ , which depends on the refractive index. Note that $\epsilon_\infty = n^2$ (Weast, 1973). The investigated refractive indices n are clearly in agreement with the experimental value (Samara, 1983), and the model of Ravindra *et al.*, (1979) agrees well for Zn films in enhancing the photo conversion. The high absorption and low reflection may be attributed to the increase in efficiency of optoelectronic devices.

3.2 Structural properties of Zn nanostructure

The typical XRD pattern of a Zn nanostructure deposited at different current densities reveals seven peaks, as shown in Figure 3. All the samples showed similar XRD patterns that demonstrate high-crystalline hexagonal (101) structures of Zn. The diffraction peaks are sharp and have a high intensity, indicating that the samples are highly crystalline in terms of their nanostructure. Decrease in distance between electrodes during deposition process results in decrease in specific energy density. Samples SRRCF01, SRRCF11, SRRCN01 and SRRCN11 are best in term of energy density as below.

The sample deposited at 2 Adm^{-2} [Figure 3(a)] shows the epitaxial growth of Zn on steel substrate, This growth can be observed from the presence of the peaks at 36.05, 38.77, 43.01, 54.11, 70.45, 81.91, and 86.39, which correspond to (002), (100), (101), (102), (111), (200), and (201) orientations, respectively.. As shown in the XRD data, the (101) direction in Figure 3 is the preferred orientation for the three samples. The peak intensity of this orientation increased and became narrow for the sample grown at 3

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Adm^{-2} . At the same time, the peak intensity of the (100) orientation was higher than that of the (002) orientation for the sample grown at 2 Adm^{-2} , which underwent reorientation. However, the peak intensity of the (002) orientation was higher in the other samples, indicating that the c-axis orientation significantly improved, as seen in Figures 3 b, c and d.

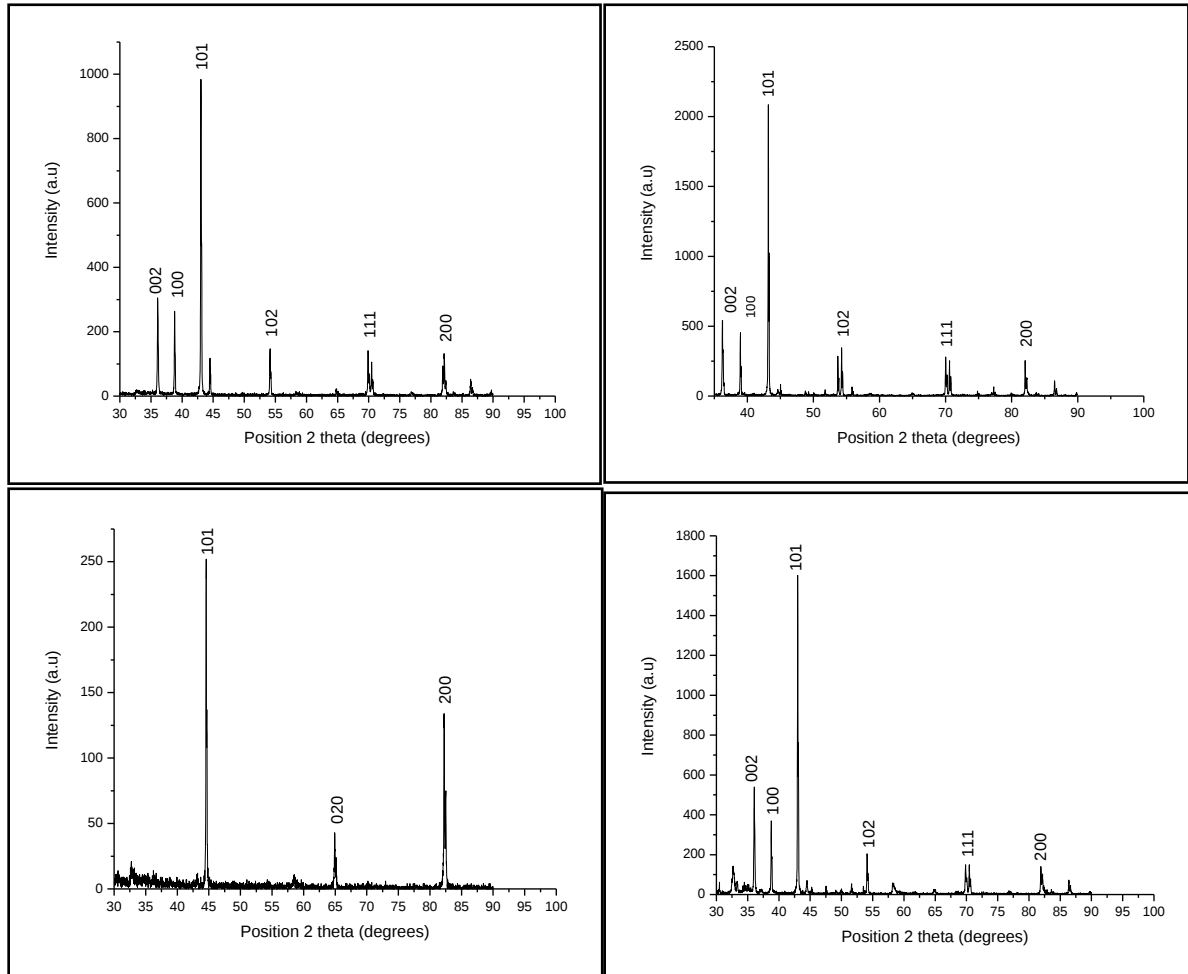


Figure 3: XRD spectrum of Zn films grown at various current densities: (a) 1 (b) 2, (c) 3 and (d) 4 Adm^{-2}

Empirical approaches have been developed (Phillips, 1973; Harison, 1989) to compute the properties of materials. In many cases, the empirical methods offer the advantage of applicability to a broad class of materials and illustrating trends. Cohen (1985) established an empirical formula for the calculation of bulk modulus B_0 , which is based on the nearest-neighbor distance. His result agrees with the experimental values. Lam *et al.*, (1987) derived an analytical expression for the bulk modulus from the total energy. This expression is different in structure from the empirical formula but gives similar numerical results. They also obtained an analytical expression for the pressure derivative B'_0 of the bulk modulus. Al-Douri *et al.*, (2004) group used a concept based on the lattice constant to establish an empirical formula for the calculation of the bulk modulus. The calculated results agree with the experimental data and other calculations. The hypothetical structure and simulation of the experimental conditions are required to use this formula practically.

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The dominant effect is the degree of covalency characterized by homopolar gap E_h (Phillips, 1973), which shows the bulk modulus can be related to the lattice constant. One reason for presenting these data in the current work is that the validity of calculations is not restricted in a computed space. An important reason for studying B_0 is the observation of clear differences between the lattice constants for different Zn samples, as seen in Table 2.

Table 2: Energy gaps (eV), lattice constants (Å), and bulk modulus (GPa) of Zn films under different current densities along with theoretical (Zhu *et al.*, 2012; Charifi *et al.*, 2007) and experimental data (Karzel *et al.*, 1996).

Current density (Adm ⁻²)	Energy gap(eV)	a=b (Å)	c (Å)	B ₀ (GPa)
0	3.2	3.2499*	5.2068* 5.2048 a	128\$
		3.249 a		166a 156.3b 183 c
1	3.4	3.2530*	5.2130*	510.233\$
2	3.42	3.2501*	5.2071*	511.828\$
3	3.44	3.2488*	5.2054*	512.545\$
4	3.46	3.2476*	5.2046*	513.142\$
5	3.48	3.2468*	5.2034*	514.138\$

*Measured value, \$ calculated value ^a[Zhu *et al.*, 2012], ^b[Charifi *et al.*, 2007] and ^c[Karzel *et al.*, 1996].

Basis of model is the lattice constant presented in Table 2. The fitting of these data gives the following empirical formula (Zhu *et al.*, 2012):

$$B_o = [3000 - 100\lambda](\frac{a}{2})^{-3.5} \quad [4]$$

Where a – is the lattice constant (in Å), and λ – is an empirical parameter accounting for the effect of ionicity; $\lambda = 0; 1, 2$ for groups IV, III–V, and II–VI respectively. In Table 2, the calculated bulk moduli values are compared with the theoretical (Zhu *et al.*, 2012; Charifi *et al.*, 2007) and experimental (Karzel *et al.*, 1996) values fitted in Figure 4. The bulk modulus of the Zn nanostructure increases as the current density increases, including the attributes of the nanostructure. We can conclude that the calculated bulk modulus is in accordance with the other results (Zhu *et al.*, 2012; Charifi *et al.*, 2007; Karzel *et al.*, 1996). These studies exhibit the same chemical trends as those found in the values derived from the experimental values, as shown in Table 2. The calculated bulk modulus agrees well with the other data.

Conclusion

Zn nanostructure was produced using the ECD technique. The optical properties were measured, revealing that the energy band gap depends on the growth parameters and current density. The defects in the Zn nanostructure obtained in the samples deposited at low and high current densities are considered the main reason for the emission in spectra. The defects can be reduced by choosing an appropriate current density, as this parameter affects the structural properties. High-crystalline Zn was then obtained by controlling the current density. The current density of 3 Adm⁻² gave the best crystallization and high intensity. The obtained results of the refractive index, optoelectric constant, and bulk modulus suggest that the Zn nanostructure is more suitable for highly sensitive.

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