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Effect of precursor concentration and growth parameters on the morphology of ZnO rods grown by hydrothermal process

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The systematic study of controllable morphology and crystallization of hydrothermally grown ZnO rod arrays by changing the precursor concentration, growth time and growth temperature was carried out. It is observed that by changing the concentration, the density and dimension of ZnO rods have been varied. On going from lower concentration to higher concentration, ZnO nanostructure changes from rod like to thin film morphology. It is also found that the length and diameter of ZnO rod follows a linear relation with growth time. As the growth temperature increases, the aspect ratio of the ZnO rods was found to be increased. The properties of ZnO rods and their growth mechanisms were studied using x-ray diffraction, HR SEM with EDAX, UV-Visible spectroscopy and photoluminescence measurements. Room temperature PL spectra show a strong UV emission peak indicating that the grown ZnO rods are highly crystalline.

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1. Introduction

ZnO is a key functional material with a wide band gap (3.37 eV) and a large excitation binding energy of 60 meV. It is a promising material for optoelectronic nanoscale devices especially in solar cell applications [1]. This material forms in different types of nanostructures (NS). There are many methods used for the synthesis of ZnO NS, like Chemical vapor deposition (CVD) [2], Pulsed laser deposition (PLD) [3], Vapor-Liquid-Solid (VLS) growth [4] and magnetron sputtering [5]. But these methods involve severe working conditions such as high temperature, pressure and complex reaction process. The simple, low cost and environment friendly technique to grow ZnO NS is the hydrothermal method [6]. As the structure of the material changes the physical and chemical properties, the understanding of growth mechanism of the desired morphology of ZnO is necessary for different applications. Pawar et al [7] reported that ZnO has high breakdown strength and excitation stability, which is more suitable for PEC applications than TiO_2. The fabrication of ZnO nanostructure from aqueous solution can be controlled by the pH of the precursor solution, concentration of zinc ions, growth temperature and growth time [8-12]. Apart from that, the ZnO seed film plays an important role in the growth of ZnO nanostructure. The thickness of the film, inclination of substrate [13], annealing temperature of the substrate [14] and presence of impurities influence the formation of ZnO nanostructures. Recently, ZnO nanorod arrays are of specific interest for use as substrates in solar cells and detection applications due to their high surface area and specific crystalline orientation and its large surface area to volume ratio. Achieving large scale and low temperature growth of vertically well aligned ZnO rods is one of the most important issues in ZnO based devices. The dense and well aligned ZnO rods on thin films synthesized by hydrothermal method can satisfy the basic requirement of good optical grade thin films for device applications and has advantages of low temperature, large scale and low cost. In the present investigation, the effect of precursor concentration, growth temperature and time on the morphology of ZnO rod grown by hydrothermal method has been systematically studied.

2. Experimental

2.1 Preparation of ZnO thin films: Sol-gel method

ZnO thin film acts as the seed layer for the growth of ZnO rods. ZnO thin film was deposited on silicon (100) and glass substrate by the sol-gel method. Before deposition, the substrates were cleaned ultrasonically in acetone, ethanol and deionized water each for 15min successively to remove dust and surface contaminations, and then dried at 100°C. After substrate cleaning processes, the substrates were seeded (film deposition) by

sol-gel spin coating method. The seed solution was prepared by mixing 0.05M zinc acetate dihydrate (Zn $(CH_3COO)_2{\cdot}2H_2O$), and 0.05M diethonolamaine (DEA) in absolute ethanol at 60°C under magnetic stirring for 2h. After 2 days of ageing, the prepared sol was used for coating. The coating was carried out at a spin rate of 2500 rpm and spin time of 30 sec followed by drying at 90°C, to evaporate solvent and to remove the organic residuals. Successive coatings have been made for 10 times on the same substrates to obtain the required thickness of the seed films. The coated films were annealed at 400°C for 30 min in a high temperature furnace to get ZnO thin films.

2.2. Preparation of ZnO rods on thin films: Hydrothermal method

The seed substrates annealed at 400°C were placed in an aqueous solution containing 0.05M zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and 0.05M hexamethylenetetramine (HMT) at 90°C for 5 h at a pH value of 6. The grown ZnO rods were then rinsed with de-ionized water and dried at 100°C for few hours.

To examine the effect of precursor concentration, equimolar precursor concentration solutions of different ranges (0.05M to 0.3M) were prepared at 90°C for 5 h. The effect of hydrothermal growth temperature was studied from 70°C to 110°C for 5 h with 0.1M zinc concentration. The influence of growth time was investigated for 3 to 18 h for 0.1M zinc concentration at 90°C.

2.3. Characterization

The crystalline structure of the ZnO nanorod arrays was analyzed using an X-ray powder diffractometer in the 2θ range between 20° and 70°. The surface morphology of the thin films was characterized by using High Resolution scanning electron microscope (HRSEM) (FEI Quanta FEG 200) instrument with EDAX. The optical properties were studied by taking optical absorption of samples using UV–vis spectrometer (Cary5E UV-VIS NIR). The samples were characterized for optical properties through photoluminescence (PL) spectra at room temperature and the data were recorded using fluorescence spectrometer (JY Fluorolog-3-11- Fluorimeter) exiting with 450W xenon lamp.

3. Results and discussion

Fig.1 shows the XRD patterns of ZnO rod arrays. The recorded XRD spectra of ZnO rods correspond to the hexagonal wurtzite structure as given in JCPDS data (Card No.36-1451). No other diffraction peaks were observed, suggesting that only single phase ZnO was formed. The higher intensity of (002) diffraction peak indicates that the ZnO rods were preferentially orientated along the c-axis.

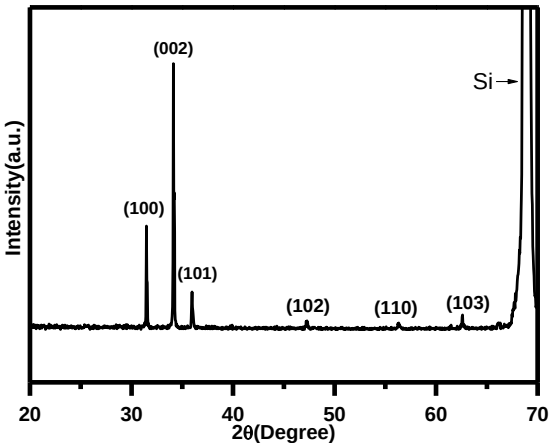

Fig.1. Powder X-ray diffraction pattern of ZnO rods with 0.1M zinc concentration grown at 90°C for 5 h.

3.1 Effect of Precursor Concentration

The length, diameter and density of the ZnO rods varied with the precursor concentration as shown in Fig.2 (a-d).Low concentration of aqueous solution yields thin rods of average length 1.5 µm. Fig.2 shows that the top ends of ZnO rods are well faceted with flat hexagonal symmetry. Hexagonal symmetry plane indicates that the rods grow along c-axis. When the concentration is high, micro-sized diameter of around 1.4 µm and average length 7 µm with densely packed c-axis aligned ZnO rods were formed as revealed from HR-SEM results. The increase in zinc concentration accelerates small bundle of ZnO nanorods coalesce together to form larger dimension of ZnO to reduce the surface energy [8]. Rods were merged together and formed thin film structure, when the concentration was increased more than 0.2M as shown in Fig.2 (d). EDAX spectrum confirms the variation of microstructure of ZnO due to the concentration of the precursor and is shown in Fig.3.

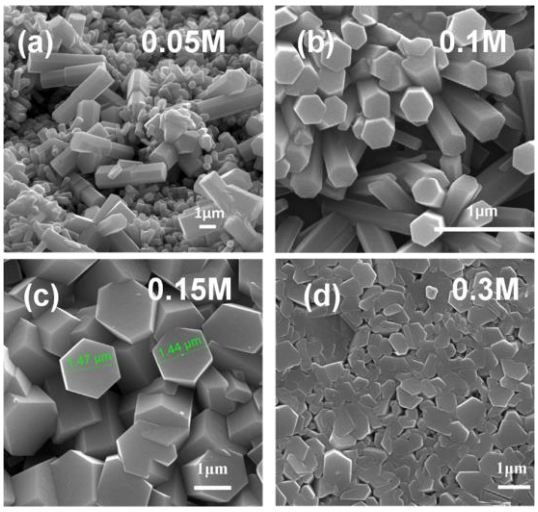

Fig.2 HRSEM images of ZnO rods grown with different precursor concentrations at 90°C for 5 h

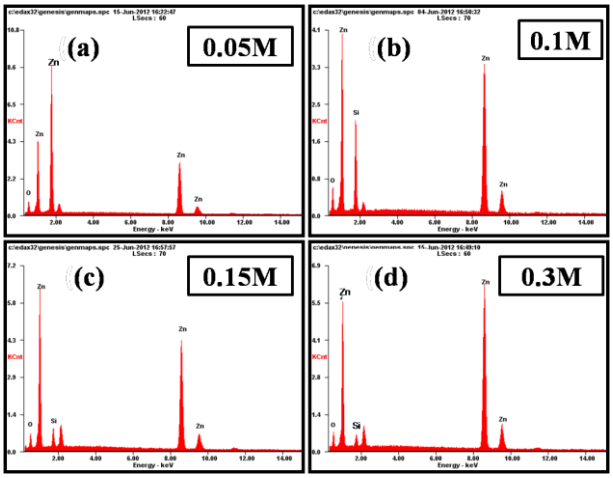

Fig.3 EDAX spectra of ZnO rods with 0.05M ,0.1M ,0.15M, and 0.3M zinc concentrations grown at 90°C for 5 h.

3.2 Effect of growth time

Since the growth time is an important factor to control the size of ZnO structure, the effect of growth time on ZnO rods was investigated with equimolar (0.1M) concentration of zinc acetate dihydrate and HMT at a constant temperature of 90°C and pH value of 6 for 3 h, 5 h and 10 h. The HR-SEM images (Fig.4a-c) reveal that the rods start emerging from the nucleation site after 3 h and lateral growth seems to be more significant than axial growth.As time increases, both axial and lateral growth increases which increase linearly the size and density of the rod as reported by Wang et al [15]. For more than 10 h, there was no change in dimension of rods, but cracks were observed on the surface of the ZnO rods as shown in the Fig.4d.

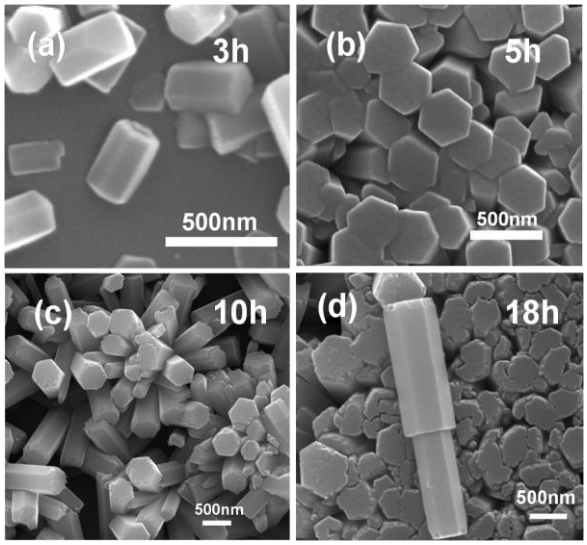

Fig.4 HRSEM images of ZnO rods (0.05M zinc concentration) grown at 90°C for 3 h,5 h,10 h and 18 h

3.3 Effect of growth temperature

The effect of hydrothermal growth temperature on the formation of ZnO rods were investigated from 70°C to 110°C for 5 h with 0.1M zinc concentration. Fig.5 shows the HR-SEM images of ZnO rods grown with different temperatures (70°C, 90°C and110°C) and plot of aspect ratio of ZnO rods vs. growth temperature. The temperature is an important factor for maintaining high aspect ratio of haxagonal shape ZnO rods. In this study, the optimum temperature for obtaining a high aspect ratio and well-defined hexagonal shape of the ZnO rods is found to be 90°C. It is evident that the rod structure does not change with growth temperature, but the size of the rod changes with temperature. The rod structures are typically 1.2 µm in length and 250 - 350 nm in diameter for growth temperature 70°C. When the temperature increases up to 90°C, length and diameter of the rod increases to around 2-3 µm and 500-700 nm respectively. At 110°C, there is no appreciable change in aspect ratio as reported by Amin et al 2011[12]. The aspect ratio of the ZnO rods can be determined by the relative growth rate of the polar surfaces and non-polar surfaces. This means that the relative growth rate of polar surface to non-polar surface at low temperatures is smaller than that at high temperatures.

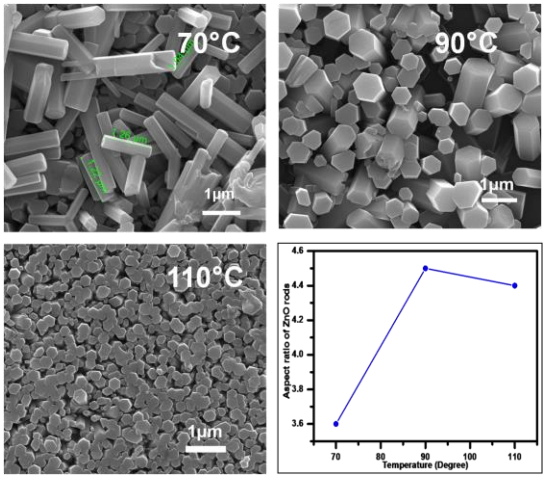

Fig.5 HR-SEM images of ZnO rods grown for different growth temperatures (0.1M zinc concentration) with growth time of 5h and plot of aspect ratio of ZnO rods vs. growth temperature.

3.4 Optical properties

Optical properties of ZnO rods are very important for many of its potential applications. Fig.6 (a) shows the optical absorbance spectra of ZnO rod arrays on thin film recorded in the wavelength range from 300 to 800 nm. The spectra reveal that ultraviolet absorption edges at approximately 380 nm were observed. The optical absorption at absorption edge corresponds to the transition from valence band to conduction band, while the

absorption in the visible region was related to some local energy levels caused by some intrinsic defects [16].

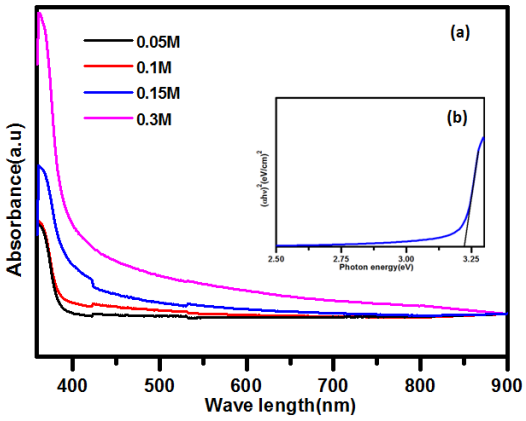

Fig.6 Optical absorbance spectra of ZnO rods with different concentrations. Inset Plot of $(\alpha h\upsilon)^2$ vs hυ of ZnO rod film with 0.1M concentration.

This spectrum reveals that low concentration ZnO rod array has low absorbance in the visible region, which is a characteristic of ZnO [17]. The absorbance has increased with increase in precursor concentration. ZnO rod arrays shows that absorption edge shift at low wavelength attributed to various factors such as electronic defects, vacancies etc.,[18].The optical band gap energy values 'Eg' are calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus hν plot as shown in fig6 (b). Band gap energy 3.22 eV is obtained for 0.1M Zn concentrated ZnO rod array film as reported by Dariani et al [19].From the plot it was determined that the film has direct band gap, and this property is suitable for photovoltaic applications [20].

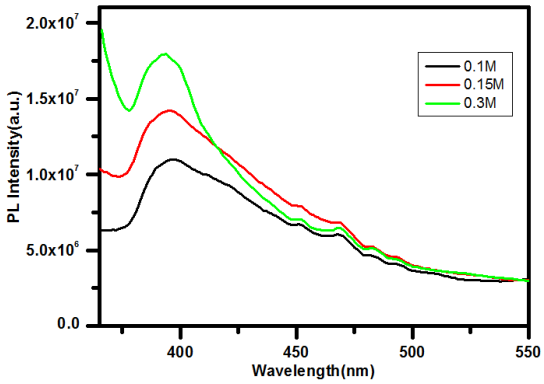

Fig.7 Room temperature PL spectrum of ZnO rod arrays with different precursor concentrations

The PL from ZnO rod array has always composed of a near-band-edge (UV) emission and a broad, deep-level (visible) emission at room temperature. The visible emission was usually ascribed to various intrinsic defects produced during the synthesis of ZnO, such as zinc vacancy and oxygen vacancy [21]. Fig.7 showed the room temperature PL spectra of the ZnO rod with different concentrations. The PL spectra reveal similar features for all samples. It shows that a strong broad UV emission peak at approximately 392 nm. This emission corresponds to the recombination of free excitons between conductive band and valence band and is called near band-edge emission [22].No other peaks such as green emissions (approximately 520 nm) were found. It should be mentioned that the green emission resulted from the radiative recombination of a photogenerated hole with electron occupying the oxygen vacancy [23].The strong UV emission in the PL spectra indicates that the ZnO rods have a good crystal quality with few oxygen vacancies.

3.5 Growth mechanism of ZnO rods

During hydrothermal process of ZnO rod synthesis, HMT hydrolysis the precursor solution to produce OH^- ions and ammonia. Then, the OH^- reacted with Zn^{2+} and thermally decomposed into ZnO. To grow ZnO structure, HMT can act as a non-polar chelating agent and attach preferentially to the non-polar surfaces (101) and (001) of zinc crystal and promotes vertical growth along (002) direction [24].The relative growth rate of polar and non polar surfaces determines the aspect ratio of as grown ZnO rod arrays. During growth process increase in precursor concentration produces more Zn $(OH)_2$ in the precursor solution and it will increases the speed of the growth. These processes are endothermic and it will hinder ZnO rod array growth, as a result thicker rod arrays were obtained for high precursor concentration .The chemical reactions of the growth mechanism of ZnO are given by H. Wang et al [25].

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \rightarrow NH_4 + OH^-$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

The growth process could be divided into three stages, as controlled by growth kinetics. The first stage is characterized by lateral growth, the second is dominated by axial growth, and the third is described as proportional growth. Moreover the growth temperature controls the mobility and diffusion length of ions on the substrate which plays an important role in the crystal growth [15].

4. Conclusions

The morphological control of ZnO nanorod arrays by adjusting the precursor concentration, growth time and temperature was studied. It is observed that zinc ion concentration changes the density and dimension of the rods. A high concentration leads to polycrystalline thin film. Initially, the growth time increases linearly and after 15 h, the ZnO rods starts collapsing. The aspect ratio of the ZnO rods increases as the growth temperature increase up to 90°C.Optical properties of ZnO nanorod arrays for

various precursor concentrations were also studied which shows that a strong UV emission peak indicating good quality of ZnO film. The properties of ZnO can be controlled by tuning the surface morphology followed by changing the growth parameters to obtain the desired nanostructures for PEC applications. High quality ZnO rods grown in this investigation can be applied on the electrode of dye-sensitized solar cell to increase the contact area between ZnO and dye to enhance the efficiency of dye-sensitized solar cell.

References

[1] V. Dhas, S. Muduli, W. Lee, S.H. Han, S. Ogale, Appl. Phys. Lett. **93,** 243108 (2008).

[2] G.Z. Wang, Y. Wang, M.Y. Yau, C.Y. To, C.J. Deng, D.H.L. Ng, Mater. Lett. **59,** 3870 (2005).

[3] C.H. Bae, S.M. Park, S.E. Ahn, D.J. Oh, G.T. Kim, J.S. Ha, Appl. Surf. Sci, **253,** 1758 (2006).

[4] T. Fang, W. Chng, W. Water, C. Lee, Physica E **42,** 2139 (2010).

[5] S.H. Jeong, B.S. Kim, B.T. Lee, Appl. Phy. Lett. **82,** 2625 (2003).

[6] N. Sakti, S. Kumari, P.S. Gupta, J. of Ovonic Research, **7,** 51 (2011).

[7] P.C. Pawar, J.S. Shaikh, A.A. Babar, P.M. Dhere, P.S. Patil, J. Solar Energy, **85,** 1119 (2011).

[8] Q. Li, V. Kumar, Y. Li, H. Zhang, T.J. Marks, R.P.H.Chang, Chem. Mater. **17,** 1001 (2005).

[9] Y.J. Lee, T.L. Sounart, D.A. Scrymgeour, J.A. Voigt, J.W.P. Hsu, J. Cryst. Growth, **304,** 80 (2007).

[10] Y. Tak, K.J. Young, J. Phys. Chem. B, **109,** 19263(2005)

[11] L. Vayssieres, Adv. Mater. **15,** 464 (2003).

[12] G. Amin, M.H. Asif, A. Zainelabdin, S. Zaman, O. Nur, M. Willander, J. Nano Materials, **2011,** 1 (2011).

[13] F. Jamali-Sheini, J. Ceram. Int., **38,** 3649 (2012).

[14] S. Liu, T. Chen, J. Wan, G. Ru, B.Z. Li, X. Qu, J. Appl. Phys. A, **94,** 775 (2009).

[15] S. Xu, C. Lao, B. Weintraub, Z. L. Wang J. Mater. Res. **23(**8), 2072 (2008).

[16] P.Singh, Ashvani Kumar, Deepak, Davinder Kaur, J. Cryst. Growth, **306,** 303 (2007).

[17] R. Chandramohan, T.A. Vijayan, S. Arumugam, H.B. Ramalingam, V. Dhanasekaran, K. Sundaram, T. Mahalingam, Mater. Sci. Engg. B **176,** 152 (2011).

[18] B.N Pawar, D.H Ham, R.S Mane, T. Ganesh, B.W. Cho, S.H. Han, Appl. Surf Sci. **254,** 6294 (2008).

[19] F. Zahedi, R.S. Dariani, Thin Solid Films **520,** 2132 (2012).

[20] B. Ergin, E. Ketenci, F. Atay, Int. J. Hydrogen Energy**1,** (2008).

[21] A. Dev, S. Kar, S. Chakrabarti, S. Chaudhuri Nanotechnology **17,** 1533 (2006).

[22] Y.C. Chi, M. Yahaya, M.M. Salleh, D.C. Fu, Sains Malaysiana **37** (3), 277 (2008).

[23] K. Vanheusden, W.L. Warren, C.H. Seager, D.K.Tallant, J.A. Voigt, B.E. Gnade, J. Appl. Phys. **79,** 798 (1996).

[24] H. Zhang, D. Yang, S. Li, X. Ma, Y. Ji, J. Xu, D. Que, Mater. Lett. **59,** 1696 (2005).

[25] H. Wang, J. Xie, K. Yan, M. Duan, J. Mater. Sci. Technol. **27**(2), 153 **(**2011).

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