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NOVEL OF ZnO NANOCACTUS ON ITO-GLASS BY ELECTRODEPOSITION METHOD

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ABSTRACT

Novels of nanocactus of Zinc Oxide (ZnO) have been synthesised by electrochemical deposition on the ITO substrate. The aqueous solutions prepared using zinc nitrate, hexamethylenetetramine at room temperature. The orientation and morphology of ZnO were observed with Field Emission Scanning Electron Microscopy (FESEM) and has a high peak intensity at c-axis (002) preferred orientations by investigate with x-ray diffractometer (XRD). The average diameter of the ZnO was estimated around 150nm and the average length of secondary growth of ZnO films was 120nm. EDAX analysis was done for nanocactus ZnO to investigate the ZnO formation with contains Zn and O elements which shown the percentage of weight and atomic values. Photoluminescence (PL) properties of ZnO were indicated the UV emission band peak at 383 nm and the deep level emission band peak at 574 nm wavelength.

Keywords: Zinc oxide, electrochemical deposition, FESEM, XRD, PL spectrum.

INTRODUCTION

ZnO is well known as II-IV semiconductor materials and have unique properties such as has wide band energy at 3.37eV and has high excitation energy 60meV at room temperature (Pearton S. J., *et al.*, 2003)(Thomas D. G. 1960). It is widely used for many applications such as in solar cells (Huang M. H., *et al.*, (2001) light emitting diodes (Li Z. W. and Gao W., 2007) and transducers (EzgFr Y. I. A. D. *et al.*, 2005). Many methods were reported to prepared Nanostructured ZnO films such as chemical vapour deposition (CVD) (Ataev B. M., *et al.*, 1999), pulsed laser deposition (PLD) (Sun X. W.and Kwok H. S., 1999), magnetron sputtering (SP) (Subramanyam T. K., *et al., 2000)*. Some of the researchers studies on the preparation of transparent zinc oxide by cathodic deposition on conductive glasses (Hartnagel H.L., 1995) that have been published. In this work, has been report the ZnO films growth and the properties were investigated after annealing process obtained by electrochemical deposition. The effect of the growth parameter on the morphology and optical properties of ZnO nanocactus films will be discussed.

MATERIALS AND METHOD

ZnO nanocactus was prepared by electrochemical deposition methods as shown in Figure-1. The electrochemical deposition systems were consists three electrode electrochemical cell and the solutions preparation with 0.01M of zinc nitrate hexaydrate ($Zn(NO_3)_2$), 0.1M of potassium chloride (KCl) and 0.01M of hexamethylenetetramine (HMT). The bath solutions were mixed together into DI water with adjustable ph=6.5. The substrate should in conductive condition, so this experiment was used Indium tin-oxide (ITO) glass as has $20\Omega/cm^{-2}$ of resistance that set up as working electrode. The platinum rod used as counter electrode while silver chloride (Ag/AgCl) as reference electrode.

Prior the electrochemical deposition process the solutions were heat up to 100°C and started to deposit by applied voltage at -1.0V in 30 min of deposition time. Finally, samples were cleaning with deionised (DI) water to remove the impurities on the substrates and dried on air.

After deposition, the substrates were annealed in oxygen gas at 500°C in 60 min. The samples were characterized by FESEM (ZEISS Supra 40VP), ZnO nanocactus of crytallinity structure was identified with x-ray diffraction (XRD (Ultima IV, Rigaku). The optical properties were investigated with Photoluminescence spectroscopy (Horiba Jobin Yvon-DU420A-0E-325).

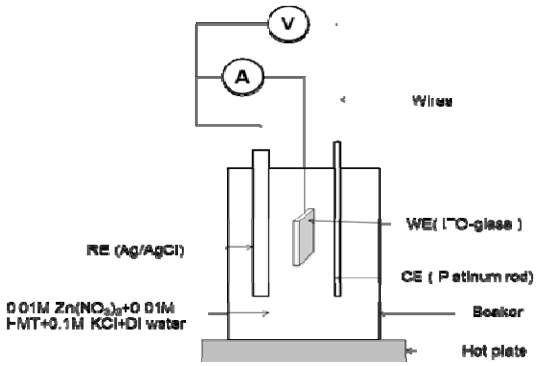

Figure-1. The schematic diagram of electrochemical deposition system set-up.

RESULTS AND DISCUSSIONS

ZnO Electrochemical Studies

The electrochemical deposition process occurred by two characteristics: solutions chemistry process and electrochemistry process, respectively. Basic reaction of oxygen reduction on surface of ITO glass which leads to the hydroxide ions appear, then zinc hydroxide was generated by OH- absorbed near the ITO substrate surface and Zn2+ in the electrolytes. Zinc hydroxide can be transited into zinc oxide when the solution temperature about 65°C (Gan X., *et al*., 2008). The mechanism of chemical reaction was summarized as:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

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

$$Zn(OH)_2^- \rightarrow ZnO + H_2O \quad (3)$$

$$Zn^{2+} + NO_3^1 + 2e^- \rightarrow ZnO + NO_2^- \quad (4)$$

As a result, the eqs. (1) Belong from electrochemistry parts while eqs. (2) and (3) correspond to the solution chemistry process.

Surface Morphology

As shown in Figure-1 gives the FESEM images of ZnO nanocactus elctrodeposition under -1.0V applied voltage. It can be seen the ZnO nanocactus have been uniformly deposited on ITO-glass substrate in 100°C bath solutions temperature in Figures 1(a) and 1(b) shows the ZnO nanocactus hexagonal shapes with an average diameter was 150nm. Secondary growth like thorns appears on the body ZnO hexagonal shapes was measured the average length 160nm and average diameter below than 10 nm

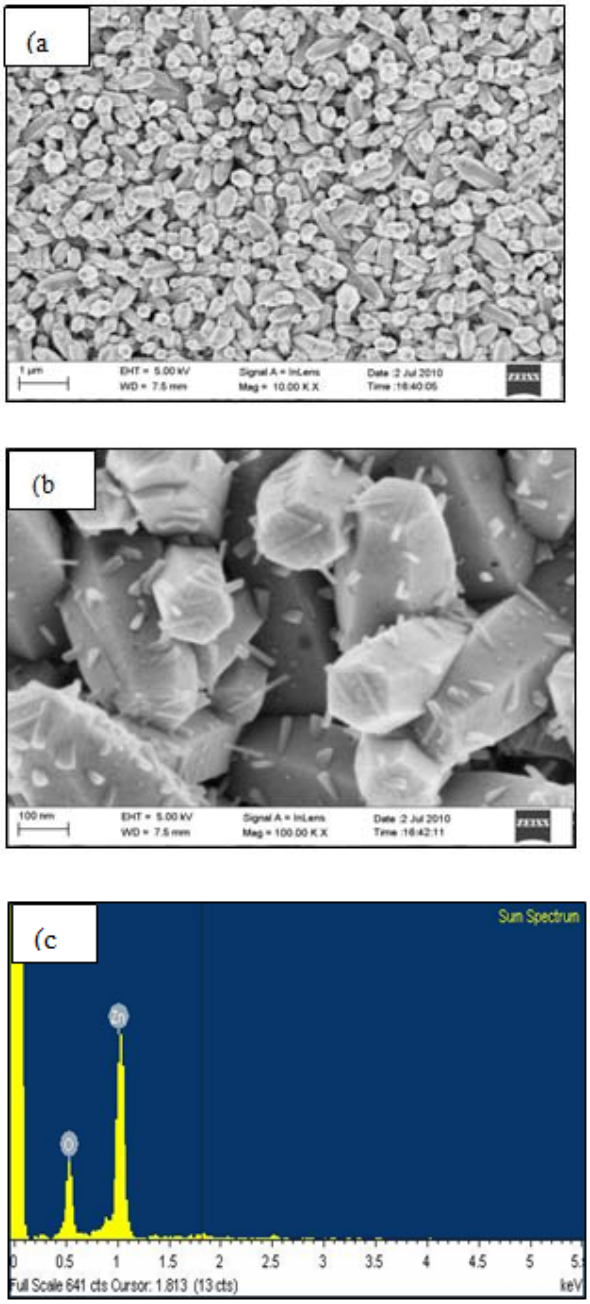

Figure-2. FESEM images of prepared ZnO nanocactus thin film at (a) 10,000 (b) 100,000 magnifications. (c) The EDAX spectrum ZnO nanocactus at 5keV.

As shown by EDAX result, the existence of small O amount in the ZnO nanocactus evidence of oxygen gas supports for the samples to growth more ZnO. Besides that, HMT also play important role in the ZnO nanocactus formation. When the solutions were heated HMT began to hydrolyze into OH- and organic molecules according to eqn. 5 (Feng Xu Y. L. *et al*.,

2010). After initiation of electrodeposition, the negative nature of the growth rates of planes, that is, $V_{(0001)} > V_{(10\bar{1}0)} > V_{(10\bar{1}\bar{1})} > V_{(10\bar{1}0)} > V_{(000\bar{1})}$.

It is corresponding the lateral growth rate at the c-axis or (0002) plane. This was suppresses in eq.1, the presence of mass of OH- became from HMT kinetically. Electrochemically, the electrodeposition process occurred so fast when NO_3^- in comparison to diffusion of Zn^{2+} to the cathode. Consequently, the ZnO was formed only at the tips of the vertical cylindrical crystals, quenching their lateral growth. Finally the ZnO nanoacactus was formed on the ITO substrate shown in eqs (5).

$$(CH_2)_6N_4 + 4H_2O \rightarrow (CH_2)_6N_4 - 4H + 4OH^- \quad (5)$$

Crystalline Structure of ZnO

The XRD patterns of electrodeposited ZnO nanocactus films are presented in Figure-3. It is shown that ZnO nanocactus has hexagonal wurtizite structure type with has space group (P63mc). Lattice parameters a=3.249Å and c=5.206Å which refer from (JCPDS card no. 36-1451). The 2-theta was evaluate from range 20° until 80° and found has six diffraction peaks. There are (100), (002), (101), (102), (103) and (112). As expected, a higher intensity is observed for the (002) diffraction peak in the XRD patterns which indicates highly oriented with c-axes being perpendicular to the ITO glass substrate. It shows evidence that by electrochemical deposition methods produced hexagonal phase ZnO nanocactus.

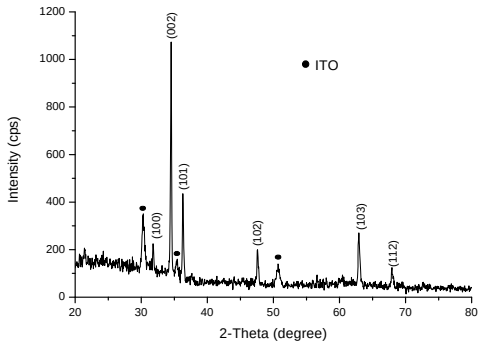

Figure-3. XDR patterns of the ZnO nanocactus by electrodeposited method after annealed.

Photoluminescence (PL) Spectrum

PL spectra were performed at room temperature in the wavelength range of 350nm to 700nm was shown in Figure-4. It can be seen that ZnO nanocactus shows two peaks of emission band. There are UV emissions or near band edge emission (NBE) peak at 383nm. UV emission band peak was contributed the free exciton recombination. At the centre of the PL curve known as the green emission or deep level emission (DLE) at 574nm wavelength. This is due defects in the crystal structure in ZnO, such as oxygen vacancy (Vo), zinc vacancy (VZn), interstitial zinc (Zni), interstitial oxygen (Oi) and antisite oxygen (OZn) (Wang J., *et al*., 2004)(Lim J., *et al*., 2004)(Leiter F., *et al*., 2003).

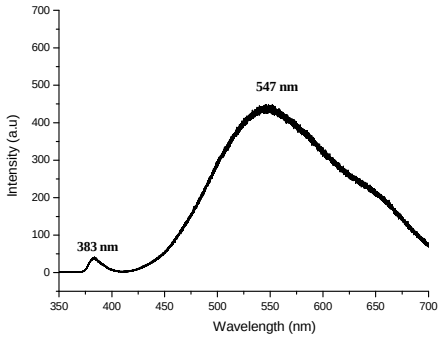

Figure 4. PL spectrum at room temperature of ZnO nanocactus structure thin film.

CONCLUSIONS

ZnO nanocactus structure thin film was successfully prepared using electrodeposition method on the ITO substrate. Uniform and secondary growths of ZnO were observed after annealed in oxygen gas at 500°C temperature. The average diameter of ZnO nanocactus structure hexagonal of 150nm and the average diameter of secondary growth of ZnO was 10 nm. XRD exhibit the sample was crystalline ZnO with high intense (002) plane. UV emission shows at 383 nm and visible emission at 574 nm were investigated by PL spectrum at room temperature. It can be conclude that, newly ZnO nanostructured were found by this method.

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REFERENCES

Pearton S. J., *et al*. 2003. Advances in wide bandgap materials for semiconductor spintronics. Materials Science and Engineering R: Reports. Vol. 40.

Thomas D. G. 1960. The exciton spectrum of zinc oxide. Journal of Physics and Chemistry of Solids. 15: 86-96.

Huang M. H., *et al*. 2001. Room-temperature ultraviolet nanowire nanolasers. Science. 292: 1897-1899.

Li Z. W. and Gao W. 2007. Growth of zinc oxide thin films and nanostructures by wet oxidation. Thin Solid Films. 515: 3323-3329.

EzgFr Y. I. A. D., Liu C., Teke A., Reshchikov M.A., Doğan S., Avrutin V., S.-J.Cho and MorkoA H. 2005. J. Appl. Phys. 98: 041301.

Ataev B. M., *et al*., "Thermally stable, highly conductive, and transparent ZnO layers prepared in situ by chemical vapor deposition," Materials Science and Engineering B: Solid-State Materials for Advanced Technology, vol. 65, pp. 159-163, 1999.

Sun X. W. and Kwok H. S. 1999. Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition. Journal of Applied Physics. 86: 408-411.

Subramanyam T. K., *et al*. 2000. Physical properties of zinc oxide films prepared by dc reactive magnetron sputtering at different sputtering pressures. Crystal Research and Technology. 35: 1193-1202.

Hartnagel H.L., Jain A.K. and Jagadish C. 1995. Semiconducting Transparent Thin Films. Institute of Physics Publishing, London.

Gan X., *et al*. 2008. Growth and characterization of ZnO-SDS hybrid thin films prepared by electrochemical self-assembly method. Applied Surface Science. 254: 3839-3844.

Feng Xu Y. L., Yan Xie and Yunfei Liu. 2010. Seed layer-free electrodeposition and characterization of vertically alinged ZnO nanorod array film. Journal Solid State Electrochemical. 14: 63-70.

Wang J., *et al*. 2004. Luminescence properties of ZnO films annealed in growth ambient and oxygen. Journal of Crystal Growth. 263: 269-272.

Lim J., *et al*. 2004. Effect of annealing on the photoluminescence characteristics of ZnO thin films grown on the sapphire substrate by atomic layer epitaxy. Materials Science and Engineering B: Solid-State Materials for Advanced Technology. 107: 301-304.

Leiter F., *et al*. 2003. Oxygen vacancies in ZnO. Physica B: Condensed Matter. 340-342: 201-204.