



The International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES14

## Pulse electrodeposition of ZnO for thin absorber solar cells

L. Atourki<sup>a\*</sup>, K. Bouabid<sup>a</sup>, E. Ihalane<sup>a</sup>, L. Alahyane<sup>a</sup>, H. Kirou<sup>a</sup>, E. EL Hamri<sup>a</sup>, A. Ihlal<sup>1</sup>,  
A. Elfanaoui<sup>a</sup>, L. Laanab<sup>b</sup>

<sup>a</sup>Laboratory of Materials and Renewable Energy, Faculty of Science, Ibn Zohr University, Agadir, Morocco

<sup>b</sup>LCS, Faculty of Science, University Mohammed V, Rabat, Morocco

### Abstract

This study reports the influence of the condition parameters on the electrodeposition of zinc oxide using  $Zn(NO_3)_2 \cdot 6H_2O$ . ZnO thin films were electrodeposited on FTO and Mo substrate, using a pulse electrodeposition technique. Thin and adherent films have been obtained after 360 cycles. The pulse electrodeposition process was investigated through voltammetry cyclic. The morphology as well as the optical properties of the films was studied by using scanning electron microscope (SEM) and optical transmittance spectroscopy.

© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Selection and peer-review under responsibility of the Euro-Mediterranean Institute for Sustainable Development (EUMISD)

*Keywords* : ZnO, thin film, Pulse electrodeposition, solar cell.

### 1. Introduction

ZnO have been considered as the most promising functional materials due to its large band gap and excellent optical properties [1]. The Zinc oxide films have a lot of important applications such as emitting devices [2], photo-sensors [3], piezoelectric transducers [4] many optoelectronic devices [5]. In thin films solar cells, Zinc oxide is widely used as a transparent conducting oxide in systems based on  $Cu(In,Ga)Se_2$  and CZTS. Furthermore ZnO provide additional optical functions like light scattering and subsequent light trapping or enhance the reflection at the back contact of a solar cell. That is due to its wide band gap and a high concentration of free electron in the conduction band. The wide bandgap is responsible for high optical transmittance and free electrons increase electrical conductivity transmittance. With these properties zinc oxide promise a high conversion efficiencies of a PV solar cell [6-13]. It is also used in several hetero junction systems like  $CuO/ZnO$  [14],  $Cu_2O/ZnO$  [15],  $CdTe/ZnO$  [16]. Different process have been developed for preparing ZnO thin films such as sputtering [17].

\* Corresponding author. Tel.: +212673212961

E-mail address: lahoucine.atourki@edu.uiz.ac.ma

spray pyrolysis [18], chemical bath deposition [19], sol gel [20] and electrodeposition [21]. Electrodeposition has some obvious advantages, such as simple and low cost processes, controllable film thickness, a good quality of film deposited and allows different shape and kind of substrate [22]. Furthermore, electrodeposition gives different size and shape of Zinc oxide such as nanorods [23], nanoflakes [24], nanosheets [25] nanowires forms[26]. The morphology and the structure of Zinc oxide electrodeposited depend strongly on the electrolyte composition [27], bath temperature [28], time of growth [29] and electrode potential [30]. Different studies reported the growth of zinc oxide thin film using electrodeposition from aqueous solution [31, 32]. In this paper we presents the result of growth of ZnO thin film on FTO and Mo substrate, using a pulse electrodeposition (PED) technique on the ZnO properties.

## 2. Materials and methods

The aqueous solution consisted of 0.01M  $Zn(NO_3)_2 \cdot 6H_2O$  and 0.1M KCl, with 5,4 value of pH. The experiment process was carried out in a simple three electrode glass cell. The working electrode was FTO glass substrate ( $1cm^2$ ). The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was Pt metal sheet ( $2 cm^2$ ).The distance between the FTO substrate and the counter electrode was maintained at 3 cm. The electrochemical studies were carried out using a VoltaLab PGZ 301 equipped with Volta Master 4 software.

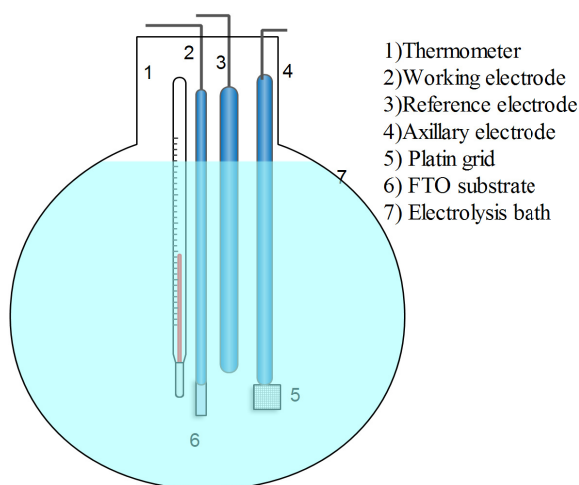


Fig.1 Devices for Electrodeposition of ZnO

Before electrodeposition the FTO substrates were cleaned ultrasonically with distilled water and acetone for 15 minutes each, and then washed with distilled water and dried in air. It is possible to use different kind of substrate such as copper, ITO or Molybdenum. The choice of FTO is justified by his good conductivity and transparency. The deposition temperature was fixed at  $65^{\circ}C$  by a thermostat, the deposited samples were cleaned with distilled water, dried at room temperature and annealed at  $350^{\circ}C$  for 1 Hour in the atmosphere ambient. The deposition time was 60 min in all the cases and without stirring.

## 3. Result and discussion

### 3.1. Chrono-ampermetry growth kinetics of ZnO

Cyclic voltammetry (CV) is an electrochemical method used in order to find the suitable region of growth potential. CV experiment was performed from the precursor solution directly on FTO coated glass. Three scans for each

sample were carried out from the open circuit potential with a negative sweep to -1.6V and then a positive sweep to +0.2 V. Scan rate was  $10\text{mV}\cdot\text{s}^{-1}$ . As shown in the figure 4 the cathodic current increases with the negative shift of electrode potential in the range -0.8 to -1.1V, where the ZnO deposition is expected. Many studies reported the electrodeposition of ZnO in this range [33]. According to these results the reduction of nitrate took place in the range between -0.8 to -1.1V. In the reverse sweeping an anodic current was observed which can be attributed to the transformation of  $\text{Zn}^{2+}$  to Zn.

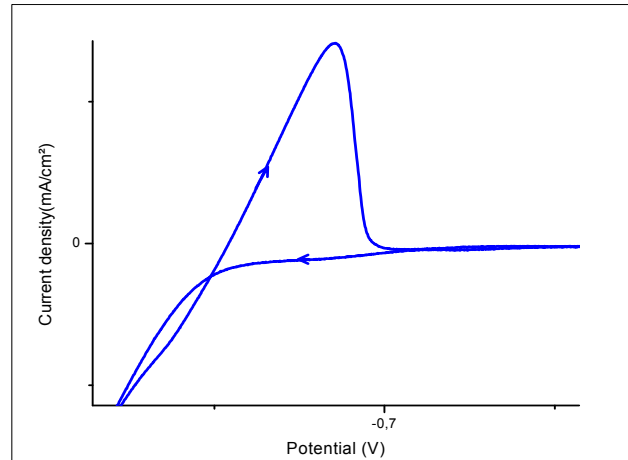


Fig.2 Voltammogram on FTO substrate from acidic solution (pH 5.4) containing 0.01 M  $\text{ZnNO}_3$  and 0.1 M KCl at temperature  $65^\circ\text{C}$ .

According to these result and other studies [34], the growth mechanism of ZnO thin films can be described by the following equations:



The Nitrate electroreduce to nitrite ions, the hydroxide ions were generated at the cathode (eq1). The zinc ions coming from dissolution of  $\text{ZnNO}_3$  reacts with hydroxide ions to form  $\text{Zn(OH)}_2$  which spontaneously dehydrated into ZnO (eq2).



The variation of the potential versus the deposition time during the electrodeposition of ZnO is shown in figure 3. The pulse and its respective durations have been fixed such that during time  $t_1$ , potential  $V_1$  (-900mV (SCE)) and during  $t_2$ , potential  $V_2$  (-1100mV (SCE)) is imposed on the working electrode. Furthermore, the time durations were varied as 3s, 5s and 7s for  $t_1$  and 7s, 5s and 3s for  $t_2$ , so as to vary duty cycles from 33% to 67%. The pulse period  $T$  was constant as 10 seconds and duty cycle  $\theta$  varied from 33% to 67%. All other deposition parameters remained constant in all cases. The wave form of pulse potential is square and the corresponding current density is differently modulated due to the presence of an electric double layer at the cathode-electrolyte interface forming a capacitor of molecular dimension [35, 36].

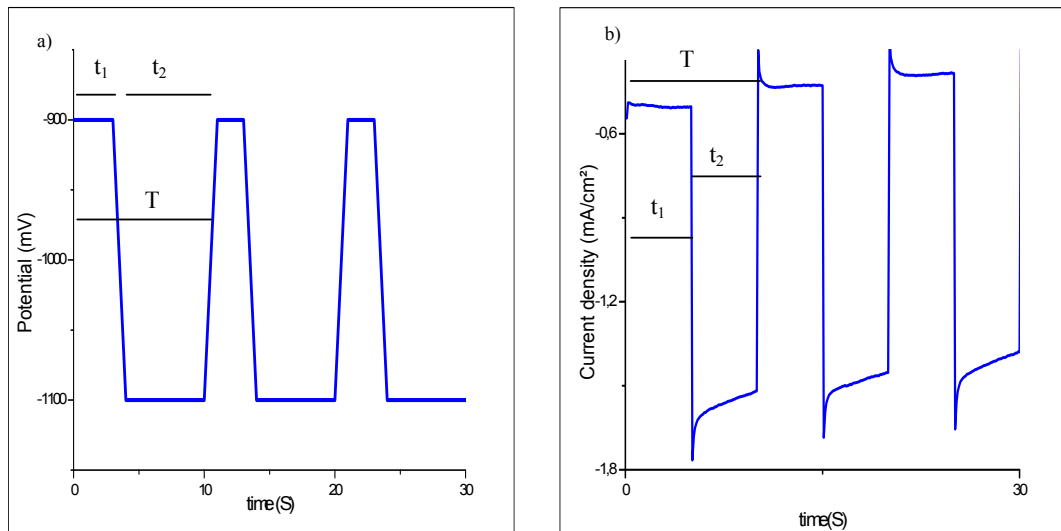


Fig.3 (a) Schematic representation of potential applied in PED, (b) Current density as function of time in the PED.

### 3.2. Morphology surface of ZnO

The influence of Pulse electrodeposition technique on the morphology of ZnO thin films was examined by scanning electron microscope (SEM) and is demonstrated in figures 5 and 6. The film thickness was estimated from SEM cross section observation (Fig.5), the film deposited have a thickness in order of 1.3 $\mu$ m. As can be clearly figure 6 Zinc oxide thin films are constituted of lamellar crystallites oriented perpendicularly to substrate surface, some holes are observed except in sample (c) grown at 67% duty cycle. The grains are randomly oriented. One can notice that the density of nuclei and grain size are strongly related to the potential and duty cycle. The density of crystallite decreased with the increasing of duty cycle. However the crystallite size increased with the increasing of duty cycle.

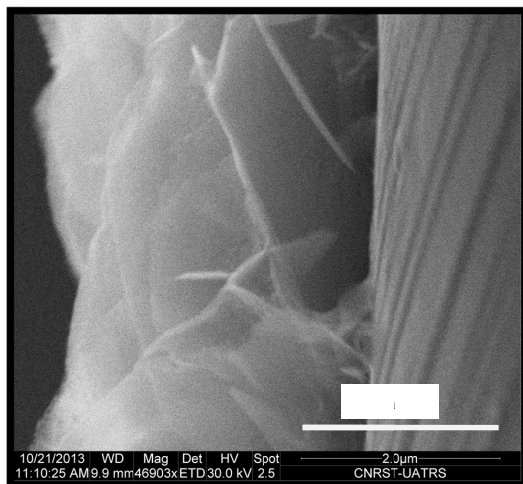


Fig.4 Cross-sectional SEM photograph of ZnO film electrodeposited on FTO glass substrate

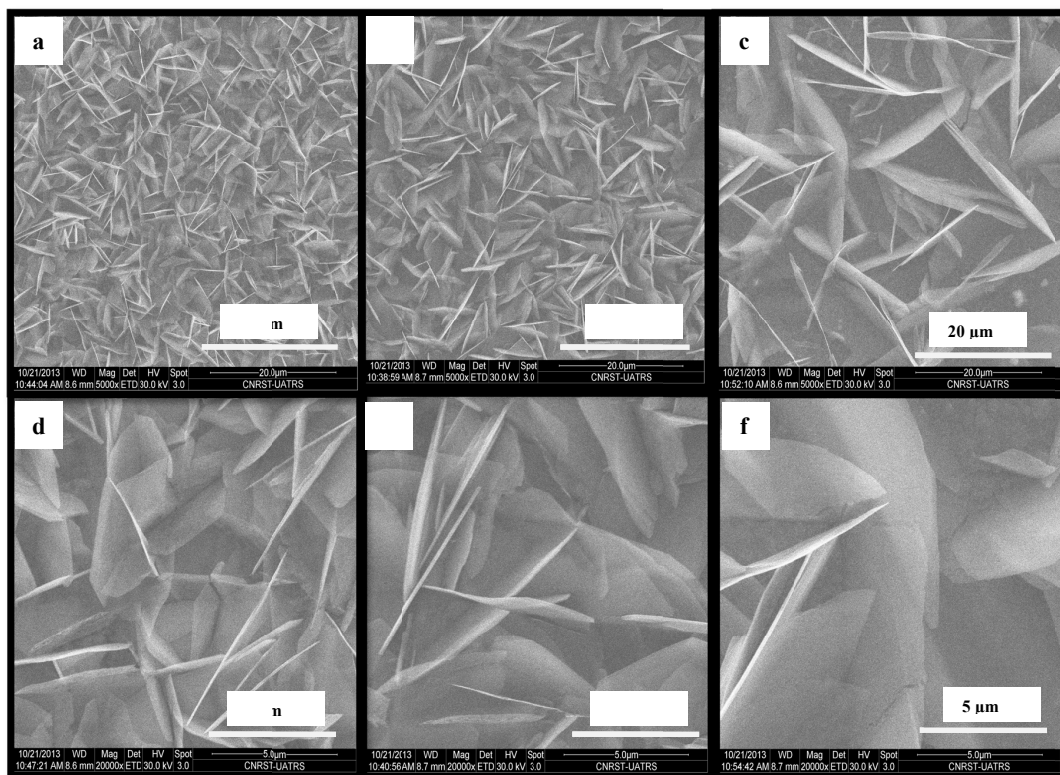


Fig.5 SEM images (top view) of ZnO pulse electrodeposited with different duty cycle. (a) and (d)  $\theta=33\%$ . (b) and (e)  $\theta=50\%$ . (c) and (f)  $\theta=67\%$ .

### 3.3 Optical characterizations

The most important main requirement for use of ZnO in solar cells is their transparency. The optical transmittance was measured at normal incidence in the wavelength range 320 to 3200 nm, using a Shimadzu UV- 3101 PC spectrophotometer. Figure 7 shows optical transmittance spectra of different samples studied, it can be seen that all films exhibit a high transparency, between 50%-70% in the visible range. The sample deposited at 50% duty cycle shows a great transparence (70%) compared to the other samples. It's maybe explained by the uniform repartition and orientation growth of ZnO crystallites as observed in SEM micrographs. Indeed, it was previously reported that the optical transparency strongly depends on the surface irregularity and the enhancement of cristallinity of the film [37]. The decrease of transmission in the other samples can be due to the existence of pores in these films.

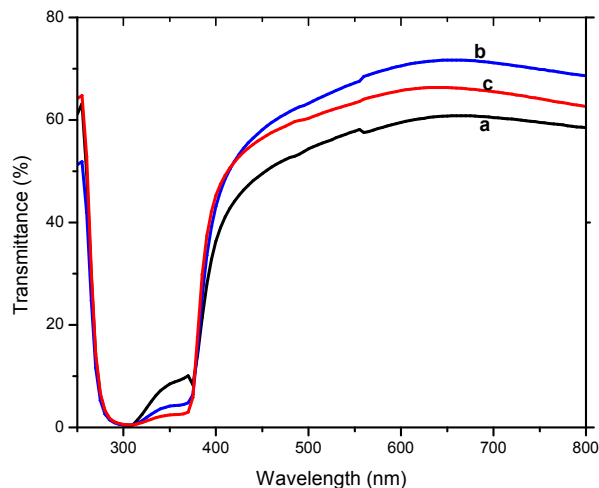


Fig.6 Optical transmittance of ZnO film grown with different duty cycle. (a)  $\theta=33\%$ . (b)  $\theta=50\%$ . (c)  $\theta=67\%$ .

## 4. Conclusion

Preparation of zinc oxide thin films was realized using a simple and inexpensive electrodeposition technique. The investigation of effect of duty cycle was realized, by using pulse electrodeposition technique from a simple nitrate bath. We found that the cycle duty strongly influences the properties of the material: morphological, electrochemical and optical. The obtained films were adherent and homogenous with a high degree of purity and good morphological and optical properties, which make PED a promising technique for preparation of a less expensive window material for solar cell.

## Reference

- [1] R.E. Marotti, P. Giorgi, G. Machado, E.A. Dalchiele, Crystallite size dependence of band gap energy for electrodeposited ZnO grown at different temperatures, *Solar Energy Materials and Solar Cells*, 2006, P. 2356.
- [2] Hartnagel HL, Dawar AL, Jain AK, Jagadish C. *Semiconducting Transparent Thin Films*. IOP Publishing Ltd.; 1995.
- [3] C.H. Xu, H.F. Lui, C. Surya, Optical and sensor properties of ZnO nanostructure grown by thermal oxidation in dry or wet nitrogen, *Journal of Electroceramics*, 2012, P. 27-33.
- [4] D.C. LOOK, Recent advances in ZnO materials and devices, *Materials Science and Engineering: B* 2001, P.383–387.

- [5] Banerjee AN, Chattopadhyay KK. Prog Cryst Growth Charact Mater 2005, P.50-52.
- [6] J. Kessler, J. Wennerberg, M. Bodegård, L. Stolt, Highly efficient Cu(In,Ga)Se<sub>2</sub> mini-modules Sol. Energy Mater. Sol. Cells, 75 (2003), P. 35
- [7] S. Nakamura, A. Electrodeposited CuInS<sub>2</sub>-based thin-film solar cells, Energy Mater. Sol. Cells, 75 (2003), p. 81
- [8] E. Ihalane, L. Atourki, L. Boulkaddat, E. El hamri, H. Kirou, L. Alahyane, A. Elfanaoui, A. Ihlal and K. Bouabid, Effect of structural variations in CIGS based solar cells from numerical analysis, Renewable and Sustainable Energy Conference (IRSEC), 2013 .
- [9] Habibe Bayhan, Murat Bayhan, An analysis of the effect of illumination to the reverse and forward bias current transport mechanisms in an efficient n-ZnO/n-CdS/p-Cu(In,Ga)Se<sub>2</sub> solar cell, Solar Energy, 2013, P.168-175
- [10] M. Buffière, S. Harel, L. Arzel, C. Deudon, N. Barreau, J. Kessle, Fast chemical bath deposition of Zn(O,S) buffer layers for Cu(In,Ga)Se<sub>2</sub> solar cells, Thin Solid Films, 2011, P. 7575-7578
- [11] M. Igalson, M. Bodegård, L. Stolt, Reversible changes of the fill factor in the ZnO/CdS/Cu(In,Ga)Se<sub>2</sub> solar cells, Solar Energy Materials and Solar Cells, 2003, P.195-207
- [12] Jaison Kavalakkatt, Xianzhong Lin, Kai Kornhuber, Patryk Kusch, Ahmed Ennaoui, Stephanie Reich, Martha Ch. Lux-Steiner, Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> from CuxSnSy nanoparticle precursors on ZnO nanorod arrays, Thin Solid Films, 2013, P. 380-383.
- [13] Hossein Movla, Eghbal Abdi, Davoud Salami, Simulation analysis of the CIGS based thin film solar cells, Optik - International Journal for Light and Electron Optics, 2013, P. 5871-5873.
- [14] Goli Nagaraju, Yeong Hwan Ko, Jae Su Yu, Facile synthesis of ZnO/CuO nanostructures on cellulose paper and their p-n junction properties, Materials Letters 2014, P. 64–67.
- [15] Jing Li, Hongbo Li, Yan Xue, Hailin Fang, Wei Wang, Facile electrodeposition of environment-friendly Cu<sub>2</sub>O/ZnO heterojunction for robust photoelectrochemical biosensing, Sensors and Actuators B: Chemical, 2014, P 619–624.
- [16] Zhao-Qing Liu, Xi-Hong Xie, Qi-Zhi Xu, Shi-Heng Guo, Nan Li, Yi-Bo Chen, Yu-Zhi Su, Electrochemical synthesis of ZnO/CdTe core-shell nanotube arrays for enhanced photoelectrochemical properties, Electrochimica Acta, 2013, P 268–273.
- [17] B. Onwona-Agyeman, M. Nakao, T. Kohno, D. Liyanage, K. Murakami, T. Kitaoka, Preparation and characterization of sputtered aluminum and gallium-co-doped ZnO films as conductive substrates in dye-sensitized solar cells, Chemical Engineering Journal, 2013, P 273–277.
- [18] M. Krunk, A. Katerski, T. Dedova, I. Oja Acik, A. Mere, Nanostructured solar cell based on spray pyrolysis deposited ZnO nanorod array, Solar Energy Materials & Solar Cells, 2008, P 1016– 1019.
- [19] S.H. Chiu, J.C.A. Huang, Chemical bath deposition of ZnO and Ni doped ZnO nanorod, Journal of Non-Crystalline Solids, 2012, P. 2453–2457.
- [20] Chien-Yie Tsay, Chun-Wei Wu, Chien-Ming Lei, Fan-Shiong Chen, Chung-Kwei Lin, Microstructural and optical properties of Ga-doped ZnO semiconductor thin films prepared by sol-gel process, Thin Solid Films, 2010, P1516 – 1520.
- [21] O. Lupan, T. Pauporté, B. Viana, P. Aschehoug, M. Ahmadi, B. Roldan Cuenya, Y. Rudzевич, Y. Lin, L. Chow, Eu-doped ZnO nanowire arrays grown by electrodeposition, Applied Surface Science 2013, P. 782– 788
- [22] Hamdane Chettah, Djamila Abdi, Effect of the electrochemical technique on nanocrystalline ZnO electrodeposition, its structural, morphological and photoelectrochemical properties, thin solid films, 2013, P.119–123.
- [23] Ming-Ta Chena, Jyh-Ming Ting, Sputter deposition of ZnO nanorods/thin-film structures on Si, Thin Solid Films 2006, P.250–254.
- [24] Yusuf V. Kaneti, Jeffrey Yue, Xuchuan Jiang, and Aibing Yu, Controllable Synthesis of ZnO Nanoflakes with Exposed (10 $\bar{1}$ 0) for Enhanced Gas Sensing Performance, The Journal of Physical Chemistry, P 13153-13162.
- [25] Qin Hou, Liqun Zhu, Haining Chen, Huicong Liu, Weiping Li, Growth of porous ZnO nanosheets by electrodeposition with the addition of KBr in nitrate electrolyte, Materials Letters, 2012, P 283–286.
- [26] J. Elias, R. Tena-Zaera, C. Lévy-Clément, Electrodeposition of ZnO nanowires with controlled dimensions for photovoltaic applications: Role of buffer layer, Thin Solid Films, 2007, P 8553–8557.
- [27] Rashid T.-R., Phan D.-T., Chung G.-S, Effects of electrolyte on ZnO nanostructures synthesized by galvanostatic electrochemical deposition and their UV sensing properties, Current Applied Physics, 2013, P1316-1320
- [28] Min Guo, ChuanYu Yang, Mei Zhang, YanJun Zhang, Teng Ma, XiDong Wang, XinDong Wang, Effects of preparing conditions on the electrodeposition of well-aligned ZnO nanorod arrays, Electrochimica Acta, 2008, P. 4633-4641.
- [29] Hamdane Chettah, Djamila Abdi, Effect of the electrochemical technique on nanocrystalline ZnO electrodeposition, its structural, morphological and photoelectrochemical properties, Thin Solid Films, 2013, P.119-123.
- [30] T. Mouet, T. Devers, A. Telia, Z. Messai, V. Harel, K. Konstantinov, I. Kante, M.T. Ta, Growth and characterization of thin ZnO films deposited on glass substrates by electrodeposition technique, Applied Surface Science, 2010, P.4114-4120 .
- [31] Satinder K. Sharma, Amritha Rammohan, Ashutosh Sharma, Templated one step electrodeposition of high aspect ratio n-type ZnO nanowire arrays, Journal of Colloid and Interface Science, 2010, P.1–9.
- [32] Ravi Chander, A.K. Raychaudhuri, Electrodeposition of aligned arrays of ZnO nanorods in aqueous solution Solid State Communications, 2008, P. 81-85.
- [33] T. Yoshida, T. Oekermann, K. Okabe, D. Schlettwein, K. Funabiki, H. Minoura, Cathodic electrodeposition of ZnO/EosinY hybrid thin films from dye added zinc nitrate bath and their photoelectrochemical characterizations, Electrochemistry, 2002, P.470.
- [34] T. Yoshida, D. Komatsu, N. Shimokawa, H. Minoura, Mechanism of cathodic electrodeposition of zinc oxide thin films from aqueous zinc nitrate baths, thin solid films 2004, P.166 – 169.
- [35] W.H. Bertain, P.J. Boody, J. Electrochem. Soc, 1962, P. 574.
- [36] R.K. Sharma, G. Shingh, A.C. Rastogi, Effect of duty cycle on properties of CIGS thin films fabricated by pulse reverse electrodeposition, Solar Energy Materials and Solar Cells, 2004, P. 201–215.
- [37] M. Izaki, T. Omi, Transparent zinc oxide films prepared by electrochemical reaction, Appl. Phys. Lett., 1996, P. 2439