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Electrochemically deposited nanostructured ZnO layers on the front side of c-Si solar cell

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ZnO nanostructures layers are deposited by electrochemical method on different c-Si solar cells structures. Acid aqueous solutions of $ZnCl_2$ (5. 10^{-3} M) and KCl (0.1 M) with pH 6.0 at temperature of 80°C is used as electrolyte using a three-electrode electrochemical cell and saturated calomel electrodes (SCE) as a reference electrode. ZnO layers deposition time varies between 20 and 90 min. An analysis of the surface morphology of such layers is performed by means of Scanning Electron Microscope (SEM). Measurements of the reflection and diffused reflection spectra of ZnO based nanostructures deposited on the front side of tree different types of c-Si solar cells is performed, as well. The obtained structural and optical properties of the ZnO electrochemical thin films deposited on the top front surface of different c-Si solar cells for different deposition time are compared. The study demonstrates that the deposition of ZnO nanostructured films results in decreasing of the specular reflection and the diffused reflection better expressed in the case of un-textured Si surface. The obtained ZnO layers can be applied as antireflection coatings in c-Si solar cells to enhance their light harvesting properties.

Key words: ZnO, nanostructure, electrochemical deposition, c-Si solar cell.

INTRODUCTION

ZnO is a unique material possessing variety of useful properties. It is among the most investigated II-VI group semiconductors with wide direct band gap of 3.4 eV and large free exciton binding energy of 60 meV [1]. ZnO possess hexagonal wurtzite structure with lattice parameters a = 3.25 Å and c = 5.12 Å [1].

Zinc oxide nanostructures are most promising one-dimensional (1D) materials received increased attention over last decade because of their exciting potential applications in optoelectronic devices, such as field effect transistors, nano-sensors, optical switches, solar cells and light emitting diodes [2-6]. Recently, J.Y Chen and K.W.Sun reported application of vertically aligned ZnO nanorod arrays as an antireflective coating on Si solar cells [7]. ZnO can be prepared with the large variety of nanostructure configurations as nano-rings, nano-springs, nano-belts, nano-combs, nano-rods, highly ordered nano-wires arrays or tower–like sticks [8] and can be synthesized by a diversity of chemical and physical methods [2-6, 9-10]. Among chemical methods are precipitation in non-aqueous solution [11], chemical–bath deposition [12, 13], hydro-thermal precipitation [13] and electrodeposition [6-8,15-17].

Electrodeposition has some advantages because it is a low cost industrially up-scalable process, relevant to different substrates for preparation of well defined nanostructures with reasonable physical parameters [2, 3, 15].

Design of novel functional configurations of the materials depends on depth understanding of connection between the electro-physical parameters of the material and particle size and morphology of nanostructure.

In this paper results from investigation of the optical and the structural properties of nanostructured ZnO thin films formed by electrochemical deposition on the top front side of c-Si solar cells are reported. The c-Si solar cell consists of ~0.4 μm n^+- type emitter on p-type Si wafer with p^+-type back surface field (BSF). Three different types of c-Si solar cells are used – type 1 – with deposited ITO film on the textures front side (ITO/(textured)n^+-Si(~0.4μm, emitter)/p-Si–base,/p^+-Si(~200μm, BSF)), type 2 - with deposited ITO film on the un-textures front side

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(ITO/(un-textured)n$^+$-Si(~0.4μm, emitter)/p-Si–base/p$^+$-Si(~200μm, BSF)), and type 3 – without deposited ITO and un-textures front side ((un-textured)n$^+$-Si(~0.4μm,emitter)/p-Si–base/p$^+$-Si(~200μm, BSF)). The obtained ZnO layers are characterized by SEM, by spectra of specular reflectance, diffuse reflection and haze ratio in reflection.

EXPERIMENTAL

ZnO nanostructured films were deposited by an electrochemical process from slightly acid aqueous solution of $ZnCl_2$ (5. 10^{-3} M) and KCl (0.1 M) with pH 6.0 at 80^0C and different deposition times (in the range of 20-90 min) using a three-electrode electrochemical cell and Saturated Calomel Electrodes (SCE) as a reference electrode. As a working electrode c-Si solar cell were used. Spectrally pure graphite rod electrode waw used as anode. The electrolyte was agitated by magnetic stirrer. The oxygen is provided in the system by supplement of H_2O_2. The deposition was carried out controlling the redox potential of the high power potentiostat system WENKING HP 96. The deposition potential was kept at -700 mV (vs. SCE). The oxygen content in solution was determined by Dissolved oxygen and temperature meter Hanna Instruments 9146. The surface morphology and the thickness of the deposited films were imaged under a Scanning Electron Microscope (SEM) Philips 515. The thicknesse of the deposited ZnO layers were between 0.50 and 1.2 μm.The optical properties (specular reflectance, diffuse reflection and haze ratio in reflection) were measured by a spectrophotometer Shimadzu UV-3600 in the range of 300 - 1200 nm employing a 60 mm integrating sphere.

RESULTS AND DISCUSSION

Despite the wide number of works, recipes and regimes for electrodeposition of ZnO, there is no adequate interpretation of the mechanism and reaction route. Deposition of thin film zinc oxide could be explained as a product of interaction of OH^- and Zn^{2+} in aqueous solution on the surface of the electrode.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O \quad (1)$$

Since the zinc hydroxide is unstable, it does dehydrate into ZnO [18]. The standard free energy of formation of ZnO is $G^{298}{}_{ZnO}$ = -361.08 kJ/mol [18].

Hydroxide ions are produced by reduction of oxygen, dissolved in electrolyte:

$$O_2+2H_2O+4e^-=4OH^-, E^o{}_{OH^-}=0.644V \quad (2)$$

Reaction (2) presents the reduction process on the oxygen electrode with standard electrode potential 0.644 V, against SCE [18].

Standard electrode potential of zinc according the reaction (3) is much more negative (-1.005 V vs SCE) than that of OH^- by equilibrium (2):

$$Zn^{2+} + 2e^- = Zn; E^o{}_{Zn2+} = -1.005\ V \quad (3)$$

The reaction of electrodeposition of ZnO depends on reduction of dissolved oxygen in the solution and can be described by four electron process according to the reaction:

$$O_2 + 2H_2O + 2Zn^{2+} + 4e^- = 2Zn(OH)_2 = 2ZnO + H_2O \quad (4)$$

The difference between standard electrode potentials of Zn and oxygen (according to the reaction (2)) is:

$$E^o{}_{OH-} - E^o{}_{Zn2+} = 1.163\ V, \quad (5)$$

while the factor G/nF for four electron process is:

$$G/4F = 0.936\ V \quad (6)$$

The comparison of the values in (5) and (6) shows that the difference between standard electrode potentials of zinc and OH^- (5) is bigger than the depolarization factor of the chemical reaction (6), $(E^o{}_{OH-} - E^o{}_{Zn2+}) > G^{298}ZnO$. This is the case of induced co-deposition mechanism by the rules described by Brener [19] and Kroger [20]. This means that at appropriate ratio of concentrations of Zn^{2+} and OH^- ($[Zn^{2+}]/[OH^-] \geq 10^2 \div 10^3$) a large interval of deposition potentials will exist, where the composition of the deposited material will be determined only by the thermodynamics of the process and will be close to the stoichiometric one.

Since the reduction of oxygen by Eq. (2) is a step determined by the potential [20], it is possible to control the overall electrodeposition process by measuring the Redox potential of the system. In the ideal case, in equilibrium the redox potential of the electrolyte determines the ability of deposition of ZnO.

In Figure 1 the dependences of both dissolved oxygen concentration (left) and Redox potential (right) on the time are shown. Initial time (T=0) corresponds to the moment of the supplying of the hydrogen peroxide into deposition solution. The curves have similar behavior – a sharp rise until 15 min is observed and then the values decrease and go to equilibrium.

In order to provide electrical conductivity of the electrolyte, the process of electrodeposition of ZnO in aqueous solutions is carried out in the electrolyte containing ZnCl and KCl. The KCl salt influences the solubility of the oxygen by Henry's Low. Another factor is the temperature of the electrolyte. In details this matter is treated in large extension by Cooper [21].

It has been reported that ZnO thin layers are obtaining at Redox potential in interval 300 ÷ 400 mV (vs SCE) [22]. At potentials below 300 mV there is no electrodeposition of ZnO because there is no enough dissolved oxygen in the solution. At potentials above 400 mV (vs SCE) the solution is over-saturated of oxygen and the deposition of zinc peroxide (ZnO_2) takes a place. In this case the deposited layers have dendrit structure with very rough surface and are non-adherent to the substrate.

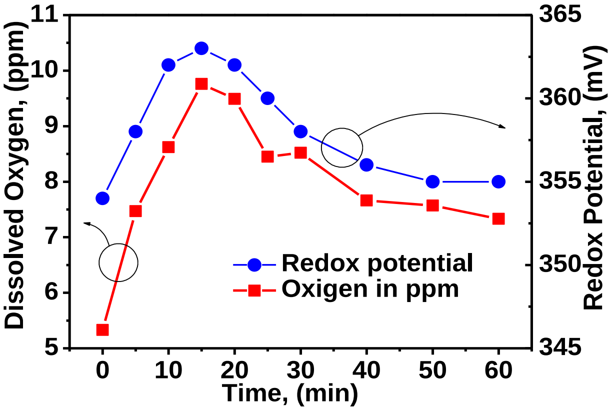

Fig. 1. Dependences of the concentration of the dissolved oxygen (left) and of the Redox potential (right) on time.

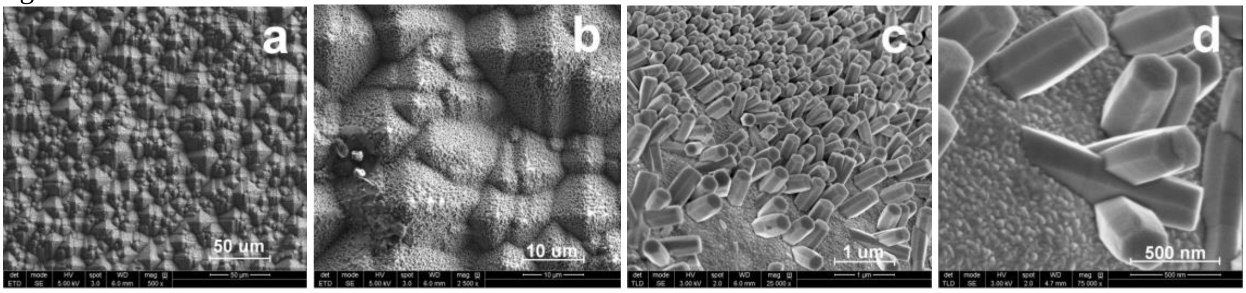

Fig. 2. SEM images (with different magnification) of ZnO electrochemical thin films deposited on textured Si-solar cells with ITO – type 1. The ZnO is deposited for 60 min.

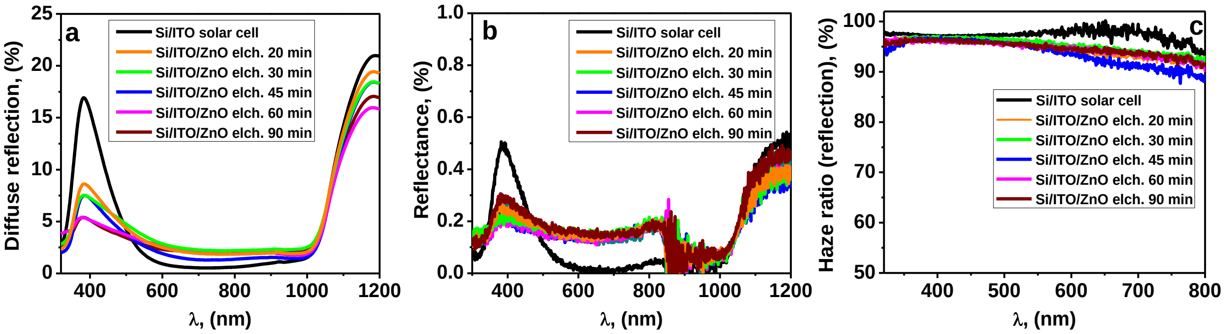

Fig. 3. Spectra of diffuse reflectance (a), specular reflection (b) and haze ratio in reflection (c) in visible region of ZnO electrochemical thin films deposited on textured Si-solar cells with ITO (type 1). The ZnO layers are deposited for different time.

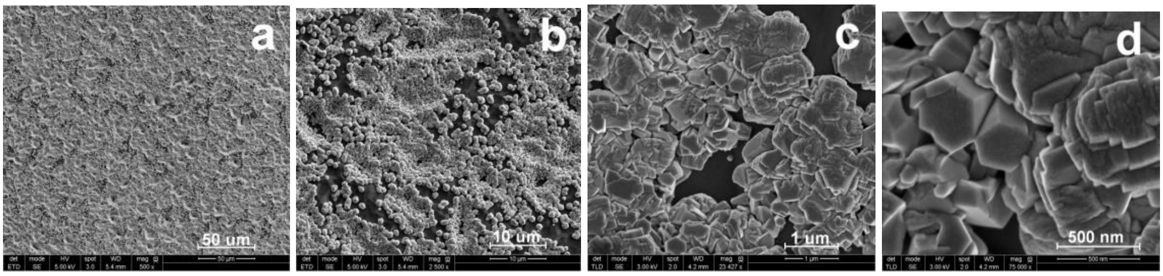

Fig. 4. SEM images (with different magnification) of ZnO electrochemical thin films deposited on untextured Si-solar cells with ITO - type 2. The ZnO layer is deposited for 40 min.

In this work the electrodeposition is carried out at cathode potential of -700 mV (vs SCE) where stoichiometric ZnO is produced. At potentials more positive than -700 mV the rate of the reaction (2), and respectively (4), is very low or does not run at all. At deep cathodic potentials, below -1050 mV, the deposition potential of zinc is reached (reaction (3)) and the layers consist of ZnO with metallic zinc.

SEM images of the surface of electrochemically deposited ZnO on the top surface of the c-Si solar cell type 1 (with ITO and textured front surface) are presented in Figure 2. It is seen that the ZnO nanowires with hexagonal shape have grown on the different side of the pyramidal etched surface of the solar cell. Similar hexagonal shape is reported in [23] and is typical for ZnO nanowires.

Figure 3 shows spectra of specular reflection, diffuse reflection and haze ratio in reflection of ZnO deposited on textured c-Si solar cell structures with ITO layers (type 1). ZnO layers are deposited for different time. The corresponding spectra of solar cells structures before deposition of ZnO are given for comparison as well.

Electrochemical deposition of the ZnO results in decreasing of the intensity of the band of reflectance at about 400 nm by about 10% and slightly increase (about 0.2%) of the diffuse reflection in the range 550 - 1000 nm compared to the value of the based structure.

Applying ZnO nanorod areas on the surface of the solar cell could increase generation of the carriers and the value of the photocurrent in the spectral range 400 - 480 nm. It seems that the deposition time of 20 and 30 min for ZnO nanostructures could be more favorable.

Figure 4 shows the SEM of the surface of solar cell structure (type 2) with a flat front surface (untextured). ZnO nanostructured layer is electrochemicaly deposited for 40 min. The column structure of electrochemical layer deposited on untextured solar cell is recognizable and the hexagonal formations are seen.

The spectra of specular reflectance, diffused reflection and haze ratio in reflection from the surface of c-Si solar cell type 2 with ZnO deposited for different time are shown in Figure 5. As in the previous case, the values of reflectance and diffused reflection at in the range 350-500 nm decrease after ZnO grown, however in the range 550 - 1000 they increased slightly (for diffused reflection from 1 to 3 %) and the haze ratio (in the range 550-800 nm) is higher compared to the sample without deposited ZnO.

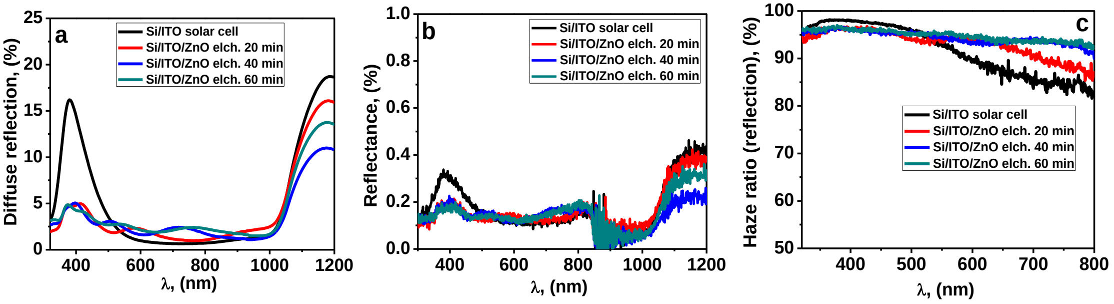

Fig. 5. Spectra of diffuse reflection (a), specular reflectance (b) and haze ratio in reflection (c) in visible region of ZnO electrochemical thin layers deposited on textured Si-solar cells with ITO (type 2). The ZnO layers are deposited for different time.

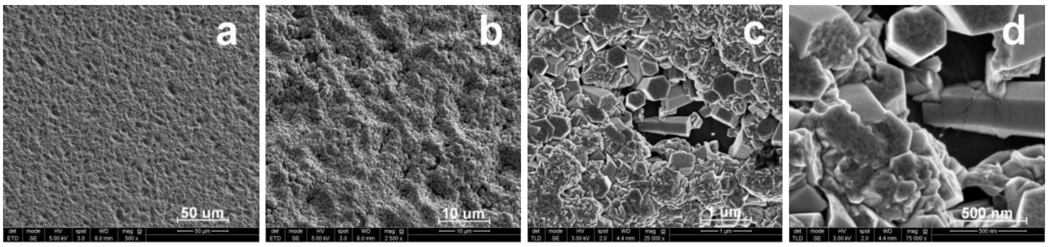

Fig. 6. SEM images (with different magnification) of ZnO thin films electrochemically deposited on untextured Si-solar cells without ITO - type 3. The ZnO was deposited for 60 min.

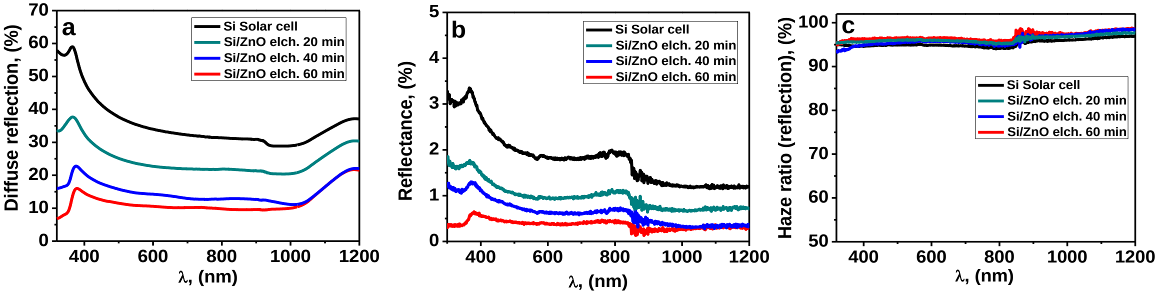

Fig. 7. Spectra of diffused reflection, specular reflectance and haze ratio in reflection of c-Si solar cells type-3 with ZnO electrochemically deposited for different time.

Similar experiments have been performed on the c-Si solar cell structure with untextured top however without front ITO layer – type 3. SEM pictures of the sample with ZnO electriochemically deposited for 60 min are shown in Figure 6. The hexagonal rods grown with different orientation to the substrate are seen.

The spectra of reflection, diffused reflection and haze ratio in reflection of the structure type 3 before and after deposition of ZnO nanowired layers are shown in Figure 7. Values of reflectance and diffused reflection decrease in the samples with deposited ZnO and with the time of deposition. The haze ratio in reflection is very high (~95%) and increases slightly after ZnO deposition.

The preliminary experiments for application of ZnO nanostructured films to solar cell demonstrate that the value of the diffused reflection and the specular reflectance can be decreased after deposition of ZnO nanolstructured layers on the top side of the c-Si solar cells. Better antireflective properties are obtained when the ZnO nanorod arrays are deposited on the front surface the c-Si solar cells with un-textured front size.

CONCLUSIONS

The study of the optical properties (diffuse reflection, reflectance and haze ratio in reflection) of nanostructured ZnO layers deposited by electrochemical methods on the front side of c-Si solar cell is performed. After deposition of ZnO layers the decrease of the reflectance is observed and this tendency increases with deposition time. Electrochemically deposited ZnO layers on c-Si solar cells with un-textured front surface results in significantly reduction of the reflectance and diffuse reflection and can be applied as antireflective coatings in c-Si solar cell.

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REFERENCES

1. V. A. Coleman, C. Jagadish , Zinc oxide bulk. Thin films and nanostructures, p. 1–5, UK, Elsevier, 2006.
2. O. Lupan, T. Pauporté, B. Viana, *Adv. Mater.*, **22,** 3298 (2010).
3. T. Pauporté, Design of solution-grown ZnO nanostructures (Ed. Z. M. Wang), Lecture Notes on Nanoscale Science and Technology, Toward Functional Nanomaterials, (vol. 5, p. 77–125, Springer Books), New York, 2009.
4. L. Luo, Y. Zhang, S.S. Mao, L. Lin, *Sens. Actuators A. Phys.*, **127,** 201 (2006).
5. O. Lupan, V.M. Guérin, I.M. Tiginyanu, V.V. Ursaki, L. Chow, H. Heinrich, T.Pauporté, J. Photochem, A. Photobiol, *Chem.*, **211,** 65 (2010).
6. T. Pauporté, D. Lincot, B. Viana, F. Pellé, *Appl. Phys., Lett.*, **89,** 233112 (2006).
7. J.Y. Chen, K.W.Sun, *Solar Energy Materials & Solar Cells*, **94,** 930 (2010).
8. Schmidt-Mende L, J. L. MacManus-Driscoll, *Mater Today*, **10**, 40 (2007).
9. C. Badre, T. Pauporté, M. Turmine, D. Lincot, *Nanotechnology*, **18,** 365705 (2007).
10. N. Wang, Y. Cai, R.Q. Zhang, *Mater. Sci. Eng. R.*, **60,** 1 (2008).
11. R. Jayakrishnan, G. Hodes, *Thin Solid Films*, **440,** 19 (2003).
12. Y. Lare, A. Godoy, L. Cattin, K. Jondo, T. Abachi, F. R. Diaz, *Appl. Surf. Sci.*, **255,** 6615 (2009).
13. M. M. Wang, S. H. Hahn, E. J. Kim, J. S. Kim, S. Kim, C. Park, *Thin Solid Films*,**516,** 8599 (2008).
14. B. Liu, H. C. Zeng, *J. Am. Chem. Soc.*, **125,** 4430 (2002).
15. T. Pauporté, D. Lincot, *Appl. Phys. Lett.*, **75,** 3817 (1999).
16. A. Goux, T. Pauporté, J. Chivot, D. Lincot, *Electrochim. Acta*, **50,** 2239 (2005).
17. T. Pauporté, D. Lincot, *J. Electroanal. Chem.*, **54,** 517 (2001).
18. D. R. Lide, H. P. R. Frederikse, in: Handbook of Chemistry and Physics, (77th ed., CRC Press, Boca Raton, FL), 1996.
19. A. Brener, Electrodeposition of alloys, Academic press (1963).
20. F. A. Kroger, *J. Electrochem.Soc.*, **12,** 2028 (1978).
21. L.H.N. Cooper, *Journal of the Marine Biological Association of the United Kingdom*, **22,** 167 (1937).
22. D. Dimova-Malinovska, P. Andreev, M. Sendova-Vassileva, H. Nichev, V. Mikli, 24th European Photovoltaic Solar Energy Conference, Hamburg, Germany (2009),
23. D. Dimova-Malinovska, K. Lovchinov, M. Ganchev, O. Angelov, J. Graff, A. Ulyashin, *Physica Status Solidi A*, **1-6** pssa.201200565 (2012).

НАНОСТРУКТУРИРАНИ ZnO СЛОЕВЕ, ОТЛОЖЕНИ ЧРЕЗ ЕЛЕКТРОХИМИЧЕН МЕТОД ВЪРХУ ФРОНТАЛНАТА СТРАНА НА ФОТОЕЛЕМЕНТИ ОТ c-Si.

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(Резюме)

Наноструктурирани слоеве от ZnO са отложени върху фронталната страна на фотоелементи от c-Si чрез електрохимичен процес в електролит от слабо кисел воден разтвор на $ZnCl_2$ (5. 10^{-3} M) и KCl (0.1 M) с pH=6.0 при 80ºC, изполвайки три електродна електрохимична клетка. Времето на отлагане на ZnO слоеве варира между 20 и 90 минути за отделните образци. Чрез метода на сканираща електронна микроскопия (SEM) е изследвана повърхностната морфология на отложените слоеве. Измерени са спектрите на отражение и дифузно отражение на ZnO наноструктурирани слоеве, отложени върху три различни вида фотоелементи с текстурирана и не-текстурирана повърхност от c-Si с ITO; и без ITO на не-текстурирана повърхност. Структурните и оптичните свойства на ZnO слоеве, отложени като горен слой в c-Si фотоелементи, са сравнени в зависимост от времето на отлагане. Резултатите от изследванията показват, че при отлагането на наноструктуриран ZnO се наблюдава намаляване на отражението и дифузното отражение, като това намаление е по-добре изразено при слоевете отложени върху не-текстурирани фотоелементи. Изследванията на свойствата на отложените ZnO слоеве могат да бъдат използвани като анти отразяващи покрития в c-Si фотоелементи за увеличаване на ефективността им.