

УДК 66.048.6-542.41

Photoactive Oxide Films and Heterostructures Preparation

Tamara N. Patrusheva* and Galina N. Shelovanova

Siberian Federal University,

79 Svobodny, Krasnoyarsk, 660041 Russia ¹

Received 6.05.2009, received in revised form 27.05.2009, accepted 17.06.2009

The nanotechnology and molecular design should be used for the Dye Solar Cells (DSC) preparation. In this paper, we present the extraction-pyrolysis technique for the photoactive oxide TiO_2 , Ti_2ZnO_4 and conductive oxide $InSnO$ films sensible by Ru-extract on glass substrate preparation. It is a low cost and large-scale technique for nanosize oxide films obtaining. The attempts to use the photoactive oxides $TiZnO$ for the protection and enhancement of the Si photovoltaic cells were made. The properties of heterostructures shown that the thin oxide film on the porous Si improve the photovoltaic performance and long time stability of solar cells.

Keywords: oxide solar cells, nanostructure films, solution technique.

Introduction

High expenses for the manufactory restrain the development of solar cells power engineering. The production cost of dye-sensitized solar cell (DSC) devices is low due to low cost material and low energy demanding production methods [1-4]. The suitable technique for a big surface coating is necessary to develop for the large-scale preparation of oxide electrodes. This problem can solve by usage of the solution technique, which additionally provides the nanostructure materials obtaining. The accumulation of the charge is more effective with the nanocrystalline oxide and the big surface area of oxide film. The usage of solution techniques provides the creation of nanosize structure and the homogeneity of oxide materials. The composite oxides of Ti, Zn, Sn, In are considered as a perspective photoactive materials. But same elements are reduced the photo effect. The diffusion of Cu in TiO_2 leads to the change of Shottky barrier [5]. Therefore, it is important to develop the technology for obtaining pure homogeneous and nanosize oxide films on big surfaces.

O'Regan and Gratzel developed dye-sensitized solar cells in 1991. The coefficient of efficiency of oxides solar cells is about 2 – 2,5 %. DSC provides the transformation of the solar energy to the electric energy with less efficiency than silicon solar cells. The oxide elements have same advantages: the protective properties of oxides increase the long time stability; the DSC reaction on a changing of the light intensity and the angle of rays is low; DSC works effective by the low light and in shade. Finally, dye-sensitized solar cells are more cheap and simple in preparation.

DSC is the photoelectric element in which the division of charges takes place on the boundary of a semiconductor with the wide band gap and an electrolyte. The TiO_2 films after the adsorption of

* Corresponding author E-mail address: pat55@mail.ru

¹ © Siberian Federal University. All rights reserved

a dye show the high ability to the light adsorption and the high velocity of the electrons transit. The solar light at the beginning is adsorbing by dye. The energy of dye molecules is carrying away to the semiconductor oxide. The appeared current carriers are going through the electrolyte to the conductive electrode.

The construction of DSC consists of two electrodes: a TiO_2 film deposited on the ITO-coated glass and the ITO-coated glass and electrolyte.. Usually a liquid electrolyte restricts the time of solar elements existence due to the leak of electrolyte. Solid electrolytes on the base of conductive polymers replace the traditional liquid electrolyte to overcome the problems of leakage and dye desorption [6,7]. In the planar construction of DSC the elements are located consecutively on the conductive glass [8].

Method and materials

TiO_2 is one of the most studied oxide semiconductor materials in this regard because of its stability in electrolytes. However, the band gap of TiO_2 (3,2 eV) limits the absorption of sunlight to the high-energy portion (UV) of the solar spectrum. It reported earlier that attempts have been made to improve the absorption of the visible light by the incorporation of substitution atoms into the lattice of TiO_2 [9].

For the large-scale preparation of solar cells, the solution techniques are more suitable. We are developing the extraction-pyrolysis technique for the elements of the DSC preparation by one technology. The distinctive peculiarity of the extraction-pyrolysis technique is in the usage of the extraction for the precursor's synthesis. After mixing the solutions of extracts and deposition on the substrate and thermal decomposition the homogeneous oxide material with set content and without impurities is obtained.

The photoactive films TiO_2 , Ti_2ZnO_4 we obtained by the extraction-pyrolysis technique. The carboxylic acids ($\text{C}_5 - \text{C}_9$) used as an extragent. The mixture of carboxylic acids is the second product of the oil remaking and has the low cost. Individual metal extracts obtained from inorganic salts and the following mixture carried out in the necessary proportion in solution that provides the homogeneity of composite oxides. The concentration of extracts defined more precisely by Atomic Adsorption measurements (AAS).

The liquid extracts deposited on transparent conducting ITO-glass sheets prepared by the same technique. Thin films deposition on glass substrates carried out by spin coating and spray techniques. After the heat treatment in air at 450 °C during 1 - 3 min the nanostructure film electrode was obtained.

The film microstructure studied using an atomic force microscope Solver P47 (NT-MDT, Russia). XRD pattern was recorded with a Rigaku RINT2400 X-ray diffraction. The photo response was measured in the dark and by using the electric lamp of 50 – 100 Wt.

The dye adsorption of the nanostructure Ti_2ZnO_4 electrode carried out by the soaking of the film in a 0.5 mM solution of Ru-extracts.

Results and discussion

Thermal investigations have shown that metal carboxylates obtained by extraction are decomposed at 300 – 450 °C without losing elements. The pyrolysis of the wetting film leads to the porous oxide layer formation. The following deposition of extracts fills pores and the continuous layer is formed.

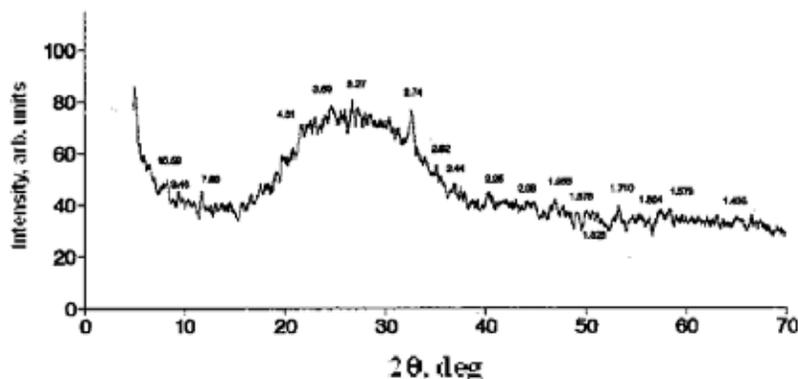


Fig. 1. XRD diagram of ZnTi₂O₄ film, prepared by extraction-pyrolysis technique after annealing at 550 °C during 10 min

After the 10-15 layers deposition the annealing at 500 – 650 °C during 5 – 30 min was made. The counter electrode InSnO prepared by the extraction-pyrolysis technique as was described above [10].

Films thicknesses were determined by the surface tension of the solution and one layer of oxide film was evaluated as about 15 – 17 nm and hence 10-layers films was about 100 nm.

Thin films TiO₂ and Ti-Zn-O obtained by the extraction-pyrolysis technique were able to photocurrent produce by the lightning with electric lamp. The composite oxide Ti₂ZnO₄ showed higher quantum yield than TiZnO₃, TiZn₂O₄ and TiO₂.

The process of the phase formation of the composite oxide Ti₂ZnO₄ was investigated by the X-ray diffraction. It was determined the crystalline phase of ZnTi₂O₄ is formed after annealing at 550 °C during 10 min (Fig. 1).

The structure of the material and the size of crystallites have a great influence on the efficiency of functional materials. Nanosize structures usually show high efficiency. The solution technique allows to obtain the nanostructure materials. Microstructure of ZnTi₂O₄ film, prepared by extraction-pyrolysis technique, show the round grains uniformed by size and form. Assemblies of grains with diameter 100 nm consist of smaller grains with diameter about 30 nm (Fig. 2).

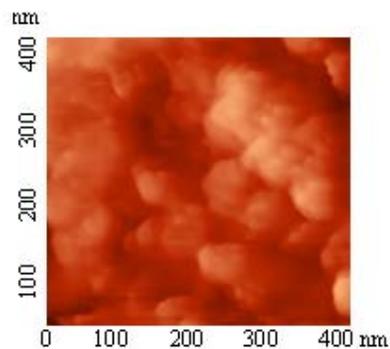


Fig.2. Microstructure of Ti₂ZnO₄ film

Photocurrent–voltage characteristics of Ti₂ZnO₄ film showed the photo activity of the obtained material. The quantity of carriers is growing under the influence of light (Fig. 3).

The optimal conditions of TiO₂ films annealing and the optimal thickness of films were established. The maximal efficiency of In_{0.9}Sn_{0.1}O - TiO₂ – Ru-extract multilayer coating on the glass was found at the annealing temperature 600 °C (Fig. 4). The increase of films thickness from 100 to 300 nm leads to increase of photocurrent.

The change of the TiO₂ active material to Ti₂ZnO₄ leads to improving of photocells characteristics (Fig. 5). Previous results of photocurrent measurements of TiO₂ and Ti-Zn-O films

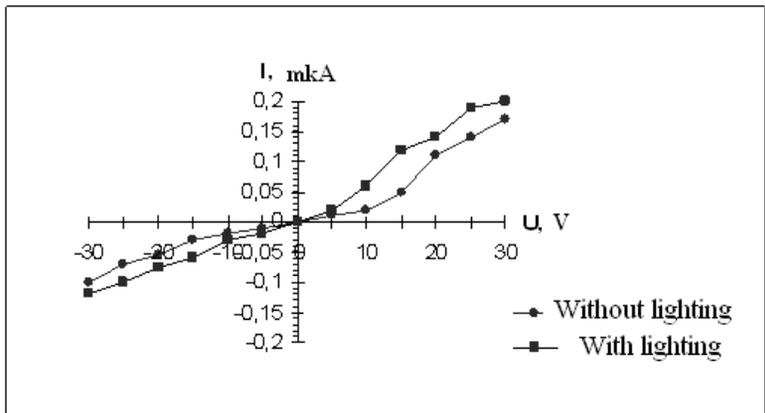


Fig. 3. Photocurrent–voltage characteristics of Ti_2ZnO_4 film on glass

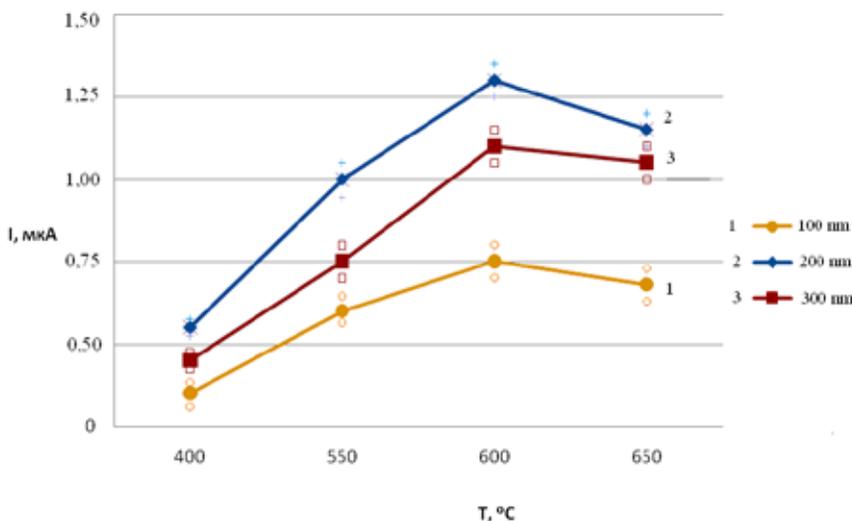


Fig. 4. Dependence of the photo response from the annealing temperature and the thickness of films in the system $In_{0.9}Sn_{0.1}O-TiO_2-Ru$ -extract

on the glass showed that Ti_2ZnO_4 composition has the maximal photo activity and exceed TiO_2 by 40 - 50 %. The efficiency of the solar cell with Ti_2ZnO_4 films exceeds the efficiency of solar cell with TiO_2 films by 45 %.

The thickness of Ti-oxide film has a big influence on the photocurrent. By the lighting of thicker film the quantity of executed electrons is increased and more electrons are able to go across the potential barrier and the photocurrent is increased. However, the increase of the photocurrent with growing of the film thickness is accomplished with the slowing down due to the increase of the mechanical tension of the film on the substrate.

The lighting by lamps of 40, 60, 100, 120 and 140 Wt is carried out during the experiment. At the low intensity of the beam, the value of the photocurrent is in the direct dependence of the light power. The sufficient power of the light for curries receive necessary energy for getting over of the potential barrier and the photocurrent appearing is about 30 - 40 Wt . The photocurrent was absent at the

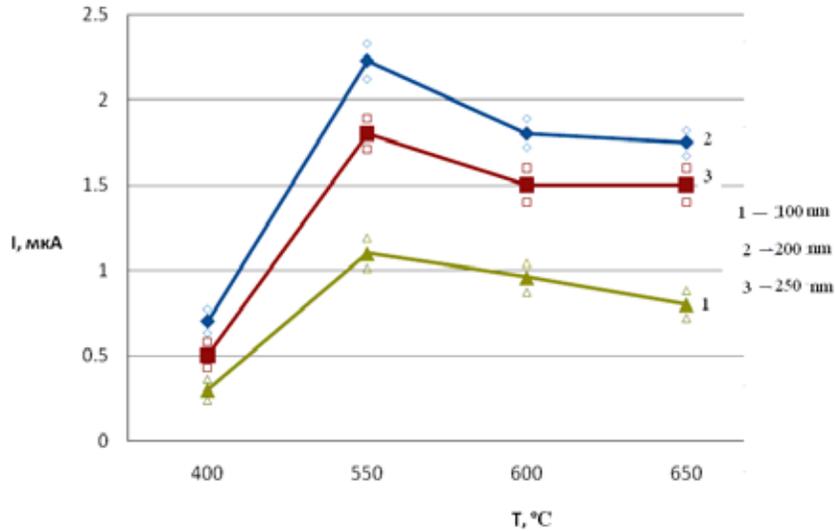


Fig. 5 Dependence of the photocurrent from the annealing temperature in the system $\text{In}_{0.9}\text{Sn}_{0.1}\text{O}-\text{Ti}_2\text{ZnO}-\text{Ru}$ -extract films on the glass

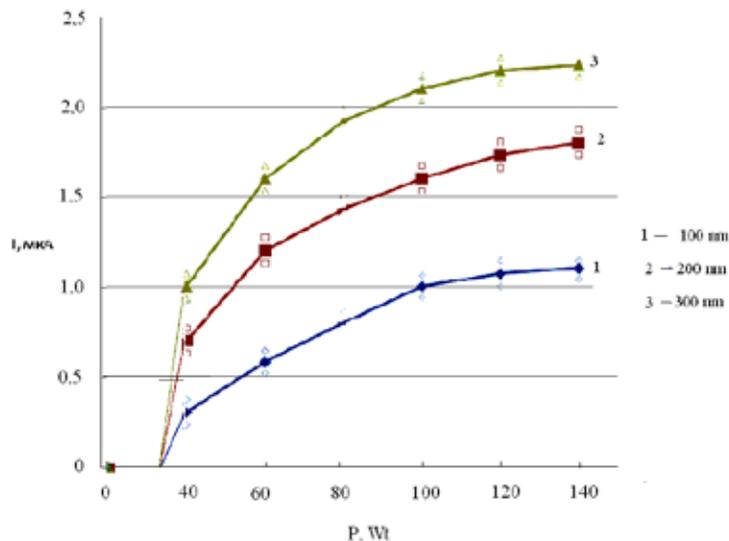


Fig. 6. Dependence of the photocurrent from the power of lighting in The solar cell element $\text{In}_{0.9}\text{Sn}_{0.1}\text{O}-\text{Ti}_2\text{ZnO}-\text{Ru}$ -extract

darkness. At the increase of lamp power, the photocurrent increased too. The growing of photocurrent lowered when the power of light had reached 100 Wt (Fig. 6).

The solar cell contained two electrodes from glass coated with $\text{In}_{0.9}\text{Sn}_{0.1}\text{O}_3$ and $\text{In}_{0.9}\text{Sn}_{0.1}\text{O}_3/\text{Ti}_2\text{ZnO}_4$ sensitized by the Ru-extract and LiOCl in the polycarbonate electrolyte was constructed. The photo current value in $\text{In}_{0.9}\text{Sn}_{0.1}\text{O}_3/\text{Ti}_2\text{ZnO}_4/\text{Ru}$ hetero-structure reached 1,5 mA/cm² an the power of the lamp 100 Wt. The efficiency of the solar cell was about 2,5 %. The efficiency of the solar cell depends on the lightening intensity and electrolyte concentrations.

In the oxide solar cells comparison with silicon solar cells the changing of light intensity leads to less change of photocurrent value. For the improving of the efficiency of solar cells the additional reflectors and accumulated light lenses are used.

Heterostructure solar cell

An alternative approach to effective solar cells is the Heterostructure cells creation. Scientists from Ioffe-FTI, Sankt Petersburg developed the first hetero transition in the thin internal layers. Heterostructure solar cells include the combination of crystalline and amorphous Si, the wide band gap window from AlGaAs on Si, multilayer structures with 2 – 5 p-n transitions and materials with different width of the band gap. Such heterostructures can increase the efficiency to the theoretical value.

One of the advantage material of solar cells energetic is porous silicon (Si-por). Si-por has a big surface area that is an important factor of the battery efficiency.

We investigated the processes of the porous Si formation by two techniques: electrochemical and electro-erosion.

The reproduction and the porosity of porous silicon depend on numerous factors such as the density of current, the type of semiconductor conductivity, the level of alloying of material, the composition of electrolyte and etc. For the reproductive formation of the porous silicon, we propose the electrical erosion technique in the flash regime. The properties of as prepared matrix depend only on the specific resistance of the semiconductor and the energy of discharge. The degradation of such porous matrix is significantly lower (Fig. 7). The diameter of pores formed by electro-erosion method is significantly more (0,1 – 0,5 mkm) than diameter of pores formed by electrochemical method (0,01-0,1 mkm)

We found that at the electrochemical formation of porous Si the obtained surface area and the photocurrent density are more than by the electro-erosion preparation (Fig. 8).

We used the porous Si formed by electrochemical method for the following experiment. The stability of the photocurrent in Si and Si-por is low (fig 8). The velocity of the degradation is increased by lowering of the pores diameter. Therefore, it is necessary to provide the protection from external factors. It is expediency to use the photoactive oxide films as protective coatings.

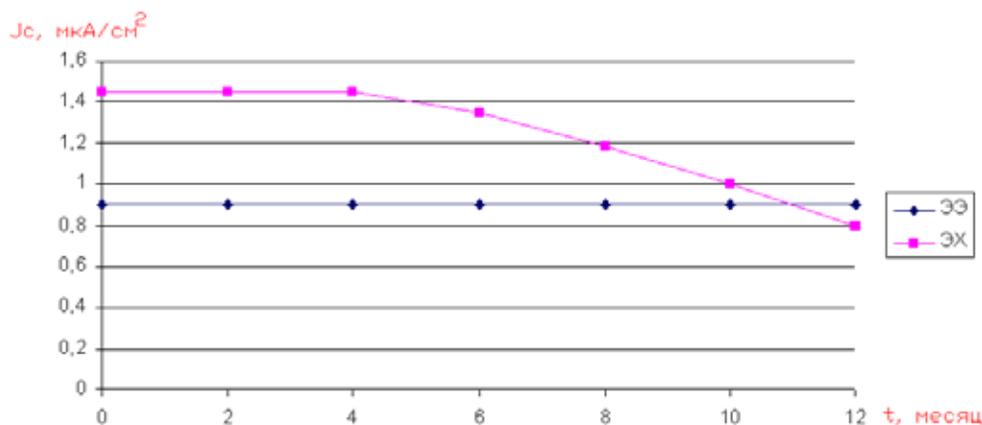


Fig. 7. The dependence of current density (Jc) from time (T) for porous Si a) EC, b) EE

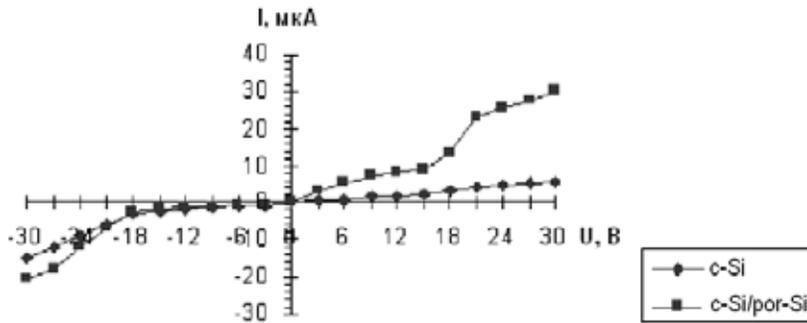


Fig. 8. Photocurrent–voltage characteristics of Si-por/Si (1) and Si (2)

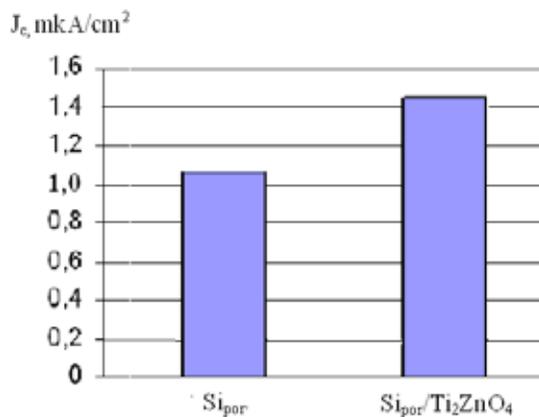


Fig. 9. Efficiency of photoactive heterostructures Si-por and Si-por/Ti₂ZnO₄

We tried to create the hetero structure of the photoactive oxide thin films with porous silicon. The surface solution process can prepare an ultrathin metal oxide film on the substrate. This process consists of three steps: chemisorptions of Ti,Zn-carboxilates, drying and annealing. Uniform metal oxide films can be prepared with reproducible thickness by this process. In the present study, we applied this process to Si porous as a substrate. Extracts of Ti and Zn mixture were selected as precursor.

We can expect the increase of the system Si-por/TiO₂ efficiency. The width of the band gap of TiO₂ is 3,2 eV. The barrier for electrons on the Si/TiO₂ boundary is 1,0 eV. The difference of band gaps between Si and TiO₂ provides the light transition from the wide band gap window without adsorption, and the total conductivity of system is increased.

Photoactive oxide films Ti₂ZnO₄ with a protective function was deposited on the porous Si by extraction-pyrolysis technique. The prepared extracts of Ti and Zn was mixed in the solution in the proportion Ti:Zn = 2:1 and deposited on the Si-por by the drop rotation.

The thickness of the oxide film evaluated by the surface tension of the solution and the pressure in the wetting film. The optimal thickness of the oxide film was determined as 30 – 50 nm. The increase of oxide film thickness decreases the photocurrent of the heterosystems Si_{por}/Ti₂ZnO₄.

The main role in the carriers generation belongs to Si. The charge transition brings about injected electrons and holes from Si and photoelectrons from the Ti₂ZnO₄ film.

The thickness and the resistivity of porous Si layer is important in Si-por/Ti₂ZnO₄ heterostructures. The dependence of the current density on the thickness of the porous Si layer (Fig. 10) shown that the optimal thickness of the porous Si layer is 3,5 mkm and resistivity 10 Om/cm.

The optimal temperature of annealing of Si-por/Ti₂ZnO₄ heterostructures was determined as 450 °C because the increase of annealing temperature leads to lowering of photocurrent.

The photo response of the heterostructure “porous Si – photoactive oxide” have been evaluated as 8,5 % by usage of pressing contacts what is more than values of the porous matrix (Fig.9).

Conclusions

For the mass production and in order to provide the quickly grow of solar power engineering the reducing of materials cost is necessary. The micro- and nano-electronic devices demand simple and low power courses of energy. Our investigations show that solar cell In_{0,9}Sn_{0,1}O – Ti₂ZnO₄ sensitized by Ru-extract allows to obtain the photocurrent 2,3 mV at the thickness of films 100 nm and the optimal temperature of annealing 550 °C.

The possibility to increase of solar cells efficiency is shown by the example of heterostructures Si-por/Ti₂ZnO₄. Because the main role in the carriers generation belongs to Si, the thickness of oxide film should be low. The optimal thickness of Ti₂ZnO₄ film with protection properties is found as 50 nm.

This work was supported by Russian Federal Found on Investigations and Krasnoyarsk Fond of Science 07-03-96803.

References

1. O'Regan B. Solar cell on the base of TiO₂/ O'Regan B., Gratzel M // Nature. – 1991 – V. 335. C. 737.
2. Miyasaka Tsutomu. Efficient nonsintering type dye-sensitized photocells / Miyasaka Tsutomu, Kijitori Yujiro, Murakami Takuro N. // Chem. Lett. 2002. – № 12. – C. 1250 – 1251.
3. Rahman M. Y. A. Effect of ionic conductivity of a PVC-LiClO₄ based solid polymeric electrolyte on the performance of solar cells of ITO/TiO₂/PVC-LiClO₄/graphite / Rahman M. Y. A., Salleh M. M., Talib I. A., Yahaya M. // J. Power Sources. 2004. – 133. – № 2. – C. 293–297.
4. Hao Sancun. The influence of acid treatment of TiO₂ porous film electrode on photoelectric performance of dyesensitized solar cell / Hao Sancun, Wu Jihuai, Fan Leqing, Huang Yunfang, Lin Jianming, Wei Yelin // Sol. Energy. 2004. – 76, – № 6. – C. 745 – 750.
5. Luo Xin-lian. Two zones conductivity of Ti oxide / Luo Xin-lian, Lan Ding, Wan Fa-rong, Long Yi, Zhou Hai-ying, Ye Ya-ping // Gongneng cailiao yu gijian xuebao = J. Funct. Mater. and Devices. 2003. – v.9. – № 4. – C. 385 – 390.
6. Kang J. Gel polymer electrolytes based on a novel quaternary ammonium salt for dye-sensitized solar cells / Kang J., Li W., Wang X., Lin Y., Li X., Xiao X., Fang S. // J. Appl. Electrochem. 2004. – 34, № 3 – C. 301-304.
7. Komiya Ryoichi. High efficient quasi-solid state dye sensitized solar cell with ion conducting polymer electrolyte / Komiya Ryoichi, Han Liyuan, Yamanaka Ryohsuke, Mitate Takehito // 21 International Conference on Photochemistry, Nara, July 26-31, 2003 : ICP 21. Nara, 2003. – C. 558.

8. Mardare Diana. On the structure of titanium oxide thin films / Mardare Diana, Rusu G. I. // An. ~Esti. Univ. Ia~Esi. Fiz. star. condens. 1999-2000. – v. 45-46. – С. 201–208.
9. Pichot F. Low-temperature sintering of TiO₂ colloids: application to flexible dye-sensitized solar cells / Pichot F., Pitts J. R., Gregg B. A. // Langmuir: The ACS Journal of Surfaces and Colloids. 2000. – v. 16 – № 13 С. 5626–5630.
10. Патрушева Т.Н., Виноградов С.А., Махновская Н.В., Романченко А.Н., Коловский Ю.В., Шелованова Г.Н., Холькин А.И. Проводящие прозрачные оксидные пенки, полученные экстракционно-пиролитическим методом // Химическая технология. – 2007. – № 5. – С. 197 – 200.