УДК 621.383:537.221

ISSN 1729-4428

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Development Organic Back Contact for Thin-Film CdS/CdTe Solar Cell

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Hybrid solar cells on the basis of CdTe photoabsorber layer and CdS buffer layer on glass/ITO substrate in combination with organic back contact layer of highly conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) were prepared using vacuum evaporation and spin-casting techniques. In order to prepare the complete solar cells, the appropriate deposition parameters and thickness of highly conductive PEDOT-PSS layers were selected experimentally. The best result was obtained by spin-coating of PEDOT-PSS aqueous dispersion which was mixed with glycerin, N-methyl-2-pyrrolidone (NMP), isopropanol and tetraethoxysilane for the enhancement of electrical conductivity of deposited PEDOT-PSS films. It was found that prepared conductive polymer film gives good ohmic back contact to the surface of p-CdTe semiconductor film in complete solar cell. For a current contact preparation to PEDOT-PSS layer, the silver suspension deposition and gold evaporation techniques were applied separately. The best obtained structure glass/ITO/CdS/CdTe/PEDOT-PSS/Ag showed so far an open-circuit voltage of around 560 mV and a short-circuit current density of around 12 mA/cm² under white light illumination with an intensity of 100 mW/cm².

Key words: Solar Cells, Hybrid Structures, CdTe, Conductive Polymer, Back Contact.

Стаття поступила до редакції 16.08.2009; прийнята до друку 15.12.2009.

Introduction

More than 95% of the solar cells in use today are made of crystalline silicon (c-Si); the average cost of the electricity generated is \$0.3/kW h. By comparison, in most parts of the United States, electricity costs about \$0.06/kW h. Thus, it costs approximately five times as much for electricity from solar cells. If the cost of producing solar cells could be reduced by a factor of 10, solar energy would be not only environmentally favorable, but also economically favorable [1].

In the field of research and development of low-cost solar energy converters, hybrid organic-inorganic solar cells in an all thin-film configuration deserve a serious investigation. For example, prospective materials for substitution of inorganic semiconductors in solar cells can be conductive polymers and photosensitive organic semiconductors [2-7].

The idea of using these materials is supported by the fact that no broken covalent bonds exist on the surface of organic semiconductors and they should not create additional centres of trapping and recombination at the interface with an inorganic photoabsorber. Furthermore, large dimensions of organic molecules should strongly limit the rate of their diffusion in inorganic layers and the formation of new impurity centres. Therefore, the efficiency of power conversion provides advantages of organic materials as functional layers and the use of good well-known inorganic photoabsorbers (CdTe, CdSe, CuInS₂ etc.) [8-11].

A stable back contact that is not significantly rectifying and has a low resistance is essential for good performance and long-term stability of CdS/CdTe solar cells. Since CdTe is a p-type semiconductor with a high electron affinity (4.5 eV) and high band gap (1.5 eV), a high work-function electrically conductive material is required to make good ohmic contact to CdTe. Most metals, however, do not have sufficiently high work-function and therefore form Schottky-barrier contacts to CdTe photoabsorber layers [12].

In the present study, a number of new hybrid solar cells based on glass/ITO/CdS/CdTe substrates and organic back-contact layers of highly conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) was prepared and investigated. In this approach, the organic layer is considered as an alternative for the traditional high working function metal back-contact layer in the conventional cell structure.

I. Experimental

For our investigations, glass/ITO/CdS/CdTe

structures were used, fabricated by Dr. G. Khrypunov (Thin Film Physics Group, ETH Zürich). It was developed a CdTe/CdS solar cell fabrication process in which all the layers are grown by physical vapor deposition (PVD) methods [13]. Briefly as described in [14], commercially available soda-lime glass coated with fluorine-doped tin oxide (FTO) or with in-house sputtered ITO is used as a substrate. CdS layer is grown in a high vacuum evaporation (HVE) chamber at a substrate temperature of 150 °C and subsequently annealed at 450 °C for recrystallisation, CdTe is then deposited at a substrate temperature of 300 °C in the same chamber without breaking the vacuum. Typical thickness of CdS is 0.1-0.5 mm and CdTe thickness is between 3 and 4 µm. CdTe/CdS junction is activated by evaporating 400-600nm CdCl₂ on to the CdTe surface and subsequently annealing the stack in air at 430 °C for 30 min.

Complete hybrid solar cells on the basis of such prepared glass/ITO/CdS/CdTe photovoltaic structure in combination with organic back-contact functional layer of highly conductive PEDOT-PSS were prepared using spin-casting technique – Chemat Technology KW-4A double-speed spin coater was applied. Conductive polymer back contact was deposited after bromine-methanol treatment of the CdTe surface (1.5% Br₂ solution in methanol during 5 sec.).

In order to prepare complete solar cells, the appropriate deposition parameters and thickness of highly conductive PEDOT-PSS layers were selected experimentally. Aqueous suspension of 1.3% PEDOT-PSS was purchased from Aldrich. The best result was



Fig. 1. Cross-sectional EbS (left part) and SEM (right part) conjugated images of glass/ITO/CdS/CdTe/PEDOT-PSS structure.

obtained by spin-coating of dispersion, where 5 ml 1.3 wt. % PEDOT-PSS aqueous dispersion was mixed with 120 μ l glycerin, 250 μ l NMP, 6.25 ml isopropanol and 81 μ l tetraethoxysilane to enhance the electrical conductivity of the deposited PEDOT-PSS films. The mixture was spin-coated on glass/ITO/CdS/CdTe substrates and dried at 40 °C in vacuum for 3 h. The average thickness of PEDOT-PSS films was about 150 nm.

All investigated photovoltaic structures were prepared in sandwich configurations

glass/ITO/CdS/CdTe/PEDOT-PSS/Au and glass/ITO/CdS/CdTe/PEDOT-PSS/Ag. To prepare a current contact onto the PEDOT-PSS layer, the silver suspension deposition and gold evaporation techniques were applied separately. The cross-sectional microstructure was observed by high resolution scanning electron microscope Leo Supra 35 with compositional contrast detector EbS. Figure 1 shows the cross-sectional view of the structure with the PEDOT-PSS back-contact layer.

Current-voltage (I-V) characteristics of complete solar cells were measured by using Autolab PGSTAT 30 potentiostat/galvanostat. White light with an intensity of 100 mW/cm^2 from a tungsten-halogen lamp was used for irradiation.

II. Results and discussion

Due to its high work-function, CdTe is a difficult material to form an ohmic contact. When a metal contact is applied on the CdTe, this often results in the formation of a Schottky barrier. The barrier acts as a diode in the opposite direction, thus blocking the photogenerated charge carriers. This phenomenon, known as back barrier, or back diode, or back surface field, can affect all major photoabsorbers such as CdTe, silicon, CuInSe₂ etc [11].

In our work, the organic layer of conductive polymer PEDOT-PSS is considered as an alternative for the traditional back-contact layer in the conventional cell structure. It should be noted, that conductive polymer PEDOT-PSS has a reasonably high work-function value of around 5 eV.

In addition, a high electrical conductivity of back contact layer is required strongly for good operation of the solar cell. For these purposes, thin films of highly conductive PEDOT-PSS were deposited onto CdTe layers by using the spin-casting technique from the special mixture of PEDOT-PSS aqueous dispersion with various additives. The PEDOT-PSS layer thickness and morphology depends on dilution, content of the precursor mixture and rotation speed. The best result was obtained by spin-coating of dispersion, where PEDOT-PSS aqueous dispersion was mixed with glycerin, NMP, isopropanol and tetraethoxysilane as described in the experimental part.

Above mentioned additives play very important role in PEDOT-PSS thin-film processing. Such, the enhancement of electrical conductivity of deposited PEDOT-PSS films by addition of the polar solvents e.g. NMP was explained as a screening effect due to the polar solvent between the dopant and the polymer main chain [15, 16]. Isopropanol is the solvent for quick-drying and wetting agent to improve the adhesion between the polymer film and substrate. The tetraethoxysilane was added for improvement of scratch resistance of spincasted polymer films.

Using lower precursor concentrations yields a thinner buffer layer making pin holes more probable and thus lowering the quality and repeatability of PEDOT-PSS films. On the other hand too thick a contact layer



Fig. 2. Electron beam-induced current (EBIC) (left part) and cross-sectional SEM (right part) conjugated images of complete glass/ITO/CdS/CdTe/PEDOT-PSS/Au solar cell.



Fig. 3. I-V characteristics of complete structures under irradiance of 100 mW/cm^2 intensity.

raises the serial resistance of the structure and bringing down the photovoltage/photocurrent. Therefore we believe that the optimal thickness of PEDOT-PSS should be in the range 50-150 nm.

Figure 1 shows the SEM micrograph from the cleavage face of the glass/ITO/CdS/CdTe/PEDOT-PSS structure. The thickness of the layers was about 1 μ m for the CdS layer, 3 μ m for the CdTe photoabsorber layer and 150 nm for the PEDOT-PSS back contact layer. It should be noted, that the deposited PEDOT-PSS layer is compact, uniform and well-adherent to the surface of CdTe layer. After PEDOT-PSS film deposition some smoothening of the CdTe surface by the amorphous polymer was observed.

The SEM EbS image obtained by using the compositional contrast detector (left part of Figure 1) show the uniform and homogenous structure of layers without the presence of the secondary phases and impurities.

Figure 2 shows the electron beam-induced current (EBIC) cross-sectional image of complete

glass/ITO/CdS/CdTe/PEDOT-PSS/Au solar cell conjugated with the SEM image of the same part of structure. It should be noted, that good uniform photogeneration in the CdTe photoabsorber layer and photoactivation of adherent PEDOT-PSS layer are observed. Relatively light interface between CdTe photoabsorber layer and PEDOT-PSS back contact layer confirms a small amount of physical defects between these layers and therefore, low recombination of photogenerated charge carriers at the interface with an inorganic photoabsorber.

Figure 3 shows the current-voltage (I-V) characteristics of the representative structures. Significant photovoltage and photocurrent of the fabricated solar cells have been observed under tungstenhalogen white light illumination with an intensity of 100 mW/cm². The incident light produced a short-circuit photocurrent density $I_{sc} = 12 \text{ mA/cm}^2$ and an open-circuit voltage V_{oc} = 560 mV for the glass/ITO/CdS/CdTe/PEDOT-PSS/Ag structure. Overall photoconversion efficiency was around 2%.

Obtained I_{sc} values are relatively high and demonstrate a good agreement with the EBIC data. It seems that at short-circuit conditions most of the photo-carriers at the interface CdTe/PEDOT-PSS do not recombine. On the other hand, the structures are not yet optimized and there is still a large room for improvement of the fill-factor. Nevertheless, the technology of hybrid organic-inorganic cells preparation is simpler in comparison with the technology of completely inorganic cells based on CdTe photoabsorber.

Good properties of cells with PEDOT-PSS back contact layer confirm expediency of using such kinds of high work-function materials in hybrid cells due to enhancing the charge carriers transfer through the structure. Also, our results demonstrate that spin-casted silver contact plate from the silver adhesive suspension is appropriate technique for photovoltaic cell preparation.

Conclusions

A new approach connected with using of organic functional layer in the solar cells structure is highlighted - hybrid solar cells based on the CdTe photoabsorber and utilizing thin film back-contact layer of the conductive polymer PEDOT-PSS were prepared and characterized. It was found that the prepared conductive polymer film gives good ohmic stable back-contact to the surface of the p-CdTe semiconductor film in a complete solar cell structure. The best structure glass/ITO/CdS/CdTe/PEDOT-PSS obtained SO far showed an open-circuit voltage of around 560 mV and a short-circuit current density of around 12 mA/cm² under white light illumination with an intensity of 100 mW/cm².

We have shown that our deposition technique gives us a way to prepare ohmic back contact layer of highly conductive PEDOT-PSS onto CdTe photoabsorber layer using relatively simple deposition method.

Acknowledgment

This work was supported by STCU under Project 4301.

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- [1] C. Goh, and M.D. McGehee // The Bridge, **35**(4), p. 33 (2005).
- [2] P. Chartier, H. Nguyen Cong, C. Sene // Solar Energy Materials and Solar Cells, 52, 413 (1998).
- [3] P.J. Sebastian, S.A. Gamboa, M.E. Calixto, H. Nguyen-Cong, P. Chartier, R. Perez // Semiconductors Science and Technology, 13, 1459 (1998).
- [4] W.U. Huynh, J.J. Dittmer, W.C. Libby, G.L. Whiting, A.P. Alivisatos // Advanced Functional Materials, 13(1), p. 73 (2003).
- [5] S. Bereznev, J. Kois, I. Golovtsov, A.Öpik and E.Mellikov // Thin Solid Films, (425), pp. 511-512 (2006).
- [6] S. Bereznev, I. Konovalov, A. Öpik, J. Kois, Synthetic Metals, 152 (2005) 81.
- [7] A. Verbitsky, Ya. Vertsimakha, P. Lutsyk, S. Studzinsky, S. Bereznev, J. Kois // Semiconductors, 40(2), 197 (2006).
- [8] A.J. Frank, S. Glenis, A.J. Nelson // The Journal of Physical Chemistry, 93, 3818 (1989).
- [9] S. Bereznev, R. Koeppe, I. Konovalov, J. Kois, S. Günes, A. Öpik, E. Mellikov and N.S. Sariciftci // Thin Solid Films, 515, Issue 15 5759 (2007).
- [10] M. Winkler, J. Griesche, I. Konovalov, J. Penndorf, J. Wienke, O. Tober // Solar Energy, 77, 705 (2004).
- [11] Y. Roussillon, V.G. Karpov, Diana Shvydka, J. Drayton, and A.D. Compaan, *Proceedings of 31st IEEE Photovoltaic Specialists Conference* 441, (2005).
- [12] S.H. Demtsu, J.R. Sites // Thin Solid Films, 510, 320 (2006).
- [13] A. Romeo, H. Zogg, A.N. Tiwari, Proceedings of Second World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, p. 1105 (1998).
- [14] G. Khrypunov, A. Romeo, F. Kurdesau, D.L. Bätzner, H. Zogge, A.N. Tiwari // Solar Energy Materials and Solar Cells, 90, 664 (2006).
- [15] F. Louwet, L. Groenendaal, J. Dhaen, J. Manca, J. Van Luppen, E. Verdonck and L. Leenders // Synthetic Metals, pp. 135-136, 115 (2003).
- [16] J. Y. Kim, J. H. Jung, D. E. Lee and J. Joo // Synthetic Metals, 126 p. 311 (2002).

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Розробка органічних контактів для тонкоплівкових сонячних елементів CdS/CdTe

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Були досліджені гібридні сонячні елементи на основі фото поглинаючих шарів CdTe та буферних шарів CdS на підкладках скло/ITO з органічними тільними контактами електропровідного пол 3,4етилендокстофену (PEDOT), що леговані пол стиренсульфонатом (PSS). Контакти виготовлялися відцентровим методом та методом вакуумного випаровування. Оптимізація параметрів осадження та товщини PEDOT-PSS шарів була проведена експериментально по значенню їх електропровідності. Було встановлено, що для отримання електропровідних PEDOT-PSS шарів відцентрованим методом водний розчин повинен містити гліцерол, N-метил, 2-пролдон(NMP), зопропанол та тетраетокслан. Біло встановлено, що виготовлені електропровідні полімерні плівки формують с напівпровідниковим шаром р-CdTe низькоомний контакт. Для виготовлення токового контакту до PEDOT-PSS шарів були використані срібна паста та плівки золота отримані вакуумним випаровуванням. Показано, що найбільш ефективні приладові структури glass/ITO/CdS/CdTe/PEDOT-PSS/Ag при потужності сонячного опромінення 100 мВт/сm2 мають напругу холостого ходу 560 мВ і щільність току короткого замикання 12 мА/сm2

Ключові слова: Сонячні елементи, гібридні структури, CdTe, електропровідні полімери, ТИЛЬНІ контакти.