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New Organic Materials for Organic-Inorganic Silicon-Based Solar Cells

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Two kinds of organic layers deposited on a silicon patterned substrate from a solution at room temperature have been investigated by scanning electron and optical microscopies, by studying the photoresponse, and by measuring the I-V characteristics. The organic pharmaceutical materials used are the following: thiamine diphosphate (vitamin B₁) and metamizole sodium (MS) (analgin). Both hybrids possess the photovoltaic (PV) properties. Investigations of the PV performance versus the solar energy power have indicated that the best samples of a MS-nSi hybrid had efficiency $EFF = 1.97\%$ for the irradiation power $E = 11.6 \text{ mW/cm}^2$ and $EFF = 1.43\%$ for $E = 63.8 \text{ mW/cm}^2$.

Keywords Efficiency; metamizole sodium; organic-inorganic hybrid; patterned silicon substrate; solar cell; thiamine diphosphate

1. Introduction

Although a lot of progress has been made in the inorganic solar cell development [1], the hybrid organic-inorganic combination is proposed as one of the most promising solar cells of the next generation. This interest is stimulated by possible compromises between the cost and conversion efficiencies [2–8]. However, it is obvious now that only Si dominates on the photovoltaic material market. The Si dominance is about 94% of market shares in various forms including a single-crystal or polycrystalline α -Si on CZ-slice ribbon amorphous films. As for the other materials, only CdTe and CIS have 6% of market shares. Organic materials are absent on the market of photovoltaic materials [2]. But they have shown to have a great potential for many important applications in various industrial fields, for example, in the varnish-paint industry, copier technique, photography, and in the field of full-color displays.

Over the past few years, some progress has been made in photovoltaics with the use of the organic materials (pigments, dyes, polymers) and the hybrid organic-inorganic structures [3–8].

Better polymer-fullerene bulk heterojunction solar organic cells have $EFF \approx 5\%$ [4]. For a dye-sensitized hybrid heterojunction based on porous TiO_2 and spiro-Me

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TAD (spiro-triarylamine), $EFF \approx 4\%$ [7]. The best result for an organic hybrid (P3HT-PPV)-nanocrystal (CdTe, CdSe) solar cells is $EFF \approx 1.7\%$ [6].

The preliminary experiments have shown that combinations of organic layer materials used in medicine with solar cell structures attributed to a technological bankrupt ($EFF \leq 5\text{--}7\%$) result in an efficiency of up to 15% [9]. The original therapeutic effect takes place, and, at the same time, a new solar cell hybrid architecture is formed.

The aim of this article is to investigate the new organic materials for the preparation of organic-inorganic silicon-based hybrids for the photovoltaic application.

2. Experimental

Two kinds of organic pharmaceutical materials were used for the formation of organic-inorganic silicon-based hybrid structures for solar cells: the thiamine diphosphate hydrochloride, vitamin B₁ ($C_{12}H_{20}N_4O_7P_2SCl$) (TD) and the metamizole sodium, analgine ($C_{13}H_{16}N_3NaO_4S \cdot H_2O$) (MS). The organic materials were purchased at a chemist's shop (pharmacy) and used without further purification. The molecular structure of organic materials is presented in Figure 1.

The chemical solution deposition was used to prepare the organic layers from a 5-% aqueous solution on Si patterned surfaces at room temperature. The substrates were cut out from an *n*-type Cz Si with a concentration of about 10^{16} cm^{-3} . A pyramidal pattern was prepared by the standard technology. The rear surface was protected by a chemically stable varnish. Then the substrate was immersed into a glass bath with the solution. The time deposition was varied from 1.0 to 50 h. The thickness of deposited layers was varied from a few nanometers up to a few micrometers according to the duration of the deposition process. An Ag paint was applied to contacts to hybrids.

It is worth to note that the liquid organic medium is not referred to homogenous media, and its identification as a solution is conditional. It is the mixture of water and a medical material in the form of a tablet which contains some additional ligands, for example, starch, lactose, *etc.* These components are absent in molecular

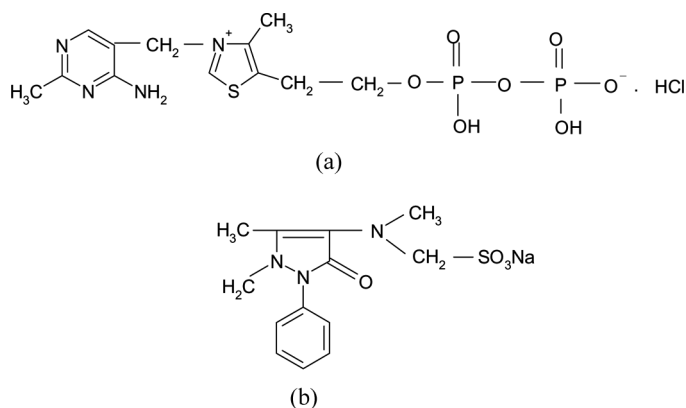


Figure 1. Molecular structure of the organic materials: a) – thiamine diphosphate containing H, C, N, O, S, P, and Cl elements; b) – metamizole sodium containing H, C, N, O, S, and Na elements.

formula. Due to these factors, some solutions can be referred to suspensions. Halogens, oxygen, nitrogen oxide (NO_2), and H_2O are the p-type ligands for organic materials. The alkali metals are *n*-type ones [2,10].

The morphological images of deposited layers were examined by optical microscopy and scanning electron microscopy (SEM).

The photoresponse (PR) spectra were measured in the short-current mode in the spectral range from 400 to 1100 nm using the standard equipment.

The photovoltaic PV parameters of hybrids were measured by a PV set under the standard test condition (STC) (100 mWcm^{-2} , 25°C , and the global spectrum corresponding to an air mass of 1.5) with a measurement uncertainty of $\pm 2.5\%$. The PV monitoring at various radiation levels was performed using the same steady-state Sun simulator as that in STC and neutral filters, i.e., without any modification of the spectral distribution of the Sun's light.

3. Results and Discussion

As shown in Figure 2, the surface morphology changes significantly with the TD organic coating thickness. At the beginning of the hybrid formation (thin organic layer $\leq 100\text{ nm}$) under the morphological stability (i.e., a thermodynamically stable surface), the hybrid contour is the same as the substrate one. The SEM image exhibits a relatively uniform coating of pyramidal surfaces (Fig. 2a). The examples of different surface morphologies of the organic layer during the growth are presented by the optical micrographs in Figures 2b–d. At the next stage of the film growth, the circular-type cells are formed with increase in the organic layer thickness (Fig. 2b). Later on, the other interesting morphology in the spherulite form is developed (Fig. 2c). The spherulite development is the process of growth of filaments in radial and circular directions. Each filament of a spherulite (Fig. 2d) contains fibrils which, in their turn, are organized from chains like nanowires and nanodots.

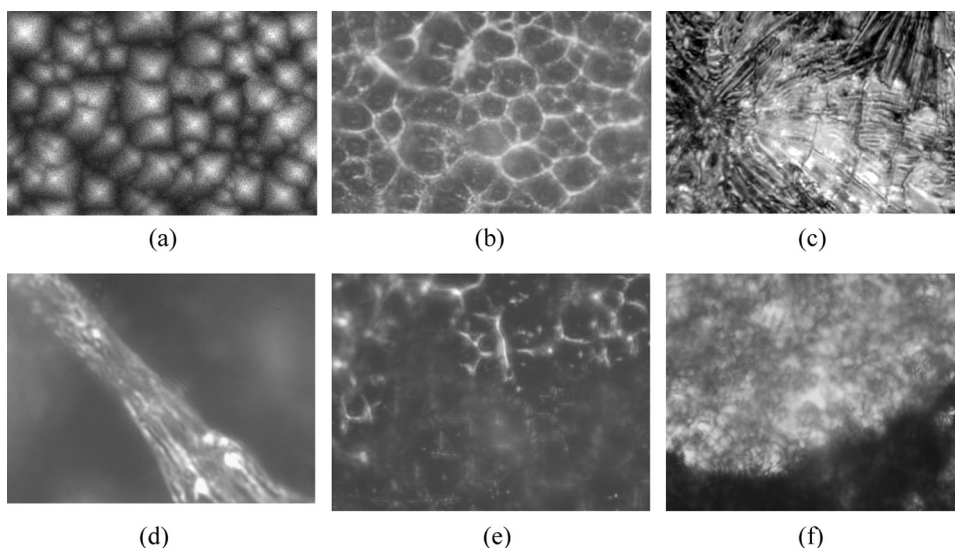


Figure 2. Typical optical image of the morphology of hybrid surfaces deposited on Si from TD (a–d) and MS (e, f) solutions.

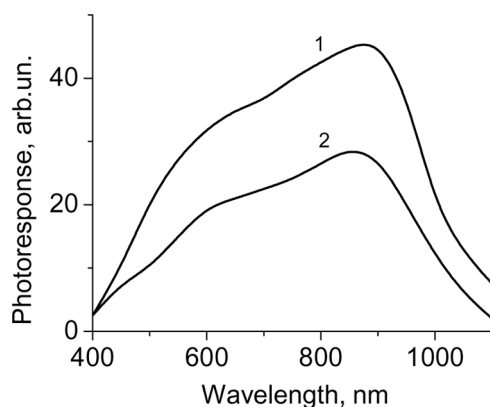


Figure 3. Typical PR spectra of an MS-Si hybrid for the morphologies of Fig. 2e (curve 1) and Fig. 2f (curve 2).

It should be noted that the morphology evolution of layers deposited from an MS solution is analogous to ones shown in Figure 2. Two fragments of such a morphology are demonstrated in Figures 2 e,f. Thus, it can be concluded that the substrate pattern has preference in the growing from these organic solutions, as well as at the inorganic deposition [11], especially during the first stage of deposition.

Two typical PR spectra of MS-Si hybrids for the morphologies of Figure 2e (curve 1) and Figure 2f (curve 2) are displayed in Figure 3.

The PV parameters at different combinations of organic-Si pairs and deposition regimes are summarized in the Table 1. It should be noted that the measurements of

Table 1. The PV parameters of organic-Si hybrids: J_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, FF is the fill factor, EFF is the solar cell efficiency.

E , mW/cm ²	J_{sc} , mA/cm ²	V_{oc} , V	FF , %	EFF , %
TD- <i>n</i> Si 24 hours				
5.2	0.92	0.068	30	0.36
12.3	3.83	0.112	28	0.96
26.9	9.06	0.152	26	1.31
63.6	18.6	0.158	25	1.16
102.7	23.86	0.161	24	0.91
MS- <i>n</i> Si 2 hours				
4.2	0.90	0.165	32	1.14
11.6	3.13	0.229	32	1.97
63.1	14.05	0.150	32	1.06
103.1	14.74	0.105	32	0.48
MS- <i>n</i> Si 50 hours				
4.2	0.61	0.105	30	0.45
11.2	2.62	0.213	30	1.40
63.8	14.15	0.211	31	1.43
102.9	18.35	0.189	30	1.02

hybrid structures were carried out without metallization, by using the front and rear pressing metallic contacts.

4. Conclusion

A new approach in the solar cell formation has been demonstrated. A PV technology based on the chemical bath deposition of heterocyclic amine (pharmaceutical materials thiamine diphosphate and metamizole sodium) onto a Si patterned substrate at room temperature is developed. As a result, the efficiency up to 2% has been achieved.

The deposition of organic layers from chemical solutions at room temperature onto a Si patterned substrate is a perspective procedure for the formation of hybrid solar cells. One of the most intriguing aspects is the use of pharmaceutical materials for the production of solar cells.

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