Sensors

Vitamin B12-functionalized patterned Si surface for solar energy conversion

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Abstract. Interaction between organic and inorganic materials is very actual both for understanding their nature and for some applications. One of directions in this area is functionalization and sensibilization of semiconductor surfaces by organic compounds for solar energy conversion. The main goal of this research is to demonstrate the possibility for immobilization of some photofunctional organic compounds on an inorganic silicon substrate at the room temperature. In particular, we have prepared a new B12–Si hybrid with the solar conversion efficiency up to *Eff* = 3.75% at the room temperature by chemical deposition of vitamin B12 on the patterned silicon substrate. Here, we report the correlation between morphology and functionality, as well as deposition mode for B_{12}–Si hybrids.

Keywords: patterned Si, vitamin B12, functionalization, solar energy conversion.

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1. Introduction

Organic modification, functionalization, and sensitization of silicon have increased enormously during the recent decade [1–4]. These resulting organic-inorganic hybrids have excited a great interest for physics, chemistry, as well as for innovative research areas in biology, communications and medicine. They are potential objects for photovoltaics (PV), optoelectronics, biosensing, as well as gene and drug delivery applications due to: (i) unique properties of both the isolated molecule and self-organized molecular assemblies or aggregations; (ii) the combination of a high absorption coefficient of organics and good Si transport properties; (iii) hybrid compatibility with well explored Si planar technology [2, 5–12]. Now, the new opportunities are opened in micro/nanometer-size silicon-based structures of the next generation with unprecedented level of functionality due to various reactions of Si with organic materials including organometallic and aromatic systems [2, 13-15].

The positive effect of deposited vitamin B1 (thiamine diphosphate hydrochloride) and other drugs on patterned n^+-p-Si solar cells was already described in our work earlier [16]. Later, deposition of B1 and metamisol sodium on patterned n-Si as well as testing the PV parameters showed that these drugs – Si hybrids – had the efficiency of solar energy conversion of about 1.0% under AM 1.5 and 0.05 Sun, respectively [17].

In this work, we study evolution of morphology, the photoresponse (PR) and photoluminescence (PL) spectra as well as PV parameters simultaneously, in order to understand the morphological effect on functionality of these hybrids.

2. Materials and methods

Czochralski grown Si wafers of {100} orientation and n-type conductivity with the dopant concentration between 10^{15} and 10^{16} cm^{-3} and an anisotropically etched surface in the shape of tetragonal pyramid were used as substrate. After protecting the Si rear surface with chemically stable varnish, the Si sample was immersed into a glass bath with B12 (its formula is presented in [18]) of 1.25% water solution. The chemical deposition was produced at room temperature under ambient laboratory condition. The deposition time was varied from 30 min up to 90 hours. Ag paint was applied as contact material to the hybrid.

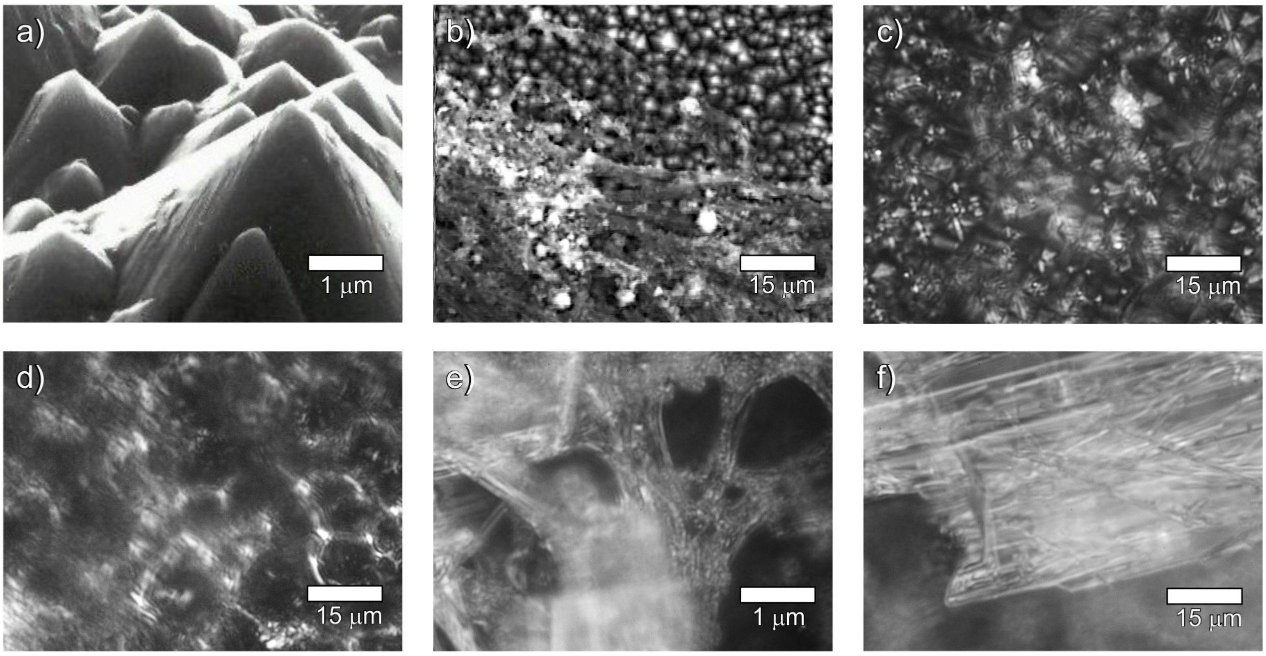

Fig. 1. Image of the hybrid surface under investigation: (a) SEM and (b)-(f) optical microscopy images of surface morphology. (a) Si patterned substrate. (b)-(f) B12–Si hybrids. (b), (c) Pyramid type. (d) Net-like shape. (e) Bunch shaped form. (f) Crystalline lamellar form. 1.5 mm scale bar presents in: (a), (e), (f) 1 μm and (b), (c), (d) 15 μm.

The surface image of resulting hybrids was characterized using scanning electron microscopy (SEM) and optical microscopy. The PR spectra were measured in the short circuit regime within the spectral range 400 to 1100 nm by using the standard equipment. In individual cases, ultraviolet PR was studied, too. Measurements of PL were performed under excitation by using 337-nm N_2 gas pulsed laser (8 ns, 1.5 kW/pulse), PL radiation was detected using a photomultiplier within 380...900 nm diapason in the photon count regime. PV parameters of hybrids were recorded at standard test condition (100 mW/cm^2, 25 °C, air mass AM 1.5).

3. Results and discussion

Typical evolution of surface morphology observed in B12 layers after their deposition is demonstrated in Fig. 1. The change of PR and PL spectra corresponding to morphological image is shown in Fig. 2. Table 1 demonstrates the results of investigations of the solar conversion efficiency *Eff* and other PV parameters versus irradiation energy.

As seen in Fig. 1, at the initial stage of B12 layer deposition (up to 0.5 hour) in stable conditions of a moving chemical front, surface morphology of B12 layer and B12 – Si hybrid (Figs. 1b, 1c) copies the patterned morphology of the substrate (Fig. 1a). In this situation, the terrace-step-kink growth mechanism is realized due to vicinal feature of {111} patterned pyramid-like substrate. It suggests room temperature deposition of films, in spite of the lattice mismatch between the substrate and films [19, 20]. The observed PR I_{sc} within the 400...1100-nm range with the maximum at λ_{max} = 900 nm (Fig. 2a, curve *1*) is typical for such structures on Si. The *Eff* versus *E* dependence (Table 1, a) has the maximum with *Eff* = 1.41% at *E* = 25 mW/cm^2, and then *Eff* value decreases to 0.76% under AM 1.5.

At the next stage (deposition time from 0.5 hour till 1.5 hour, *i.e.*, with increasing the layer thickness), evolution of morphology takes place (Fig. 1d) from the pyramid shape to surface of a circular, square or rhombic net shape as a result of filament connection of pyramid vertexes. For this "quasi-equilibrium" morphology (Fig. 1d), the I_{sc} increase (Fig. 2a, curve *2*) is observed in comparison with the former case. At the same time, I_{sc} is detected in the ultraviolet range with λ_{max} = 276, 315 and 365 nm. The I_{sc} peaks correspond to the absorption peaks of B_{12}. This result is shown in the insert of Fig. 2a.

The hybrid indicates *Eff* = 3.75% at *E* = 25...70 mW/cm^2, which decreased to 3.0% under AM 1.5 (Table 1, b). It is interesting to note that the internal structure of micro-filament is complex. As shown in the filament fragment (Fig. 1g), each filament contains microfibers, which in their turn are organized from chains as nanowires and nanodots. In this moment, the film growth mediated substrate has no preferences, and film morphology is determined by the self-organized process. When time deposition is further increased (up to 2.5 hour), the surface morphology of hybrid is characterized by the presence of bunch shaped fibres joined together in one or more points with ball fragments (Fig. 1e). In this case, I_{sc} is decreased over the whole spectral range (Fig. 2a, curve *3*). At the same time, the efficiencies of the hybrid are *Eff* ≈ 0.8% under AM 1.5 and *Eff* = 2.72% at about 24 mW/cm^2 illumination (Table 1, c).

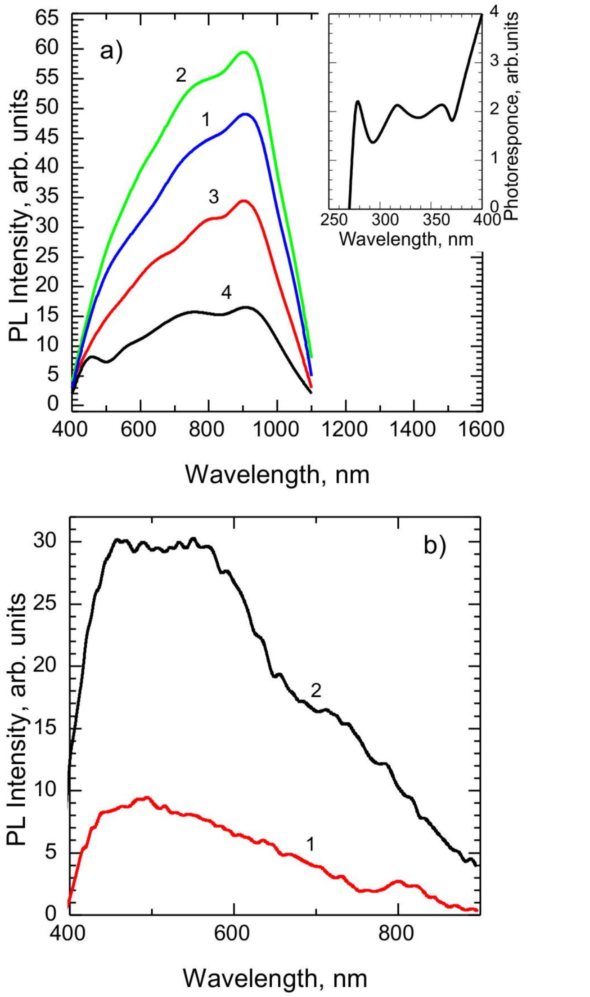

Fig. 2. Photoresponse (a) and photoluminescence (b) spectra of B12–Si hybrids at various times of deposition and different morphologies.
a: (*1*) $t = 0.5$ h, pyramid-like morphology (Fig. 2b,c); (*2*) $t = 1.5$ h, net-like morphology (Fig. 1d); (*3*) $t = 2.5$ h, bunch shaped form (Fig. 2e); (*4*) $t = 90$ h, crystalline lamellar form (Fig. 1f). The insert shows the photoresponse spectra in 250–400 nm range for net-like morphology.
b: (*1*) $t = 1.5$ h, net-like morphology (Fig. 2d), (*2*) $t = 2.5$ h, bunch shaped form (Fig. 2e).

Morphology shown in Fig. 1f corresponds to more thick coating of the pyramid pattern of Si substrate during B12 layer formation. The time of deposition is changed from 2.5 to 90 hours, and the film surface is characterized by lamellar structure (Fig. 1i). PR demonstrates further decrease of I_{sc} value and the additional I_{sc} peak at $\lambda = 450$ nm. There is a weak dependence of *Eff* versus the illuminating power. Here, *Eff* is about 0.6% under AM 1.5 (Table 1, d). Thus, optimum morphology formation improves the PV parameters.

The photoluminescence spectra (Fig. 2b) of hybrids with different morphology also have considerable differences both in peak positions and emission efficiency. According to Fig. 2b, curve *1*, the hybrid spectrum of thinner B12 layer with morphological image

Table 1. Power energy irradiance effect on PV parameters of B12–Si hybrids in dependence on the deposition time* and morphology**.

E, mW/cm^2	I_{sc}, mA/cm^2	V_{oc}, V	FF	*Eff*, %
a				
106.1	14.69	0.190	0.29	0.75
66.3	8.18	0.186	0.42	0.96
24.9	5.62	0.190	0.33	1.41
11.7	1.94	0.137	0.36	0.81
b				
104.1	33.44	0.255	0.37	3.01
63.6	21.74	0.283	0.39	3.75
23.8	7.61	0.292	0.40	3.75
11.4	2.83	0.263	0.36	2.33
4.8	0.42	0.066	0.24	1.10
c				
107.7	26,53	0.089	0.35	0.77
67.6	25.43	0.124	0.32	1.50
25.1	12.64	0.181	0.30	2.72
12.1	5.48	0.168	0.32	2.42
4.9	1.27	0.114	0.41	1.21
d				
106.6	16.87	0.125	0.30	0.59
65.4	11.12	0.116	0.31	0.62
25.1	3.86	0.093	0.34	0.49
12.2	1.23	0.074	0.23	0.17

* (**a**) 0.5 h, (**b**) 1.5 h, (**c**) 2.5 h, (**d**) 90 h;
** (**a**) Pyramid-like morphology (Figs. 1b, 1c); (**b**) net-like morphology (Fig. 1d); (**c**) bunch shaped form (Fig. 1e); (**d**) crystalline form (Fig. 1f).

shown in Fig. 1d is more structured. It has two maxima: one at $\lambda = 500$ nm and another at $\lambda = 800$ nm. Not far from the first peak, there are two shoulders: the shortwave one near $\lambda = 435$ nm and the longwave one at about $\lambda = 535$ nm with weak fine structures. For thicker B_{12} layer with morphological image analogous to Fig. 1e, PL is characterized by a broad peak situated within $\lambda =$ 450...550 nm spectral range (Fig. 2b, curve *2*). The peak position at $\lambda = 800$ nm is transformed into a shoulder. Besides, the emission efficiency increases by 3 to 4 times.

5. Conclusions

The possibility of the functionalization and sensibilization of patterned silicon surfaces by vitamin B12 (cyanocobalamin) at the room temperature has been proved. The example of correlation between morphology and functionality, as well as deposition mode for B12–Si hybrids was demonstrated. In particular, we obtained the new B12–Si hybrids with solar conversion efficiency of up to *Eff* = 3.75% at the room temperature by chemical deposition of vitamin B12 on the patterned silicon substrate. This relatively simple and controlled procedure for fabrication of B12–Si hybrids with the patterned surface and interface may open a number of practical possibilities for photovoltaic application. Optimization of deposition time with corresponding surface morphology is a promising way to improve PV parameters.

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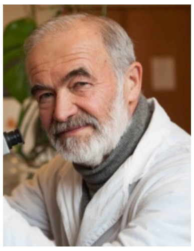

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