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FORMATION OF SELF-ORGANIZED ORGANIC-INORGANIC HYBRIDS

The morphology features and peculiarities of current-voltage characteristics of self-organized organic–silicon hybrids were investigated. The organic layers were formed by chemical bath deposition at room temperatures of phosphorus doped n-type FZ Si-patterned substrate. The pattern was formed by etching in anisotropic etch on the base of aqueous solution of potassium hydrate KOH and isopropyl alcohol. The following aqueous solutions of organic heterocyclic aromatic compounds were used for hybrids formation: sulfacyl sodium, procainamide hydrochloride (novocain) and lamotridgine. These hybrids have shown different types of morphology. This depends on substrate properties, time deposition and organic concentration in water solution. The photovoltaic effect of organic-pattern silicon is the result of chemisorptions of functional amine, amide, carboxyl, thiols and halogen groups on silicon pattern-type surface. At the same time these results have proven that the substrate of start and classic morphology in pyramid form is favored for formation of organic-silicon hybrids for photovoltaic application.
Keywords: organic-inorganic hybrid solar cell, current–voltage characteristic.

Introduction

Organic modification, functionalization and sensitization of silicon have increased enormously during the last decade [1–6]. Such resulting organic-inorganic hybrids have attracted great interest for physics, chemistry as well as for innovative research areas in biology and medicine [7, 8]. They are potential objects for photovoltaics, optoelectronics, biosensing, gene and drug delivery applications due to: 1) unique properties of both the isolated molecule and self-organized molecular assemblies or aggregations; 2) the combination of high absorption coefficient of organics and good Si transport properties; 3) hybrid compatibility with well explored *Si* planar technology [9–16].

Now new opportunities are opening in micro-/nanometer-size silicon based devices of next generation with unprecedented level of functionality using various reactions of Si with organic materials including organometallic and aromatic systems [1–4, 17–20].

This article deals with the self-organized aromatic heterocyclic organics on the silicon patterned substrate with non-classic pyramide type morphology used usually in photovoltaics and some photoelectric properties of such organic-silicon hybrids. The technology used for fabrication of organic-silicon hybrids is enough simple and differs by preparation at room temperature, using of water solutions of organic components and lack of vacuum equipment.

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Experimental details

Phosphorus doped *n*-type FZ silicon (the resistivity is 2Ω·cm) was used for patterned surface preparation. Substrate was etched in anisotropic etch on the base of aqueous solution of potassium hydrate KOH (180 g/l) and isopropyl alcohol (5 % (vol.)). Some etching regimes were studied with difference in temperature, space wafer orientation and presence of wolfram incandesce lamp.

The conditions for pattern silicon substrates are summarized in Table 1.

Table 1

Conditions for formation of patterned surface on Si-wafers

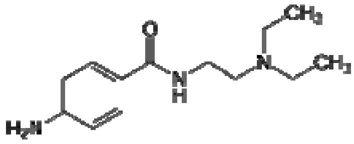
№ of substrate	Temperature, °C	Time of treatment, min	Orientation	Illumination	Additional chemicals
1	48–65	45	Horizontal	Without	No
2	45–60	45	Horizontal	Without	Isopropyl alcohol
3	64–71	30	Vertical	74 Wt	No

Architecture of organic-inorganic hybrid solar cell was consisted of:

1) microstructured silicon substrate with pattern surface;
2) back metal contact;
3) organic material: heterocyclic aromatic compounds;
4) electroconducting painted contact.

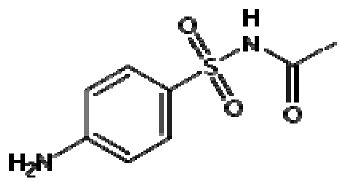
Self-organized organic-inorganic hybrids are formed by chemical bath deposition of the heterocyclic aromatic compounds at room temperature from water solutions. Molecular formulas of substances grown on Si are resulted below.

Procainamide hydrochloride (novocain) – $C_{13}H_{21}N_3OHCl$ [20]:

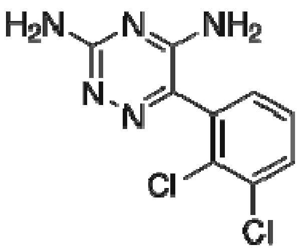


HCl

Sulfacyl sodium (sulfacetamide) – $C_8H_{10}N_2O_3S$ [21]:



Lamotridgine – $C_9H_7Cl_2N_5$ [21]:



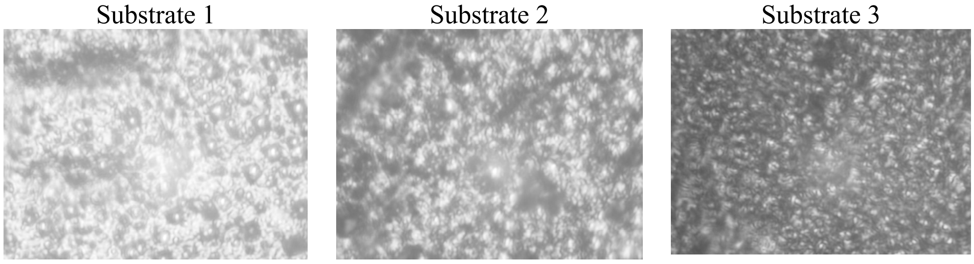
Silicon substrates [100] was etched in KOH-water solution as long as the net was formed at its surface. The previous investigations have shown that such morphology was optimal from the hybrid functionality point of view [5, 19].

The surface morphology of the films was examined with optical microscopy (OM). The peculiarities of current-voltage characteristics (CVC) of organic-silicon hybrids were analyzed by differential and injection approaches [21, 22].

Results and discussion

The optical images of the surface morphology of substrates are presented in Fig. 1. We can see the more homogeneous pattern on substrate 2 and 3.

Substrate 1 Substrate 2 Substrate 3



a *b* *c*

Fig. 1. Optical image of silicon substrate pattern after etching in KOH-water solution: *a–c* – wafers 1–3 (see Table 1) respectively

As example of surface morphology the sulfacyl sodium-silicon hybrid is presented in Fig. 2. The deposition time of self-organised organic film changed from 20 to 50 min. The surface morphology changed from separate organic fragments (Fig. 2, *a*) through organic net (Fig. 2, *b* and 2, *c*) to filament carpet (Fig. 2, *d*).

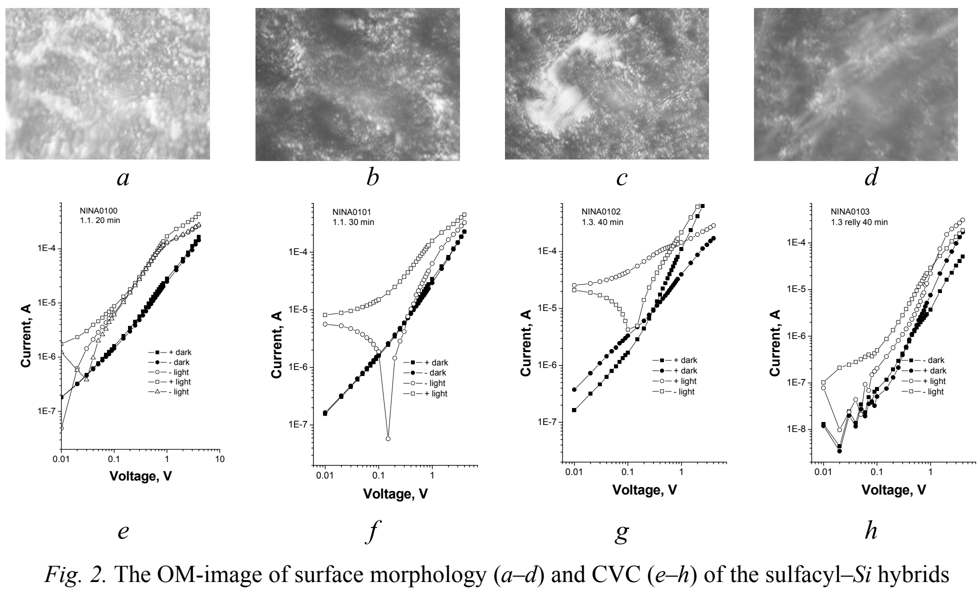


Fig. 2. The OM-image of surface morphology (*a–d*) and CVC (*e–h*) of the sulfacyl–*Si* hybrids obtained on substrate 1: *a–d* and *e–h* – for 20, 30, 40 and 50 min respectively

Simultaneously measured CVCs-show increase of the short circuit current I_{sc} (I_{sc} = 1,5 10^{-6} A, I_{sc} = 7,1·10^{-6} A, I_{sc} = 2,0·10^{-5} A for deposition time 20, 30 and 40 min respectively) and increase of open circuit voltage V_{oc} (V_{oc} = 0,03 V, V_{oc} = 0,15 V, V_{oc} = 0,1 V for deposition time 20, 30 and 40 min respectively). The photovoltaic parameters of hybrids under investigation are summarized in Table 2.

Table 2

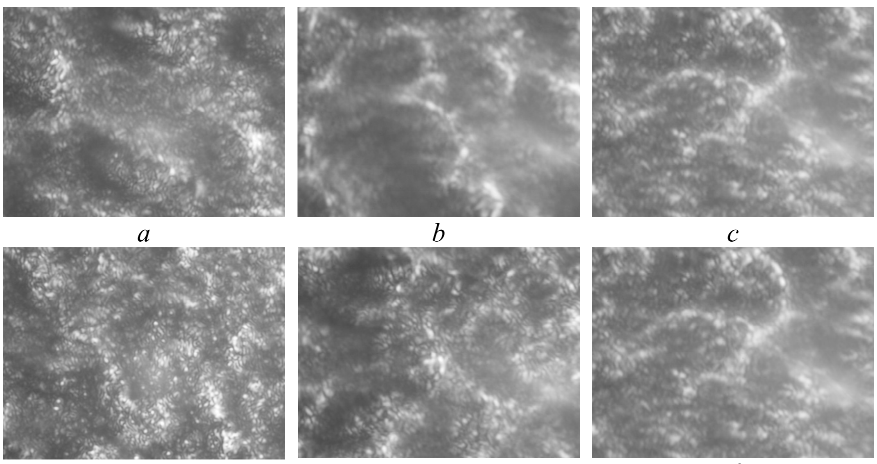
Photoelectric parameters of organic-silicon hybrids with different organics on various substrates under illumination by white light from a halogen lamp with an intensity of about 30 W/m^2

№ of substrate	Deposition time, min	Sulfacyl sodium		Procainamide hydrochloride		Lamotridgin	
		V_{oc}, V	I_{sc}, A	V_{oc}, V	I_{sc}, A	V_{oc}, V	I_{sc}, A
1	20	0.03	$1.5 \cdot 10^{-6}$	-	-	0.05	$1.5 \cdot 10^{-5}$
	30	0.15	$7.1 \cdot 10^{-6}$	0.06	$7.0 \cdot 10^{-6}$	0.10	$5.5 \cdot 10^{-6}$
	40	0.10	$2.0 \cdot 10^{-5}$	0.09	$3.5 \cdot 10^{-7}$	0.05	$8.5 \cdot 10^{-6}$
	50	-	-	0.15	$2.0 \cdot 10^{-7}$	-	-
2	20	-	-	0.05	$1.3 \cdot 10^{-7}$	0.04	$1.2 \cdot 10^{-5}$
	30	0.08	$7.0 \cdot 10^{-6}$	0.03	$20 \cdot 10^{-7}$	-	-
	40	0.08	$1.0 \cdot 10^{-6}$	0.02	$3.0 \cdot 10^{-7}$	-	-
	50	-	-	-	-	-	-
3	20	-	-	-	-	0.15	$6.0 \cdot 10^{-6}$
	30	-	-	0.09	$1.5 \cdot 10^{-5}$	-	-
	40	-	-	-	-	-	-
	50	-	-	-	-	-	-

There is the similar behaviour for hybrids: sulfacyl sodium on substrate 2, procainamide hydrochlorideon substrate 1, lamotridgine on substrate 1 and 2.

Effect of substrate on the surface morphology of different organics at 30 min. chemical bath deposition is presented in Fig. 3. Morphology of organic layers on substrate 3 is differing from one on substrate 1 and 2. May be this is due to activation of surface during etching with illumination. Such effect needs further investigation.

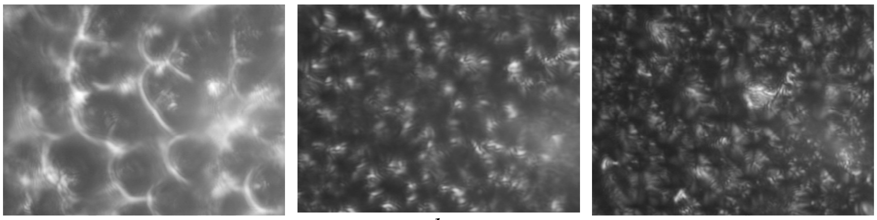
Sub-strate **Sulfacyl** **Procainamid** **Lamotridgin**



1: *a* *b* *c*

2: *d* *e* *f*

3



g *h* *i*

Fig. 3. Effect of substrate on the surface morphology of different organics at 30 min sedimentation: sulfacyl (*a*, *d*, *g*); procainamid (*b*, *e*, *h*); lamotridgin (*c*, *f*, *i*)

Conclusion

Once more it is shown that the self-organized organic-inorganic hybrids formed by chemical bath deposition of the heterocyclic aromatic compounds at room temperature from water solutions have shown different types of morphology. This depends on substrate properties, time deposition and organic concentration in water solution.

The photovoltaic effect of organic-pattern silicon is the result of chemisorptions of functional amine, amide, carboxyl, thiols and halogen groups on silicon pattern-type surface [20]. At the same time these results have proven that the substrate of start and classic morphology in pyramid form is favored for formation of organic–silicon hybrids for photovoltaic application.

Досліджено морфологічні властивості та особливості характеристик струм–напруга для самоорганізованих кремнійорганічних гібридів. Органічні шари було одержано хімічним осадженням за кімнатної температури легованих фосфором візерункових кремнієвих субстратів FZ n-типу. Візерунок формували витравлюванням в анізотропних травниках на основі водного розчину гідрату калію KOH та ізопропилового спирту. В подальшому для отримання гібридів використовували водні розчини органічних гетероциклічних сполук: сульфосаліцилового натрію, гідро хлориду прокаінаміду (новокаїну) і ламотріджину. Ці гібриди показали різну морфологію. Вона залежить від властивостей субстрату, часу осадження та концентрації органічної складової у водних розчинах. Фотогальванічний ефект кремнійорганічного рисунка є результатом хемосорбції функціональних груп амінів, амідів, карбоксилу, тріолів та галогену на поверхні кремнію. Водночас, ці результати підтверджують,що субстрат початкової і класичної морфології у вигляді піраміди кращий для утворення кремнійорганічних гібридів фотогальванічного застосування.

Ключові слова: *органіко-неорганічна гібридна сонячна комірка, характеристика струм–напруга.*

Исследованы морфологические свойства и особенности характеристик ток–напряжение для самоорганизующихся кремнийорганических гибридов. Органические слои были получены химическим осаждением при комнатной температуре легированных фосфором узорчатых кремниевых субстратов FZ n-типа. Узор формировали вытравливанием в анизотропных травителях на основе водного раствора гидрата калия KOH и изопропилового спирта. В дальнейшем для получения гибридов использовали водные растворы органических гетероциклических соединений: сульфосалицилового натрия, гидрохлорида прокаинамида (новокаина) и ламотритриджина. Эти гибриды показали различную морфологию. Она зависит от свойств субстрата, времени осаждения и концентрации органической составляющей в водных растворах. Фотогальванический эффект кремнийорганического *рисунка является результатом хемосорбции функциональных групп аминов, амидов, карбоксила, триолов и галогена на поверхности кремния. В то же самое время, эти результаты подтверждают, что субстрат начальной и классической морфологии в виде пирамиды является предпочтительным для образования кремнийорганических гибридов фотогальванического применения.*

Ключевые слова: органико-неорганическая гибридная солнечная ячейка, характеристика ток–напряжение.

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