PEDOT:PSS Carbon Nanotube Nanocomposites and Textured Interfaces for Enhanced Si Solar Cell Efficiency

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Motivation

- Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) thin polymer films can be obtained by spin-coating on large areas using room-temperature vacuum-free techniques.
- PEDOT:PSS is a *p*-type semiconductor. It forms a heterojunction when in contact with *n*-type silicon
- PEDOT:PSS thin films have high light transmission and electrical conductivity [1].
- Thus, solar cells based on the PEDOT:PSS/Si heterojunction are promising due to the ease of fabrication and low cost, but need to improve their efficiency and stability.
- Silicon surface texturing is used to reduce optical losses and improve the photoelectric parameters of solar cells. Various types of microrelief are formed by the method of chemical etching of semiconductor surfaces, for example, such as quasigrating type [2], inverted pyramids [3], porous ("black") silicon [4], etc.
- The addition of carbon nanotubes (CNT) to PEDOT:PSS increases the conductivity without significantly affecting the transmission of the polymer layer [5].

Experimental details

Flat Si substrate: factory-polished *n*-Si (100), KEF 0.5-2.4 Ohm·cm.

Pyramidal type: *n*-Si (100), wet anisotropic chemical etching in an aqueous solution of 2% KOH and 10 vol% IPA at 80°C (25-30 min.). The expected angle between {111}Si and {100}Si planes is 54.735° [6].
Parameters of the resulting pyramids: base of the pyramids ~1-15 µm, height ~0.7-10.5 µm (Fig.1a).

Quasigrating type: *n*-Si (110), wet anisotropic chemical etching in 20% KOH at 70°C (90 min).
The period of the relief is ~3-15 µm (Fig.1b).

Inverted pyramids: *n*-Si (100), chemical etching in a solution of $CuSO_4{\cdot}5H_2O{:}HF{:}H_2O_2{:}H_2O$ at 45°C (12-15 min). Concentrated HNO_3 was used to remove copper from the sample.
The size of the inverted pyramids is ~1-5 µm (Fig.1c).

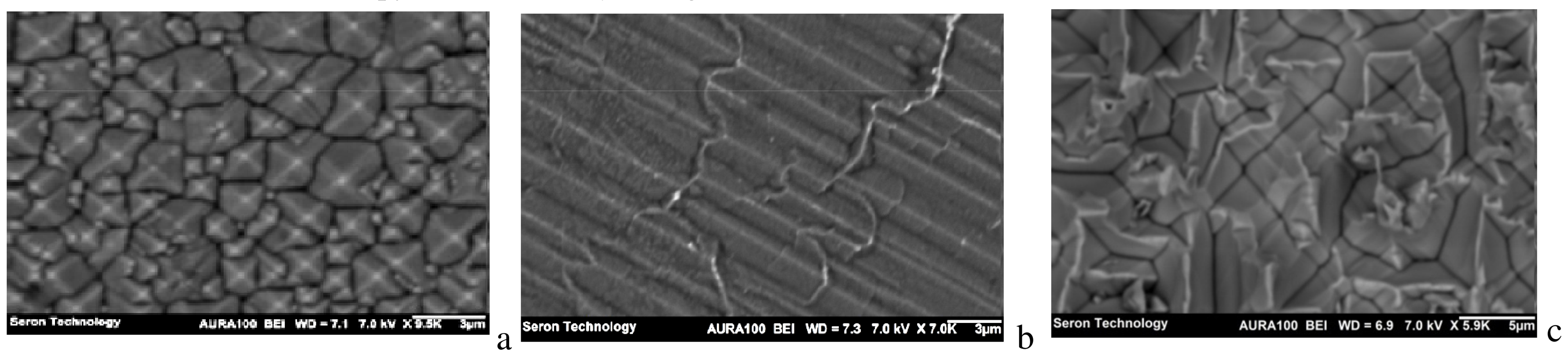


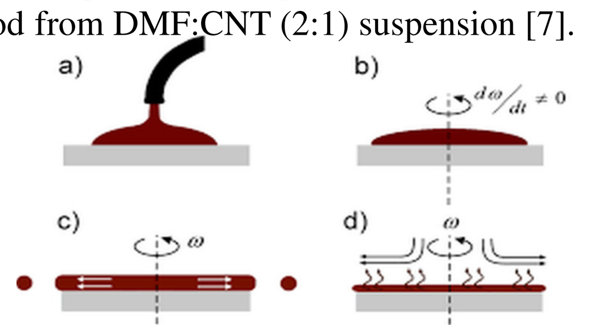
Fig. 1. SEM images of microtextured Si surface of the pyramidal (*a*), quasigrating (*b*) and inverted pyramids (*c*) type.

Composite films based on PEDOT:PSS

Method-1: PEDOT:PSS–CNT mixture: a small amount (8 mg) of CNTs was added to PEDOT:PSS (1 ml) followed by treatment with ultrasonic bath.

Method-2: separate deposition of CNT films followed by PEDOT:PSS film deposition was performed. Two CNT layers of CNT were deposited on Si substrate surface by deep-coating method from DMF:CNT (2:1) suspension [7].

PEDOT:PSS transparent conductive films



PEDOT:PSS (3.0-4.0% in H_2O, Sigma Aldrich) polymer formulation with small fraction of additives to improve wetting was used for the fabrication of PEDOT:PSS/Si heterostructures.

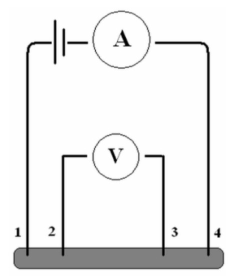
Films with a target thickness of 100-200 nm were obtained by **spin-coating** procedure and posterior annealing at a temperature of 130°C for 30 min [8].

Film thickness and optical parameters:

Spectroscopic ellipsometer SE-2000 (SEMILAB LTD)
Rotating compensator ellipsometer
Ellipsometry in reflectance mode
Optical reflectance & transmittance modes
λ = 250-2100 nm, φ = 20 - 90°

Film conductivity: Electrochemical work station CH660E (CH Instrument, USA)

Collinear 4-point probes method



Electrical and photoelectrical characteristics:

simulated AM1 irradiation, 136 mW/cm²

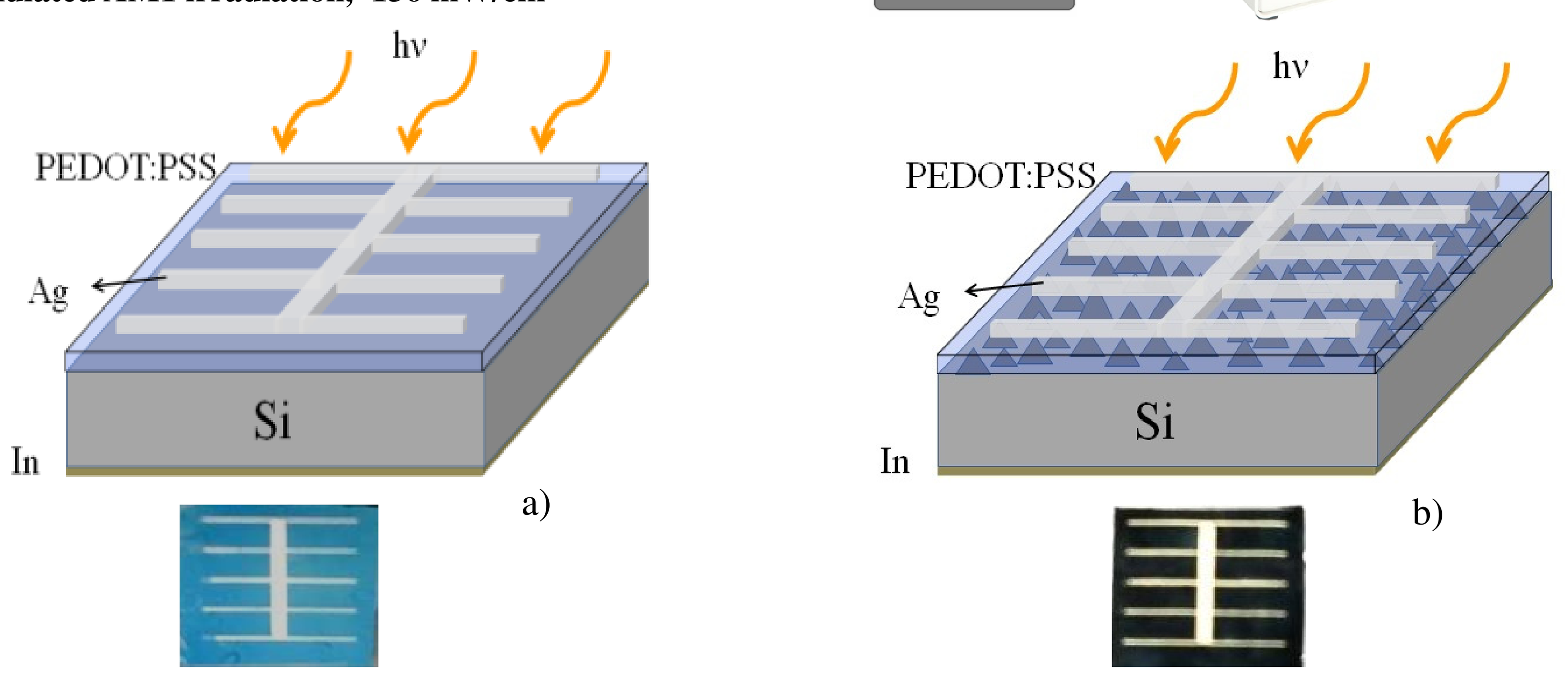
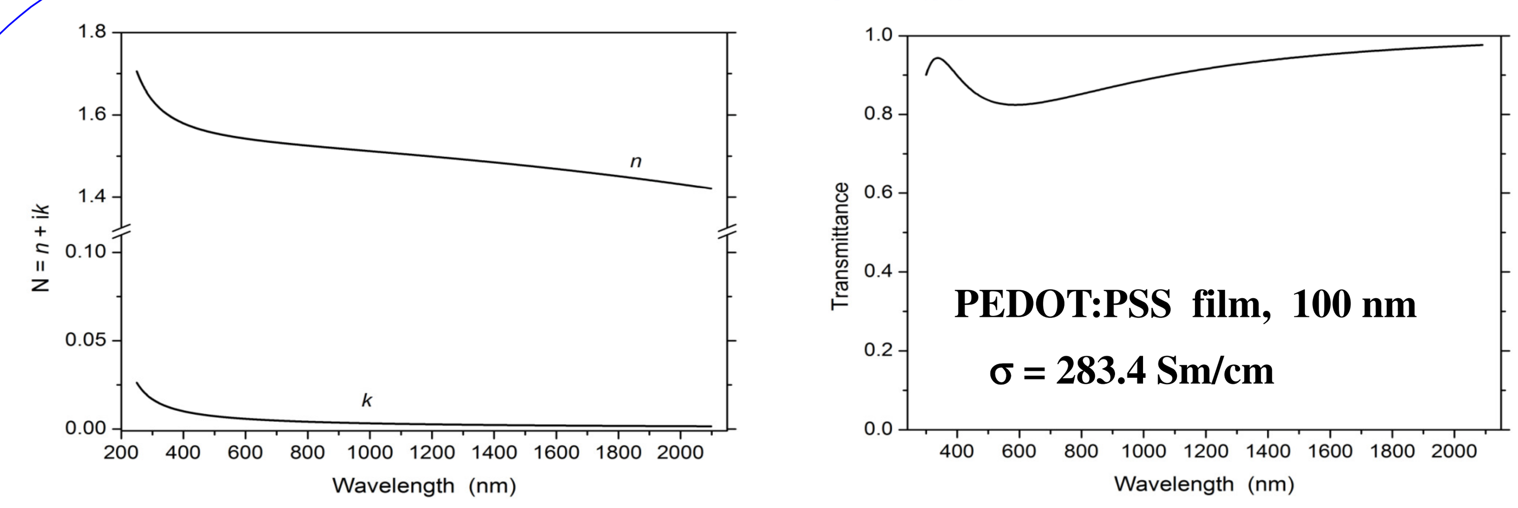


Fig. 2. Schematic representation and front-surface imaging of PEDOT:PSS/Si based solar cell structures on flat (*a*) and pyramid-textured (*b*) Si surfaces, including an Ag grid as top contact and back ohmic In contacts. Sample size 6×6 mm.

PEDOT:PSS



Photoelectrical characteristics of PEDOT:PSS/Si solar cell heterostructures with pyramidal, quasigrating and inverted pyramids type microreliefs

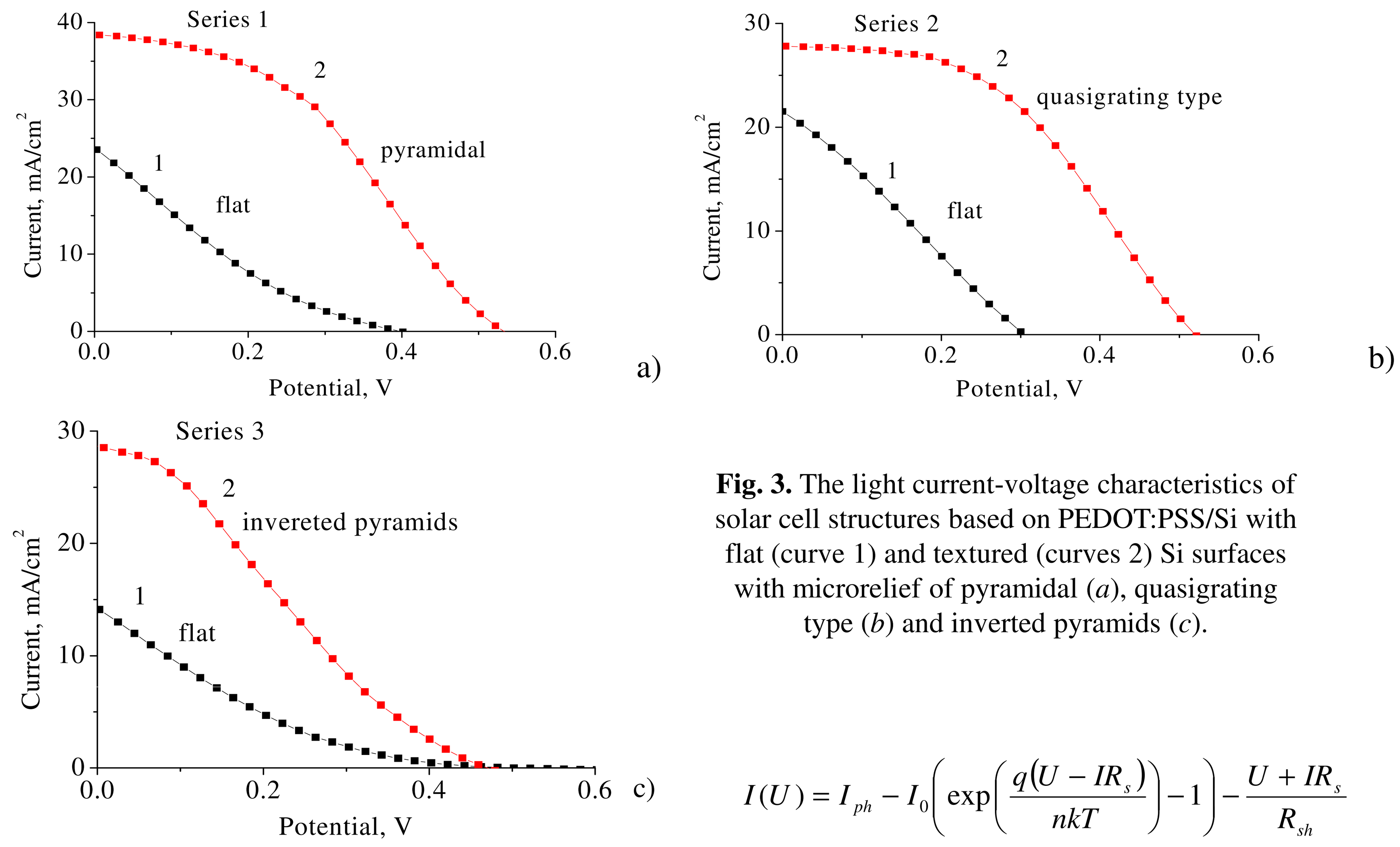


Fig. 3. The light current-voltage characteristics of solar cell structures based on PEDOT:PSS/Si with flat (curve 1) and textured (curves 2) Si surfaces with microrelief of pyramidal (*a*), quasigrating type (*b*) and inverted pyramids (*c*).

$$I(U) = I_{ph} - I_0\left(\exp\left(\frac{q(U - IR_s)}{nkT}\right) - 1\right) - \frac{U + IR_s}{R_{sh}}$$

Table 1. Photoelectrical parameters of PEDOT:PSS/Si solar cell heterostructures.

№	Active interface morphology	Open circuit potential, mV	Short circuit current, mA/cm²	Serial resistance, Ohm	Shunt resistance, Ohm	Fill factor, %	Max efficiency, %
Series 1							
1	Flat	398.2	23.759	157.6	46.2	17.9	1.25
2	Pyramidal	532.3	38.433	50.8	511.4	40.8	6.14
Series 2							
1	Flat	304.5	21.516	50.8	69.4	26.55	1.28
2	Quasigrating type	520.0	27.835	41.5	513.6	45.31	4.82
Series 3							
1	Flat	504.6	14.225	1535.9	69.3	14.29	0.75
2	Inverted pyramids	469.5	28.663	122.5	197.3	25.07	2.48

Nanocomposites of PEDOT:PSS with carbon nanotubes

(Series 4)

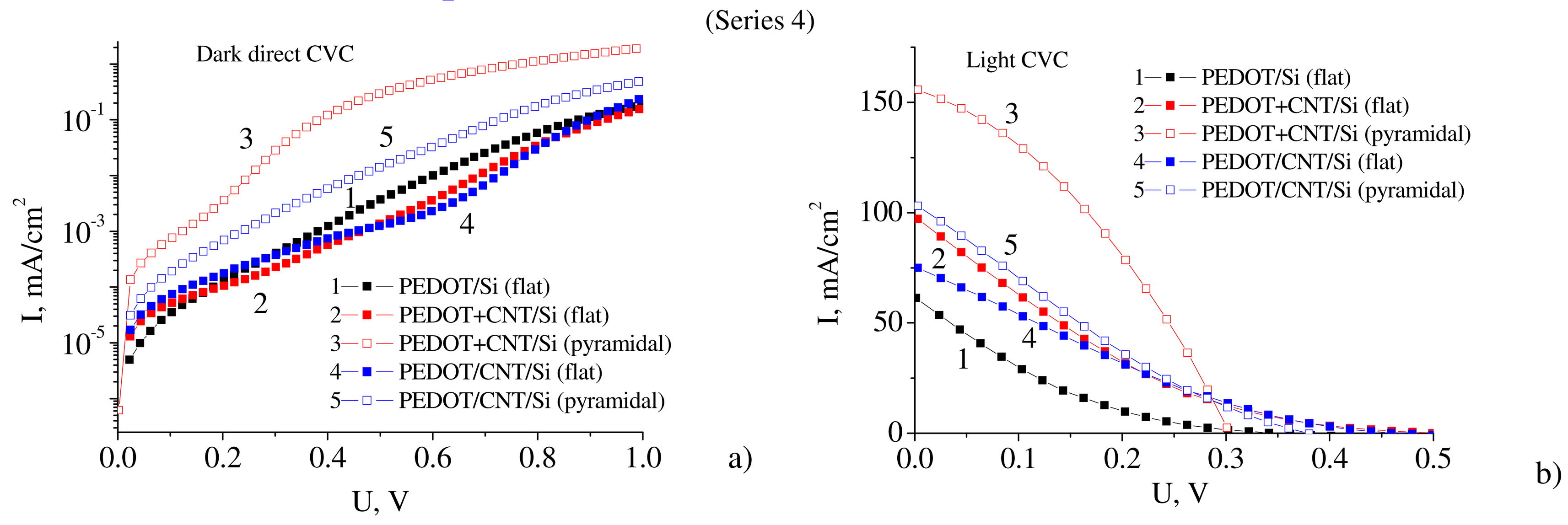


Fig. 4. The dark direct (a) and light current-voltage (b) characteristics of photosensitive element heterostructures based on PEDOT:PSS/Si with flat (1, 2, 4) and textured (3, 5) Si surfaces with pyramidal microrelief.

Table 2. Photoelectrical parameters of photoconverting heterostructures with PEDOT:PSS-CNT composite layers.

№	Sample structure	Open circuit potential, V	Short circuit current, mA/cm²	Serial resistance, Ohm	Shunt resistance, Ohm	Fill factor, %	Max efficiency, %
Series 4							
1	PEDOT/Si (flat)	0.3464	30.84	7084.9	586.5	14.02	1.10
2	PEDOT+CNT/Si (flat)	0.4983	49.1	7841.1	559.3	14.35	2.58
3	PEDOT+CNT/Si (pyramidal)	0.3037	50.4	205.5	1244.9	35.09	3.95
4	PEDOT/CNT/Si (flat)	0.4619	37.75	6631.3	971.2	18.64	2.39
5	PEDOT/CNT/Si (pyramidal)	0.3786	51.97	1737.9	676.6	20.11	2.91

Conclusions

- A comparison of the photoconversion efficiency of PEDOT:PSS/Si heterojunction type converters on silicon with different type of surface microreliefs showed that the highest efficiency is achieved with pyramidal relief converters.
- Microtexturing of the silicon single crystal surface by wet chemical anisotropic etching in KOH solution resulted in heterostructures with increased short circuit current, open circuit potential, shunt resistance, and decreased series resistance.
- The efficiency of the heterojunction with a microtextured pyramidal type interface is increased approximately 5 times due to reduced optical loss for light reflection and additional chemical surface etching.
- One of the ways to further increase the efficiency of photoconversion in this type of heterostructures is to find ways to improve the conductivity of the organic semiconductor film. Improving the characteristics of photoconverting elements was achieved by creating a composite film with the addition of carbon nanotubes to the PEDOT:PSS polymer layer.

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