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Hetero- and low-dimensional structures

Fabrication and conductivity of thin PEDOT:PSS-CNT composite films

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Abstract. In this work, two methods for fabrication of composite conductive films, consisting of single-walled carbon nanotubes (SWCNTs) and PEDOT:PSS, in order to obtain films with high conductivity and transparency for their use in solar cell structures based on Si have been compared. The thickness and optical parameters of the films were determined using the spectro-ellipsometric measurements within the spectral range 0.6…5.0 eV. The electrophysical parameters were obtained from the four-point probe measurements. Our results showed that the method for deposition of SWCNTs and PEDOT:PSS in layers enables to obtain films with a much higher conductivity (220…306 S/cm) as compared to the method of applying a film from their mixture (6…209 S/cm).

Keywords: PEDOT:PSS, SWCNT, composite films, conductivity, optical properties, layer-by-layer deposition.

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1. Introduction

Conducting polymer film PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) has high transparency and electrochemical stability [1]. It is widely used in organic electronics, in particular, to create photosensitive heterostructures such as organic/inorganic semiconductors that are easy to manufacture owing to vacuum-free, low-temperature technology, and promising characteristics [2]. PEDOT:PSS is also used in supercapacitors, organic light emitting devices (OLEDs), touch screens, organic solar cells [3–6]. It is known that addition of carbon nanotubes to PEDOT:PSS greatly increases the conductivity and transmission of the polymer layer, which is used in optoelectronic devices. To achieve the best results, the choice of the method for applying these layers is especially important. Recently, much attention has been attracted by the methods for obtaining transparent conducting films of the hybrid type, consisting of carbon nanotubes (CNTs) and a transparent conducting polymer PEDOT:PSS. These hybrid films with high transmittance and low sheet resistance are used in optoelectronic and photovoltaic devices [7–13].

Two methods of deposition of a flexible transparent conductive electrode based on SWCNT (single-walled CNTs) / PEDOT:PSS were proposed in the paper [7]. In the first method, the PEDOT:PSS layer was deposited onto the previously deposited layer of carbon nanotubes, and in the second method, one layer of a mixture of SWCNTs and PEDOT:PSS was deposited. It turned out that the layer-by-layer structure showed a lower sheet resistance (60…70 Ohm/SQ) with the high transmittance close to 81% at 550 nm.

To manufacture solar cells based on c-Si, a PEDOT:PSS-CNT composite film with various concentrations of CNTs was deposited using the centrifugation method [8]. These heterojunction solar cells showed the open circuit voltage 588.6 mV, a short-circuit current density 25.3 mA/cm^2 and the fill factor close to 60–79%, which gives the photoconversion efficiency of 9.05%.

Almost the same value of efficiency (9.24%) was obtained in the study of solar cells based on a composite CNT-PEDOT:PSS/*n*-Si film at the open circuit voltage close to 576 mV [9].

A significant decrease in sheet resistance was also obtained from 800 to 150 Ohm/SQ, when CNTs were added to the PEDOT:PSS:DMSO mixture, the DMSO concentration being 5 wt.% with the film thickness 150…170 nm [10].

In [11] CNTs were deposited onto glass substrates by sputtering, and thin PEDOT:PSS layers were deposited onto CNTs by centrifugation. This manufacturing method provided the low sheet resistance close to 82…92 Ohm/SQ (due to the PEDOT:PSS particles that efficiently filled up the voids between CNTs), neutral color and high transmittance (within the range 80–85%).

However, these higher efficiency values were obtained with layer-by-layer deposition of PEDOT:PSS and CNTs layers for manufacturing the solar cells [12, 13]. In [13], SWCNTs were deposited by immersing a Si substrate into a dilute solution of SWCNT in toluene and with various concentrations of nanotubes. Then, a PEDOT:PSS solution mixed with 1 wt.% Triton and 5 wt.% dimethyl sulfoxide (DMSO) was applied by centrifugation. The SWCNT layer was used as an interlayer that improves the performance of PEDOT:PSS/Si solar cells. An energy conversion efficiency close to 12.14% was achieved with the optimized SWCNT layer thickness.

In this work, we compared two methods of fabricating the hybrid conductive films consisting of SWCNT and PEDOT:PSS with an emphasis given to their optical properties studied by spectroscopic ellipsometry for their use in solar cell structures based on Si.

2. Experimental methods

Factory polished *n*-Si (100) phosphorus-doped wafers (resistivity of 1…10 Ohm·cm) were used as substrate for film depositions. The surface were preliminarily cleaned by boiling in isopropyl alcohol for 5 min (T = 75…80 °C). Oxide and impurities from the silicon surface were removed in a solution of 10% HF:Triton X100 = 20:1, then washed with ethyl alcohol and distilled water.

Transparent conducting polymer PEDOT:PSS (3.0…4.0% in H_2O, high-conductivity grade, Product No. 655201, Sigma Aldrich) was used for film fabrication.

For the first type of conductive transparent films based on PEDOT:PSS, a colloidal solution of CNT (with different concentrations) in PEDOT:PSS was prepared. Stable enough suspension of CNT in water-based PEDOT:PSS can be prepared in a mixture with dimethylformamide (DMF) and 4% Triton X100. Therefore, preliminary suspended for 5–7 minutes with ultrasonic bath CNT in DMF (1:20) with addition of 4% of Triton X100 were mixed with PEDOT:PSS with following ultrasonic bath homogenization. The v/v ratios of PEDOT:PSS and other components are presented in Table 1. Thin films on the substrate were produced by spin-coating technique at a rotation speed of 3000 rpm for 30 s, and annealing at the temperature of 135…150 °C for 1 min (Fig. 1a).

Table 1. Thickness and electrical parameters of composite PEDOT:PSS + ((DMF + SWCNT) + 4% Triton X100) film.

PEDOT:PSS to (DMF+SWCNT) ratio	*d*, nm	R_{SQ}, Ohm/SQ	ρ, Ohm·cm	σ, S/cm
(1:1)	418	3696.5	0.155	6.5
(2:1)	335	1060.3	0.036	28.2
(4:1)	313	530.7	0.017	60.2
(6:1)	312	517.0	0.016	62.1
(8:1)	220	217.5	0.005	209.0
(10:1)	225	258.6	0.006	172.0
pure PEDOT:PSS	222	169.7	0.004	265.5

Table 2. Thickness and electrical parameters of PEDOT:PSS/SWCNT film.

Number of SWCNT layers	*d*, nm	R_{SQ}, Ohm/SQ	ρ, Ohm·cm	σ, S/cm
0	222.0	169.7	0.004	265.5
1	279.3	162.1	0.0045	220.9
2	276.8	118.9	0.0033	303.9
4	375.5	88.8	0.0033	300.0
8	328.0	99.5	0.0033	306.5

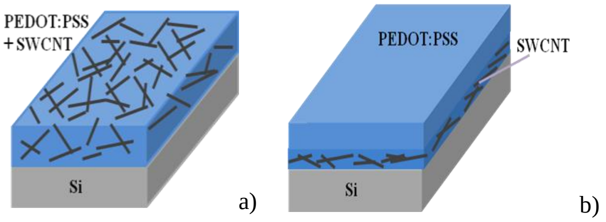

Fig. 1. Schematic representation of the structures design based on PEDOT:PSS+SWCNT and PEDOT:PSS/SWCNT composites films on the flat surface of Si.

For the second type of PEDOT:PSS based transparent conductive films, separate deposition of CNT film (with different thickness of CNT) and PEDOT:PSS was performed. SWCNT layers (1, 2, 4, and 8 layers) were deposited by deep-coating method from DMF:SWCNT (20:1) solution by exposition of Si substrate for 1 min (Table 2). A layer of PEDOT:PSS was also applied by centrifugation (like to the first method). The following method resulted in fabrication of PEDOT:PSS/SWCNT/Si type structures (Fig. 1b).

3. Results and discussions

The electrical d.c. conductivity of films was measured using the four-point probe method (CHI660E, CH Instruments) with the probes spaced in line with 1 mm distance. The thickness and optical parameters of the films were determined from the multiangle spectroscopic ellipsometry measurements (SE-2000, Semilab) in the spectral range 0.6…5.0 eV at three angles of light incidence (65, 70 and 75°) and optical reflectance/transmittance spectroscopy (Tables 1 and 2).

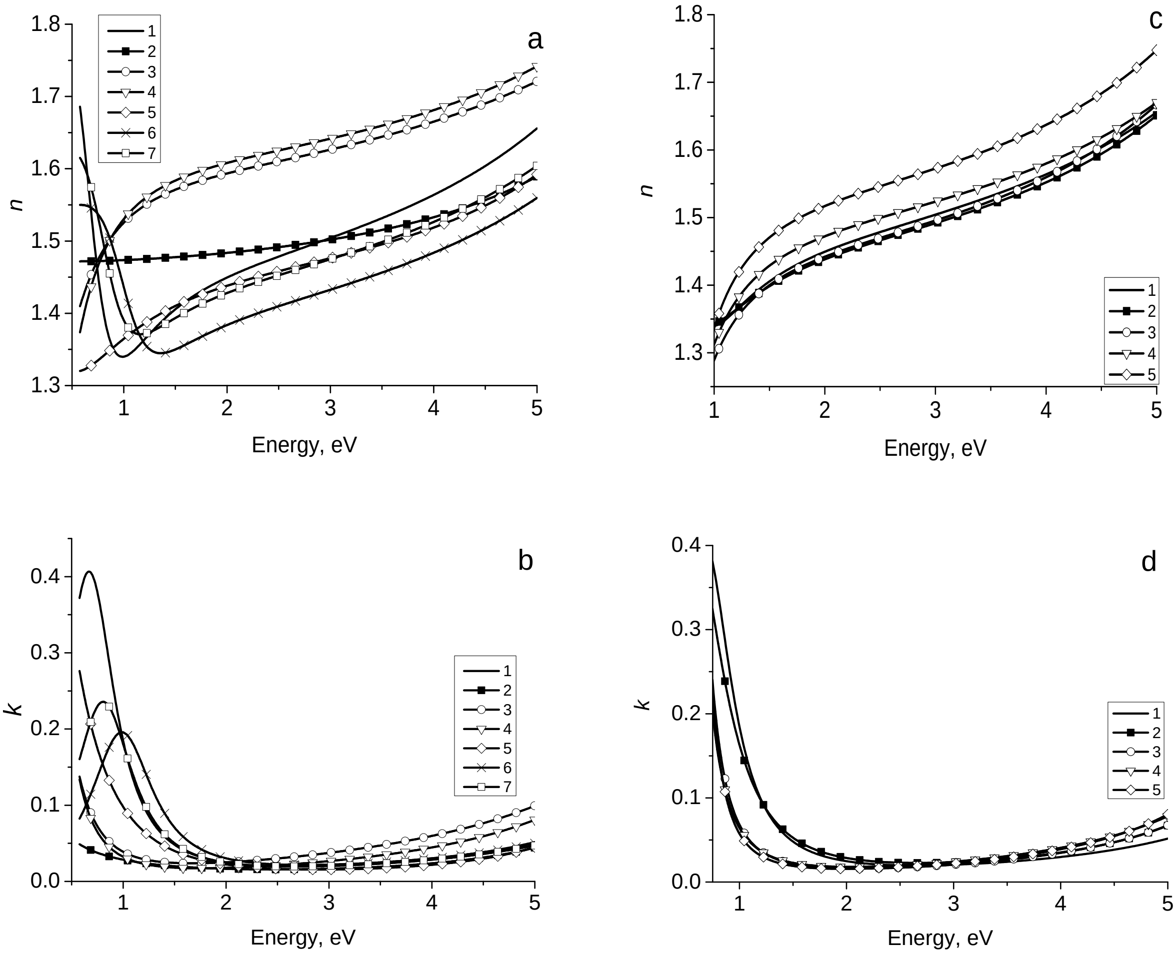

Fig. 2. The dependences $n(\lambda)$ and $k(\lambda)$ for conductive films PEDOT:PSS + ((DMF + SWCNT) + 4% Triton X100) with the PEDOT:PSS to (DMF + SWCNT) ratio: pure PEDOT:PSS (*1*), (1:1) (*2*), (2:1) (*3*), (4:1) (*4*), (6:1) (*5*), (8:1) (*6*), (10:1) (*7*) (a, b) and PEDOT:PSS/SWCNT with number of SWCNT layers: 0 (*1*), 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*) (c, d).

The dielectric function $\varepsilon(E)$ of the composite PEDOT:PSS films was modelled as the sum of the Cauchy and Drude components: $\varepsilon(E) = \varepsilon_C(E) + \varepsilon_D(E)$. The Cauchy component, $\varepsilon_C(E) = n^2$ (Eq. (1)), is often used to describe the optical properties of dielectrics [14] and makes a major contribution to the refractive index of PEDOT:PSS in the region of their transparency:

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 , \qquad (1)$$

where A, B and C are the empirical coefficients, and λ is the wavelength.

The Drude component, $\varepsilon_D(E)$, (Eq. (2)) describes interaction of light with free carriers:

$$\varepsilon_D(E) = 1 - \frac{E_p^2}{E^2 - iE \cdot \Gamma} , \qquad (2)$$

where E_p is the plasma energy of free carriers, E – energy of incident light quanta, and Γ – damping parameter of plasma oscillation.

Fig. 2 shows the dependences $n(\lambda)$ and $k(\lambda)$ for conductive films PEDOT:PSS + ((DMF + SWCNT) + 4% Triton X100) and PEDOT:PSS/SWCNT. The main effect on the optical parameters, when including CNT into the composite, is manifests itself in increasing the absorption coefficient k of the composite within the high-energy (ultraviolet) spectral range due to π-π^* absorption by carbon nanotubes, and within the low-energy range (near IR) – due to the increased plasma frequency of composite. But photons with the energy lying within the range of increased absorption coefficient k do not make any significant contribution to photoconversion of solar radiation.

From the dependence of the film conductivities, it can be seen that the second method with layer-by-layer deposition of SWCNT and PEDOT:PSS provides obtaining the films with stable higher conductivity values of 220…306 S/cm (Fig. 3, Tables 1 and 2).

For Si-based photovoltaics, the photosensitivity range of silicon from ~400 up to 1100 nm (1.1…3.0 eV) is important. From the viewpoint of optical

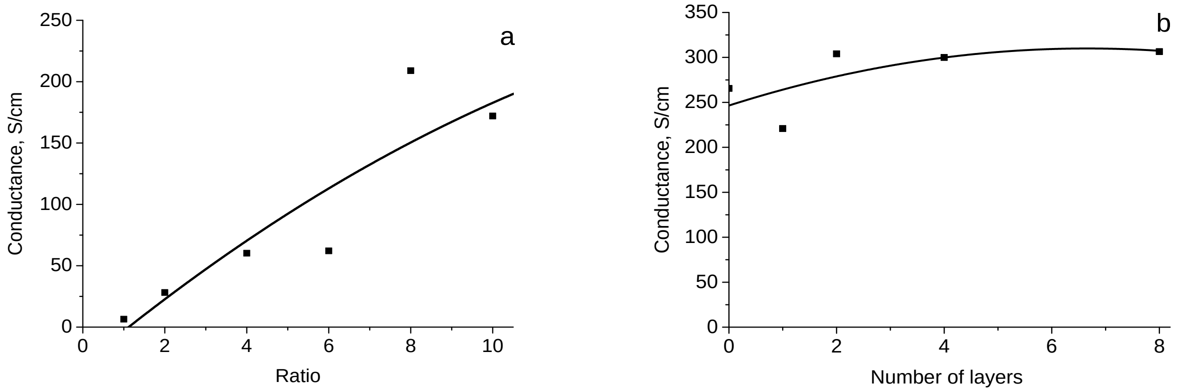

Fig. 3. Dependence of the conductivity of composite films PEDOT:PSS + SWCNT on PEDOT:PSS to (DMF + SWCNT) ratio (a) and PEDOT:PSS/SWCNT on the number of SWCNT layers (b).

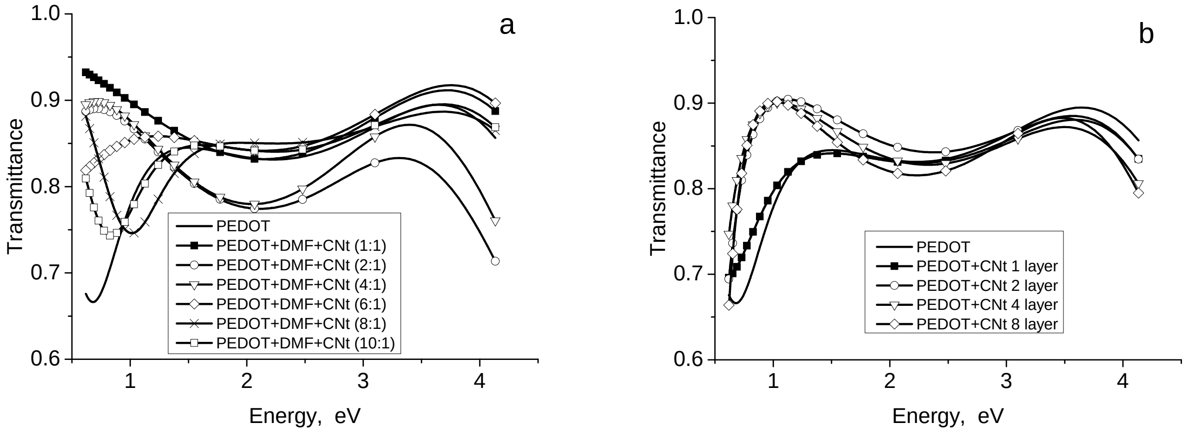

Fig. 4. Calculated transmittance of composite films PEDOT:PSS + SWCNT (a) and PEDOT:PSS/SWCNT (b) with 100-nm thickness.

characteristics, it is important to have high transparency of upper current-carrying electrode in this range. And in terms of electrical parameters of this layer, it is desirable to ensure its high conductivity. The increase in conductivity caused by free carriers is accompanied by an increase in absorption coefficient in the near-IR region of the spectrum due to the increase in the concentration and, accordingly, in the plasma frequency of free carriers.

Therefore, in such cases, it is necessary to choose a compromise value of conductivity, so as not to observe a strong cut of light transmission in the long-wave range of sensitivity of the solar cell.

Fig. 4 shows the dependence of transmittance on photon energy of 100-nm films on the glass substrate calculated with $n(\lambda)$ and $k(\lambda)$ obtained from spectro-ellipsometric measurements. For most of the films, the transmittance value lies within the range 80 to 90%, but the higher T value, in average, we obtain for the films prepared using the second method, especially in the NIR region lower than 1 eV. This is caused by the lower $k(\lambda)$ value for these films in this range.

4. Conclusions

Two methods for fabrication of composite conductive films, consisting of single-walled carbon nanotubes and PEDOT:PSS, were compared to obtain films with higher conductivity and transparency for their use in solar cell structures based on Si. The thickness and optical parameters of the films were determined using spectral ellipsometry within the energy range 0.6…5.0 eV.

The electrophysical parameters were obtained from the four-point probe measurements. Our results have shown that the method of sequential deposition of SWCNT then PEDOT:PSS enables to obtain films with a much higher conductivity (220…306 S/cm) as compared to the method based on application of films prepared from the colloidal solution of SWCNT and PEDOT:PSS (6…209 S/cm).

The transmittance of the films of both types has shown the high value close to 80…90%, but it is a bit enhanced in the NIR range for the films with sequential deposition of SWCNT and PEDOT. This is related with the lower value of extinction coefficient $k(\lambda)$ for these films in this range.

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Виготовлення та провідність тонких композитних плівок PEDOT:PSS-CNT

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Анотація. У цій роботі порівнюються два методи виготовлення композитних провідних плівок, що складаються з одностінних вуглецевих нанотрубок (SWCNT) та PEDOT:PSS, для отримання плівок з високою провідністю та прозорістю для їх використання в структурах сонячних елементів на основі Si. Товщину та оптичні параметри плівок визначали на основі спектральної еліпсометрії в спектральному діапазоні 0.6…5.0 еВ. Електрофізичні параметри були отримані за допомогою вимірювань 4-зондовим методом. Наші результати показали, що метод пошарового осадження SWCNT та PEDOT:PSS дозволяє отримувати плівки з набагато більшою провідністю (220…306 S/cm) порівняно із способом нанесення плівки з їх суміші (6…209 S/cm).

Ключові слова: PEDOT:PSS, SWCNT, композитні плівки, провідність, оптичні властивості, пошарове осадження.