# МАТЕРИАЛЫ ЭЛЕКТРОННОЙ ТЕХНИКИ
# ELECTRONIC ENGINEERING MATERIALS

## Synthesis Peculiarities of Electrically Conductive Materials on Metallized Polyimide as Elements of Flexible Solar Cells

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## Особенности синтеза электропроводных материалов на основе металлизированных полиимидов как элементов солнечных батарей и микросистемной техники

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The properties of metallized polyimide films with high electric and optical characteristics have been presented. The preparation process features of organic solar cells have been considered. The optimum conditions for obtaining a multi-layered electrode – anode from polyTEOS – poly(tetraethoxysilane as active and semi-conductive layer, also, for an active layer P3HT (poly(3-hexythiophene-2,5—diyl)/PCBM ([6,6] – phenyl-C61-butyric acid methyl ester) for increasing power conversion efficiency as a material with volumetric hetero-junction, as well as a conductive metal layer for cathode preparation, have been established. One of the possible solutions to increase the light absorption in ultra-thin active layer may be metal nano-particles use. The metallized silver polyimide films have been recommended for production of organic solar elements.

*Keywords:* polymer; solar element; film; metallization; transparent electrode; active layer.

Представлены свойства металлизированных полиимидных пленок с высокими оптическими и электрическими свойствами. Рассмотрены технологические особенности получения органических солнечных элементов. Установлены оптимальные условия для получения многослойной структуры со следующими слоями: polyTEOS – поли(тетраэтоксисилан) активный

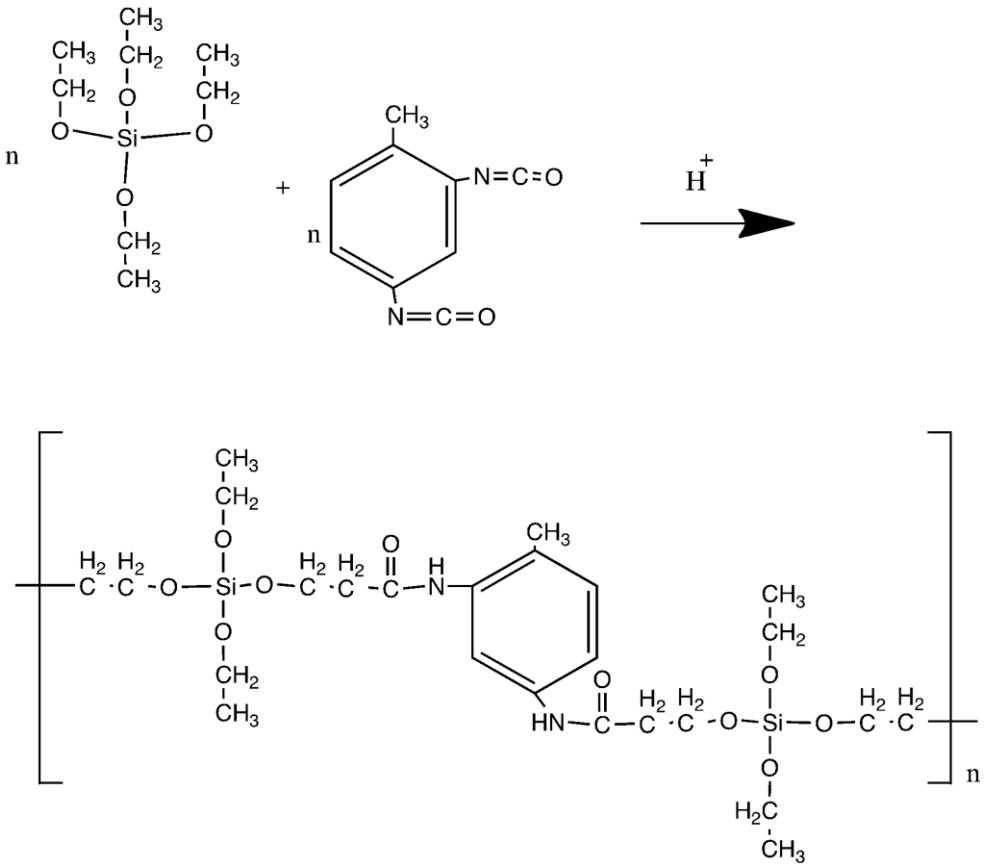
адгезивный и полупроводниковый слой анода и активный слой P3HT (поли(3-гексилтиофен-2,5-диил) / PCBM ([6,6] – фенил-C61-метиловый эфир масляной кислоты) как материал с объемным гетеропереходом для повышения эффективности преобразования электроэнергии, а также проводящий металлический слой катода. Одно из возможных решений, позволяющих увеличить поглощение света в сверхтонких активных слоях, – применение металлических наночастиц. Металлизированные серебряные полиимидные пленки рекомендованы для производства органических солнечных элементов.

*Ключевые слова:* полимер; солнечный элемент; пленка; металлизация; прозрачный электрод; активный слой.

**Introduction.** Usually, the term «solar cell» is meant more united photovoltaic cells (solar cells). Such semiconductor devices directly convert solar energy into direct electric current (DC) [1]. Production of photovoltaic cells and solar collectors is growing rapidly in many different directions [2]. The conversion efficiency is dependent on the electrical characteristics of an inhomogeneous semiconductor structures and optical properties of solar cells, among which the most important role played by photoconductivity. It is due to the phenomena of internal photoelectric effect in semiconductors irradiated by sunlight [3]. An organic solar cell is a type of polymer solar cell that uses organic electronics, and branch of electronics that deals with conductive organic polymers or small organic molecules. In recent years intensive research to create organic film compositions based on electro-active polymers which combine high mechanical properties, chemical resistance to aggressive media, and the ability to form strong elastic films have been developed [4, 5]. The layer of organic semiconductor is situated between two electrodes; typically, at least one of the electrodes is transparent [4]. Main disadvantages of organic semiconductor systems are sustainable work for long-term function, limitation in space and respectively in the coefficient of efficiency to maximum 9–10%. Nanostructured materials are being investigated and developed as versatile components of optoelectronic devices with the ability to manipulate light (via plasmonic enhancement, photonic crystals, and so on) and control energy flow at nearly the atomic level. Nano-structured solar cells are the type of third- or next-generation solar cell. They hold great promise towards new approaches for converting solar energy into either electricity (in photovoltaic devices) or chemical fuels. There are challenges to overcome, but currently there is no even medium-term stability for this type of cells. As a type of classical conducting polymers, polyanilines have been widely studied in the past decades due to their high conductivities, environmental stabilities and ease of synthesis for multiple energy-related applications such as sensors, super capacitors and organic light-emitting diodes [6, 7]. Polyanilines with good solution processabilities in commonly used solvents can be prepared through internal or external doping [8]. For instance, when doped by sulfonic acid, polyanilines can be dissolved into water, and the water soluble polyanilines can be used as the p-type materials in organic solar cells. For improvement in electron and hole collections for further process cycle efficiency (PCE) enhancement, insertions of inter layers between the active layer and the electrodes have been made [9]. However, prolonged exposure of this kind of device to air can lead to the sensitive metal cathode oxidation in the air, resulting in a polymer solar cell **(**PSC) degradation. In order to alleviate this problem, an approach involved an inversion of the conventional polymer solar cell (c-PSC) device architecture is employed, in which a less air-sensitive high work function metal (Ag, Au) is used as the back hole collecting electrode [10]. The aim of this work is the multilayered structure formation based on polyimide film substrate with the fol-

lowing layers: polyTEOS – poly(tetraethoxysilane) active adhesive and semiconductive layer, also for an active layer of P3HT (poly(3-hexylthiophene-2,5-diyl)/ PCBM ([6,6] - phenyl-C61-butyric acid methylester), for increasing power conversion efficiency responsible for p-n junction, and as well as conductive metallic layer.

**Experiment & Research.** The process of obtaining organic solar cells has been considered. It is established that the optimum conditions for obtaining a transparent electrode are as follows: poly(tetraethoxysilane) (polyTEOS) was prepared on a surface of the initial polyimide film in a solution of iso-propanol (6 vol.%) from tetraethoxysilane and toluene-2,4-diisocyanate (TDI) monomers. Process of polyTEOS polymerization proceeds in acidic conditions on the surface of polyimide films which were immersed into the reaction solution in a flask you can see in the scheme of *in situ* polymerization of polyTEOS onto polyimide film substrate:



There are SEM images of polyTEOS polymerized on the surfaces of polyimide depending on various concentrations of TEOS in a reactor during the synthesis (Fig.1). There is homogeneous distribution of polyTEOS on the substrate surfaces with obvious silicate area increasing as the concentration in a reactor grows from 5.0 to 7.5 up to 10.0 wt% of co-monomers in the iso-propanol reactive solution.

P3HT/ PCBM mixture in chloroform [10] were cast on to polyTEOS-modified polyimide film dropping the solution on to the substrate rotating by means of a roto-film machine. The optimum thickness of photo active layer is about 90 nm (at 3500 rpm rotation) and post-annealing temperature is 150 $^{o}$C as it is shown in Fig.2. The optimization of all steps of the production of organic solar cell, resulting in increased power conversion efficiency to 3.3% has done.

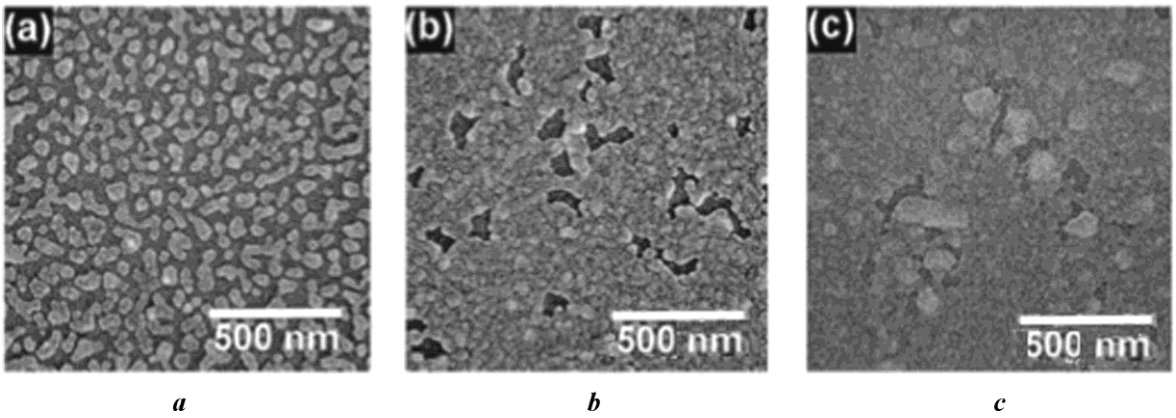



*Fig.1.* SEM images of polyTEOS-modified (specially pretreated by gilding) polyimide films under various concentration of the initial monomers (TEOS and TDI) concentration: (*a*) 5.0 wt%; (*b*) 7.5 wt%; (*c*) 10.0 wt%

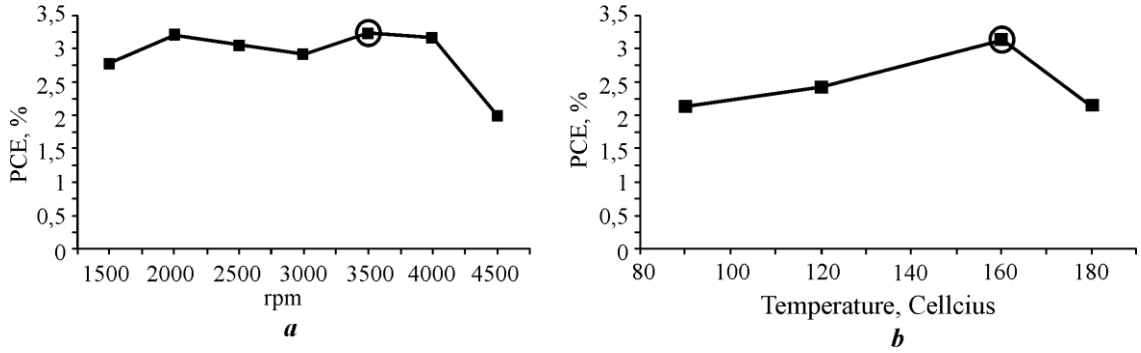
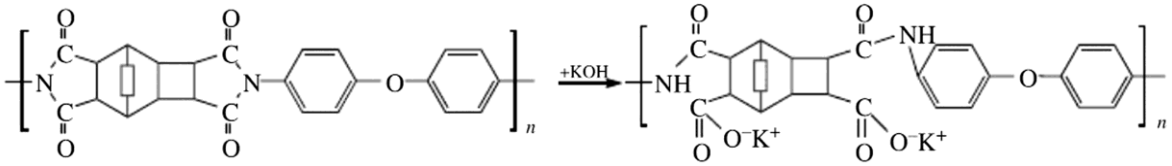
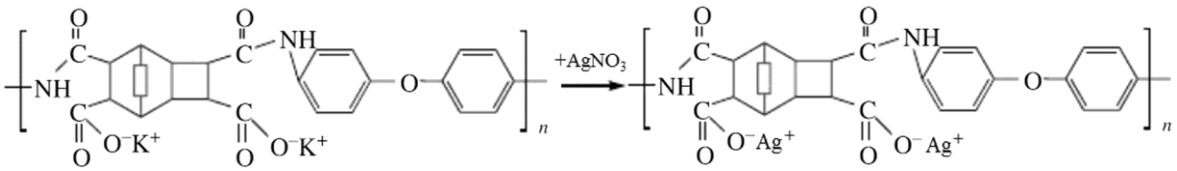



*Fig.2.* Thickness characteristics of photoactive layer depending vs rotation rate (*a*); thickness of photoactive layer depending vs drying temperature. Optimum conditions are shown by red circles (*b*)

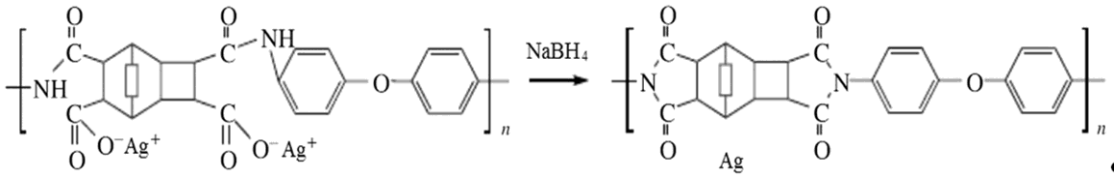
The metallization process of the polyimide (PI) films has been studied [8,10]. The polyimide (PI) film with pre-degreased surface was subjected to swelling in acetonitrile for 20 minutes. Next step was an alkaline hydrolysis




in 0.2 M KOH solution, where in the mixture of «water : so-propanol» was (20:1). PI film was kept in the alkaline solution for 20 minutes to open imide cycle and substitute proton by potassium ions for the further introduction of silver ions. Then, PI film was rinsed with distilled water and was transferred to 3% solution of $AgNO_3$. The so-called chelation process was performed for 30 minutes. During this step potassium ions were substituted by silver ions from the solution:



The last step was the reduction of silver ions to metallic ones made with 0.1% $NaBH_4$ in «iso-propanol : water» (1:20) solution by its spraying onto the surfaces of the final film:




The resulting samples were annealed at 85 °C for 4 hours. Kinetics of metallization process which chemically represented in Fig.3 was depicted by means of AFM Integra Spectra at various exposure times from the beginning up to the final 30 min exposition. The process of potassium ions substitution with vice versa silver ions accumulation into the surface of polyimide during exposure is obviously visible.

The final composite based on multilayered structure (Fig.4) showed photo-transitional characteristics (Fig.5).

The sample with fixed two contacts and connected to a voltmeter was placed in an ultraviolet camera with regulated irradiation intensity.

Maximal result in 0.27 V was reached at about 300 Hz frequency of UV radiation which represents about 3.5% efficiency of the converted radiation to the electrical one. Voltage shows growing with UV intensity increasing up to 300 Hz. The further decreasing happens due mainly to destruction of either silver or polymeric layers at high UV intensity. The metallized polyimide films with additional coating from Ni, Au and Rh have been studied too. It has been found that the temperature dependence of the specific surface resistance in themetallized films at the temperature from 25 up to 160°C was in the well agreement with linear law. The specific surface resistance at 20°C and temperature coefficient showed low values and was 0.16 – 2.24 W and $0.69 \cdot 10^{-4}$ – $19.18 \cdot 10^{-4}$ $K^{-1}$ respectively. The film reflection coefficient in visible spectrum field at wavelength of 530 nm was 75% and essentially enlarged with wavelength increasing.

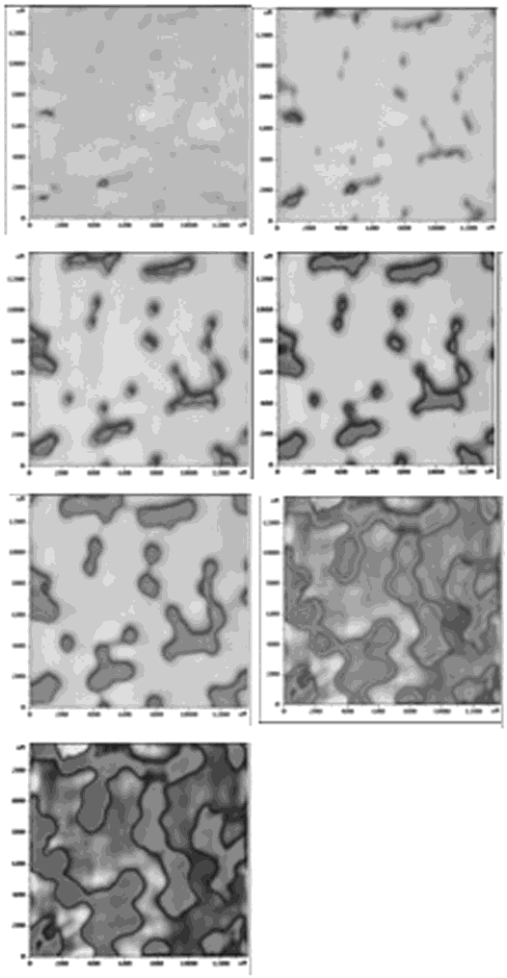


*Fig.3.* Micrographs of PI film surface during metallization process under the following exposure time from the left to the right: 0; 5; 10; 15; 20; 25; and 30 min respectively

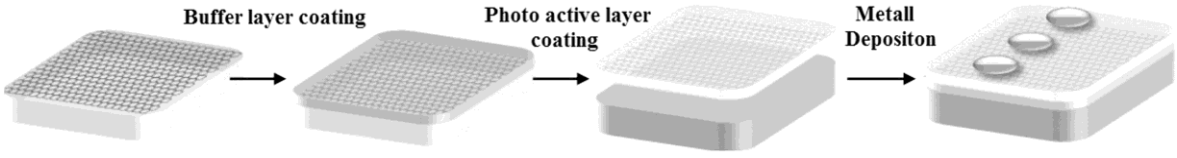



*Fig.4.* Structure of manufacturing solar cell

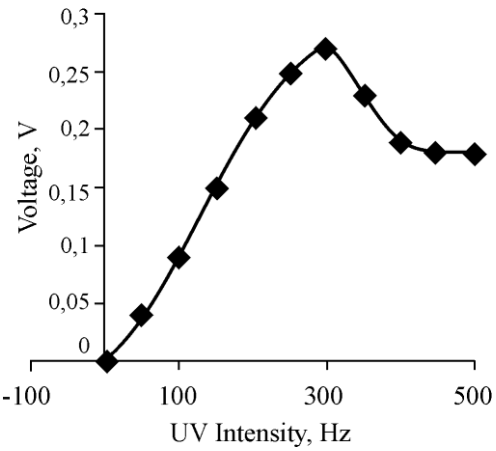



*Fig.5*. Voltage characteristics of the final composite solar cell structure depending vs intensity of UV irradiation

**Conclusion.** Partially compensate the low efficiency of today's organic solar cells is possible by light absorption increasing in ultra-thin active layers, namely using metal nano-particles. The probability of exciton dissociation into an electron and hole increases due to the large electromagnetic field in the vicinity of the nano-particles. The optical properties of metallic nano-particles are largely dependent on their size, so it is possible to «tune» the absorption maximum of such a cell in various regions of the electromagnetic spectrum.

Results on the formation of a multilayer structure based on a polyimide film substrate have been presented. Formation of such layers as polyTEOS – poly(tetraethoxysilane) active adhesive and semiconductive layer, active layer of P3HT (poly(3-hexylthiophene-2,5-diyl)/ PCBM ([6,6] - phenyl-C61-butyric acid methylester) for increasing power conversion efficiency responsible for *p–n*-junction; and as well as conductive metallic silver layer. The chemical process of polyimide films metallization by silver was studied. Thickness of the active and metal layers has been optimized. Process cycle efficiency (PCE) was calculated using voltage variations and exposure modes of the metalized polyimide films. Of course, PCE remains a problem for this type of technology. Traditional silicon batteries reach 20% efficiency or more. The results presented in this paper showed the conversion efficiency of ultraviolet energy into electrical energy about 3.5%, which is a good result for organic solar cells. In addition, the problem of waste, which is relevant for silicon solar cells, in the case of organic batteries is not as prevalent. Processing thereof is very simple and safe.

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