

MONOLAYER POLYMER PHOTOCELLS. THE OPPORTUNITIES

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Abstract: The conversion of solar energy into electricity is in the focus of a large number of scientists. Because of the problems caused by the use of fossil fuels, the use of renewable and environmentally friendly energy sources is desirable, and in some countries the use of a certain percentage of such energy sources becomes a legal obligation. Today there are commercially available silicon solar cells with prices ranging from 800 USD/kW (about 10 m²/kW) and efficiency in the range of 10-20%. The main obstacle to a wide use of these energy sources is the high price of such generated electric power in comparison to the costs of electricity from classical sources (hydro, thermal and nuclear power plants). Technological progress has been made in the development of polymer-based organic photovoltaic (OPV) solar cells, and their energy efficiency is approaching the value of 10%, whereas the price per unit of output can be significantly lower than silicon solar cells. A shortcoming of OPV solar cells is their short life, and that is why they did not find a wider application. A single-layer polymer photovoltaic is characterized by a simple design and potentially very low production cost. It can be assumed that because of these properties, the polymer monolayer photocell can become a cheap substitute for widespread photocells based on classic semiconductors. In this article, the existing published achievements in the development of a monolayer polymer solar cell are presented, and also the original solutions that are the result of investigations conducted by the authors.

Keywords: Photocell, energy.

1. HISTORY

The demand for environmentally friendly energy sources has recently caused the intensive development of technologies, the purpose of which is the conversion of solar energy into electricity. However, after the first discovery of photoelectric currents between metal electrodes that are immersed in an electrolyte (Edmund Becquerel in 1839), it may be argued that the significant discoveries in this area of science occurred about every 10 or 20 years until the mid-20th century. The first solid-state photocell was reported in 1876 (W. Adams and R. Day, selenium - platinum contact). The first large area photocell, selenium-gold, was reported by C. Firtts in 1894. In addition to the experimental results, the development of theoretical and quantum physics has contributed to a better understanding of these phenomena; in 1905 Albert Einstein explained the photoelectric effect using discrete quantized packets of light energy; a model of the rectifying effect (bar-

rier) at the metal-semiconductor contact was introduced by Goldman and Brodsky in 1914, and an improvement on this theory was followed about 15 years later (in the 1930s) by Neville Mott, Walter Schottky and others. The improvement of the quality of the silicon crystal in the 1950s enabled the development of semiconductor electronics (*p-n* junction), and also improvements in the quality of silicon-based photocells. The first *p-n* junction solar cell, based on silicon, was produced in 1954 with an energy conversion efficiency of 6%. Most of the solar cells on the market today are based on silicon with an efficiency in the range 10-20%, while multi-junction photo cells in experimental conditions showed up to 40% efficiency [1]. Monolayer photocells characterize photo-induced exciton in a single layer (material), commonly a composite. The lifetime of excitons must be long enough so that the separation of the charge takes place using the contact potential of the applied electrodes. A report, which first pointed out the large potential of the

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described designs of monolayer photocells, was published by O'Regan and Grätzel in 1991 [2]. The monolayer photocell that shows the largest efficiency, are the dye-sensitized solar cell (DSSC) containing ruthenium dyes with an efficiency of energy conversion of up to 13% [3].

2. THE WORKING PRINCIPLES

The working principle of a photocell is based on the absorption of a quantum of light in a material; at the same time the energy of the absorbed quantum of light must be sufficient to cause separation of the

charges. In the case of the p - n like solar cells (multilayer), the photo-excited electron has to overcome the contact barrier between the two materials, i.e. to move from one (p) to another (n) material. The existence of such a contact barrier (contact potential) is a necessary condition for the creation of photo-induced voltage between the two materials. In monolayer photocells the separated charges live for a while in the same material (layer) where they originated, and are then separated into different directions to different electrodes with suitably chosen contact potentials. A symbolic illustration of multilayer and monolayer photocells is presented in Figure 1.

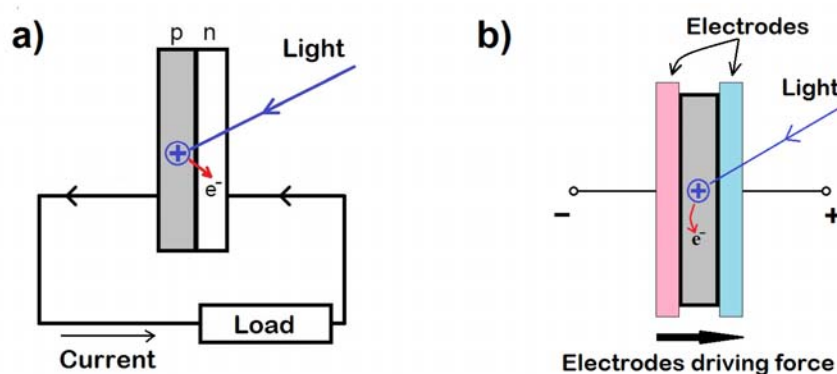


Figure 1. Photovoltaic systems: a) p - n junction; b) monolayer

The high price of electricity produced from photocells is the reason why this form of energy cannot now replace traditional sources of electricity (hydro, thermal and nuclear power plants). The process of producing quality semiconductors for these purposes is complex and still very expensive. There are expectations that monolayer photocells will start dominating the market because of their low price. The ability to generate excitons when illuminated by visible light is shown by a variety of materials from the group of ceramics, polymers and their composites [4]. However, the short lifetime of excitons and the energy losses during electron transport (to and from the electrodes) are usually the main causes of the lower energy efficiency of monolayer photocells compared to the p - n junction photocells. One of the advantages of the monolayer photocells is the simple achievement of a higher spectral efficiency. An increase in the spectral efficiency in p - n junction photocells was achieved by multiple layers, which dramatically increased their production costs. In monolayer photocells the spectral efficiency is effectively achieved by adding fillers or dyes in the composite [5].

The dye-sensitized solar cells (DSSCs) are a particularly interesting group of organic photocells. The design of this type of photocell is simple, a dis-

persed dye on a suitable metal oxide (TiO_2 , ZnO , SnO_2) surface [2]. The working principle of a DSSC is based on the absorption of a quantum of light and exciton formation in a suitable chosen dye. Because of a low energy level conduction band, for example in TiO_2 , the excited electron from the dye can irreversibly cross into this band [6]. The further course of the separated charge is achieved by direct contact between the TiO_2 and a (usually) metal electrode. A suitable method for discharging (neutralization) of the positive charge in the dye is the use of an iodine electrolyte between the dye and the other (transparent) electrode [2,6].

Because of this design, DSSCs can be classified as p - n like photocells. However, the good efficiency of 13% [3] in these photocells is achieved in one layer produced by mixing ruthenium dyes with TiO_2 nanoparticles, and such a design can be characterized as a monolayer photocell design. The efficiency of other types of monolayer photocell is significantly lower than 13% [7].

In this article we want to introduce the possibility of a new type of monolayer photocell. The essence of our idea is a different collection mechanism of photo-induced charge in an illuminated material than that presented in Figure 1. The operation of this photocell is based on a collection of currents

originating from relaxations of photo-induced charges, Figure 2. The relaxations are stimulated by the application of short pulses of electric voltage to the electrode system that is otherwise used for the collection of relaxation currents. For this kind of technical solution of a photo cell, the excited electrons do not need to be in the conduction zone of the material, in our case the polymer. The work-time

period of the cell consists of the time of application voltage excitation, and the time of collection of the relaxation current. The presented technical solution has been patented and more technical details can be found in the patent document P-2015/0529 submitted on 10 August 2015 in the Serbian Intellectual Property Office.

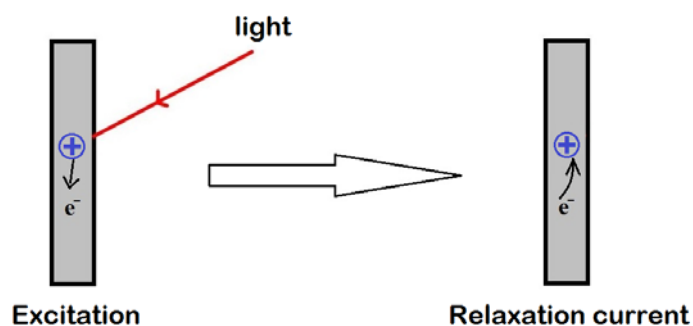


Figure 2. Generation of relaxation current in the illuminated material

The idea of the utilization of relaxation currents that originate from a photo-induced charge is obtained on the basis of the conclusions of the analysis of the photodielectric surface properties of polyolefins, which is presented in the following section. The possibility that cheap polymers, such as polyethylene (LDPE) and polypropylene (iPP), have potential application for the design of photocells can be of great technological importance.

3. SURFACE PHOTODIELECTRIC PROPERTIES OF LDPE AND IPP

The influence of UV radiation on the surface AC conductivity of LDPE and iPP was investigated. The samples were taken with surface positioned Al electrodes and with hot immersed electrodes of Khantal (Fe - 96%). Figure 3 shows the samples with hot immersed Khantal wires. The expected results were observed, where brief illumination of

the polymer surface at room temperature increased the real and imaginary part of the surface AC conductivity of the polymers. This increase in AC conductivity is a consequence of the UV initiated radical which we confirmed using electron paramagnetic resonance (EPR) spectroscopy, where UV excited electrons probably contributed to the development of the AC conductivities.

The percentage changes in conductance and susceptance of LDPE and iPP due to UV-vis illumination (380-430 nm) are presented in Figure 4, where measurements were taken in the heating mode (5 K/min). The results in Figure 4 show the expected photo-induced increases in conductance at certain temperatures and frequencies in LDPE and iPP. Bearing in mind the small changes in susceptance (Figure 4a,b), one can conclude that the photo-induced increase in conductance of the investigated polyolefins is primarily due to the free photo-induced charge.

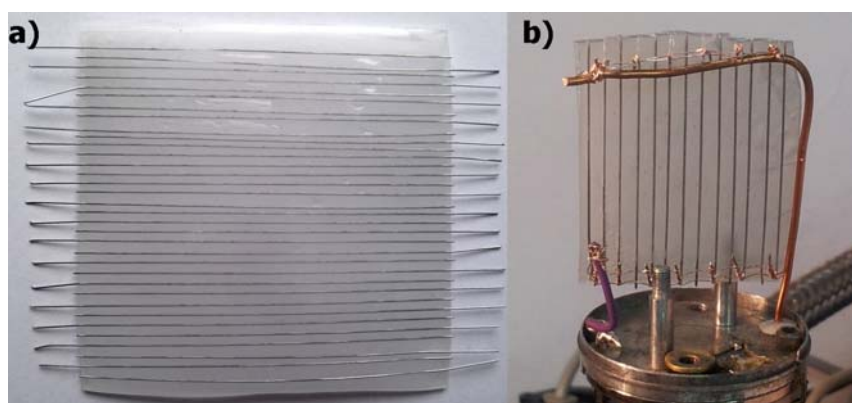


Figure 3. A sample with hot immersed Khantal wires: a) as prepared and b) mounted in the cell for measurements

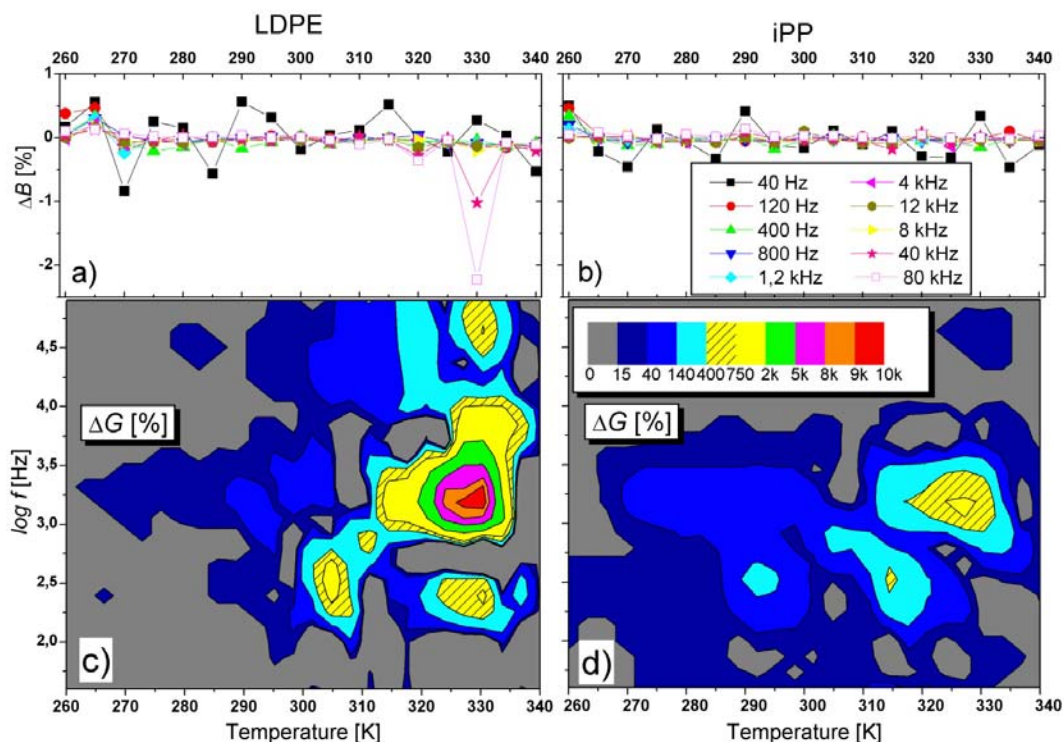


Figure 4. A temperature-frequency map of photo-induced AC conductivity in LDPE and iPP; susceptibility: a) LDPE and b) iPP; conductance: c) LDPE and d) iPP

At temperatures slightly higher than room temperature and longer illumination times, a decrease in the value of the real part of the AC conductivity (Conductance - G) was observed and, depending on the temperature and frequency, G can reach zero and even move into the negative part of the measuring range. This result was repeatedly confirmed in two laboratories with different LCR

bridges (Hameg 8118 - Faculty of Physics, University of Belgrade and Agilent 4284a - Vinča Institute of Nuclear Sciences, Serbia).

Figure 5 shows the typical changes in the real part of the AC surface conductivity, where the experiment was carried out at 50 °C, and where the LDPE sample was illuminated by UV light for the periods between 5 and 15 minutes.

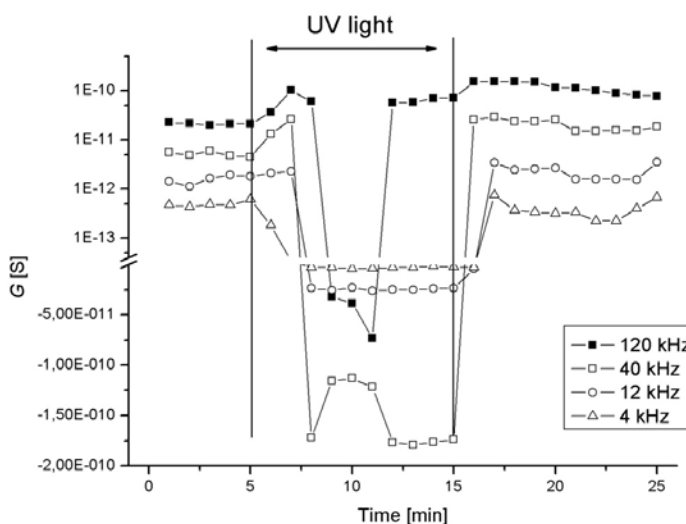


Figure 5. Changes in G as function of time at 50 °C in LDPE, where the sample was exposed to UV light for periods between 5 and 15 minutes.

The appearance of negative values of surface conductance depends on several parameters: measuring frequency, temperature and UV exposure time. This phenomenon existed, regardless of whether the electrodes were placed on the surface or hot immersed. To understand the behaviour of the amplitude of the AC conductivity, the experiment was repeated so that the sample during illumination was excited by a function generator, while the excitation voltage and the resulting current through the sample were monitored using a two-channel oscilloscope. The current through the sample was fed with a high frequency nano ampere amplifier. The current through the sample during UV exposure could be shifted through an angle greater than $\pi/2$ relative to the excitation, and the LCR bridges of such a response pattern of sinusoidal voltage excitation showed negative conductance values. The samples were analyzed after the experiment using Fourier-transform infrared spectroscopy, and no chemical changes due to the temperature and UV treatment were observed. Based on this, we can conclude that this phase shift was the result of the relaxation of the UV-generated charge on the polymer surface.

The results presented in this section indicate that a relaxation of UV-vis generated charge in non-polar polymers, like polyolefins, can be expressed. Relaxation currents that originate from photo-induced charges were clearly observed, and this motivated us to design a solution for the operation of a photocell that will produce a collection of relaxation currents.

4. THE OPPORTUNITIES

As already noted, the high cost of electricity obtained from photocells is the basic reason for the limited use of this form of energy. Another problem related to the production of solar electricity is storage. The non-continuous process of producing electricity from solar panels, and the problem of storage of energy generated in this way (high prices of batteries), present a problem for small consumers. However, there are good solutions for the storage of generated electricity on an industrial scale, such as the reversible hydro power plants, or the production of hydrogen. The determining factor for the broader use of photocells is not their energy efficiency, but the price per unit of installed electric power. Existing estimates indicate that the electric energy produced from solar panels will become a significant source of energy only when the price of the installed capacity drops below 100 USD/kW, which is about ten times less than today's price (800 USD/kW). In

this context, the design of cheap and environmentally friendly photocells becomes the only logical direction that leads to their wider use. Due to the simple design and potentially very low production price, monolayer photocells should replace the existing silicon based photocells on the market. It is, however, necessary to improve their physico-chemical stability and environmental acceptability. The monolayer stimulated photocell based on a collection of relaxation currents, which is briefly described in this paper, presents an attempt to design a low-cost photocell, and its effectiveness will be checked in subsequent research.

5. ACKNOWLEDGMENTS

This work was supported in part by the Ministry of Education and Science, Republic of Serbia (Project Nos. 171029), and in part by the National Research Foundation, South Africa (Grant No. 88301).

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ПРЕДНОСТИ ЈЕДНОСЛОЈНИХ ПОЛИМЕРНИХ ФОТОЋЕЛИЈА

Сажетак: Конверзија соларне енергије у електричну енергију је у фокусу интереса великог броја научника. Због проблема узрокованих употребом фосилних горива, пожељна је употреба обновљивих и еколошки прихватљивих извора енергије, а у неким земљама је употреба тих извора енергије у одређеном проценту постала законска обавеза. Данас постоје комерцијално доступне силиконске соларне ћелије са цијенама у опсегу од 800 USD/kw (око 10m²/kW) и ефикасности у обиму од 10–20%. Главна препрека за ширу употребу ових извора енергије је висока цијена електричне енергије произведене на тај начин у поређењу са трошковима електричне енергије из класичних извора (хидро, термалне и нуклеарне енергане). У развоју органских фотонапонских соларних ћелија (OFN) на бази полимера постигнут је технолошки пргорес, те се њихова енергетска ефикасност приближава вриједности од 10%, док цијена по јединици произведене енергије може бити значајно нижа од цијене енергије произведене од силиконских соларних ћелија. Недостатак OFN соларних ћелија је у њиховом кратком вијеку трајања, те због тога нису нашле ширу примјену. Једнослојне полимерне фотоћелије карактерише једноставан дизајн и потенцијално ниски трошкови производње. Може се претпоставити да због ових својстава једнослојна полимерна фотоћелија може постати јефтина замјена за широко распрострањене фотоћелије засноване на класичним полупроводницима. У овом раду су представљена постојећа објављена достигнућа у развоју једнослојне полимерне соларне ћелије, као и оригинална рјешења која су резултат истраживања вршених од стране аутора.

Кључне ријечи: фотоћелија, енергија.

