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Electrical and photoelectrical properties of P3HT/n-Si hybrid organic-inorganic heterojunction solar cells

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ABSTRACT

A detail analysis of electrical and photoelectrical properties of hybrid organic-inorganic heterojunction solar cells poly(3-hexylthiophene) (P3HT)/n-Si, fabricated by spin-coating of the polymeric thin film onto oxide passivated Si(100) surface, was carried out within the temperature ranging from 283 to 333 K. The dominating current transport mechanisms were established to be the multistep tunnel-recombination and space charge limited current at forward bias and leakage current through the shunt resistance at reverse bias. A simple approach was developed and successfully applied for the correct analysis of the high frequency C-V characteristics of hybrid heterojunction solar cells. The P3HT/n-Si solar cell under investigation possessed the following photoelectric parameters: I_{sc} = 16.25 mA/ cm², $V_{oc} = 0.456 \text{ V}$, FF = 0.45, $\eta = 3.32\%$ at $100 \text{ mW/cm}^2 \text{ AM } 1.5 \text{ illumination}$. The light dependence of the current transport mechanisms through the P3HT/n-Si hybrid solar cells is presented quantitatively and discussed in detail.

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1. Introduction

The interest in fundamental and applied research of conducting polymers as well as organic and hybrid organic/inorganic hybrid heterostructures has been rapidly increasing during the last decades [1-3].

Organic/inorganic hybrid heterojunctions merge advantages of both organic and inorganic semiconductors by unique combination of high quality electrical properties of inorganic materials with the film-forming properties of polymers. The fabrication of organic/inorganic hybrid semiconductor heterojunctions allows the development of a new class of semiconductor devices, which are very prospective for application in low cost flexible electronics, optoelectronics and photovoltaics.

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However, in spite of many advantages of hybrid heterojunction solar cells, there are a few drawbacks which have to be overcome in order to fabricate stable hybrid heterojunction solar cells with the compatible efficiency comparing with conventional c-Si homojunction solar cells and high quality CdTe or CuInSe2 thin film inorganic heterojunction solar cells [4]. One of the reasons of the relatively low efficiency of hybrid heterojunction solar cells is the lack of knowledge about electrical processes which take place in organic/inorganic heterojunction solar cells and thus determine their photoelectrical parameters.

There are many interesting works dedicated to the fabrication and analysis of new hybrid heterojunction solar cells based on different materials [5–12]. However, most of them are focusing on the design and configuration of organic/inorganic heterostructures in order to increase their photoelectric efficiency. At the same time much less attention is paid on the analysis of the dominating current transport mechanisms, DC and AC electrical properties as well as their dependence on different external conditions

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 that is very important for the operation of high quality optoelectronic devices. Therefore, a gap between the level of the efficiency of experimental hybrid solar cells and that of the understanding of physical and chemical processes exists. It is quite obvious that the gap has to be closed in order to create favourable conditions for the further development of high efficient hybrid heterojunction solar cells.

This paper reports the results of a detail analysis of DC and AC electrical as well as photoelectrical properties of planar hybrid heterojunction solar cells P3HT/n-Si within the temperature range from 283 to 333 K.

2. Experimental part

Single crystal n-doped Si(100) substrates (ρ = 6 Ω cm, n = 7.4 × 10¹⁴ cm⁻³) were ultrasonically cleaned in isopropanol and rinsed in deionized water (ρ = 10⁸ Ω cm). The substrates were etched in 5% HF solution during 5 min in order to eliminate the native oxide. Afterward, the freshly H-terminated Si(100) substrates have been oxidized under laboratory conditions (T = 300 K, RH = 18%) for 10 h in order to obtain an oxide passivated Si(100) surface with low density of interface states [13]. The thickness of the SiO₂ layer d_{SiO_2} amounts to about 2 nm as measured by means of an ellipsometer (SENTECH SE850).

The P3HT thin film was deposited onto oxide passivated Si substrates by spin-coating (2000 rpm, 30 s) of 2 mg P3HT solved in 5 ml 1-2-dichlorobenzene solution. Afterwards the P3HT/n-Si hybrid heterostructures were transferred to a vacuum chamber and annealed at 373 K and 10^{-7} mbar for 1 h. A semitransparent Au front contact was deposited by thermal evaporation. The back electrical contact to the n-Si(100) substrates was prepared outside the vacuum chamber by means of an In—Ga eutectic. The active area of the fabricated P3HT/n-Si hybrid solar cells was $0.2 \, \mathrm{cm}^2$.

The morphology of the surface of the P3HT thin film on the Si substrate and the cross-section of the heterostructure under investigation were analyzed by means of a scanning electron microscope (SEM) Hitachi S 4100. The structural properties of the P3HT/Si surface were inspected by using Raman spectroscopy (LabRAM micro Raman, Dilor, excitation wavelength 632.82 nm).

Current–voltage (*I–V*) characteristics of the P3HT/n-Si heterojunctions were measured by a high current source measuring unit Keithley 238 at different temperatures in the dark and under illumination. The temperature control was carried out by a thermal inducing vacuum platform ThermoChuck TP0315B. The light source was an AM1.5 solar simulator (Steuernagel). The capacitance–voltage (*C–V*) characteristic was measured by a Keithley 590 CV Analyzer at an AC frequency of 1 MHz at 293 K.

Optical properties of the P3HT thin film and semitransparent Au front contact were measured by a Perkin Elmer UV/VIS/NIR spectrometer Lambda 19 within the wavelength range from 300 to 1500 nm. The spectral distribution of the apparent quantum efficiency of the hybrid heterojunctions under investigation was measured using a monochromator SPEX 270 M within the wavelength region from 300 to 1150 nm. The calibration of the

monochromator was carried out by means of a calibrating Si solar cell (Fraunhofer ISE CalLab PV Cells).

3. Results and discussions

3.1. Morphology and structural properties

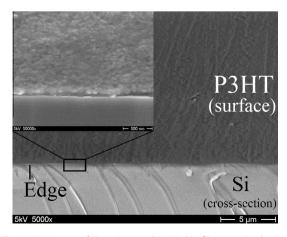
The surface and the cross-section SEM images of a P3HT thin film spin-coated onto Si substrate are shown in Fig. 1 at the angle of 30°. It is seen that the polymer thin film is not uniform over the surface, mainly due to the high rotation velocity during the deposition that decorates stripes. However, any pinholes in the thin film were not observed. The thickness of the P3HT layer varies from 40 to 60 nm.

The Raman spectrum of the surface of the P3HT/Si hybrid heterostructure is shown in Fig. 2. The first three peaks $298 \, \mathrm{cm}^{-1}$, $520 \, \mathrm{cm}^{-1}$ and $942 \, \mathrm{cm}^{-1}$ originate from the Si substrate [14]. The two sharp peaks at $1378 \, \mathrm{cm}^{-1}$ and $1442 \, \mathrm{cm}^{-1}$ and the small one at $1512 \, \mathrm{cm}^{-1}$ result from the C–C stretching vibrations and C=C skeleton stretching of the thiophene rings, respectively. The small and broad peak at about $2886 \, \mathrm{cm}^{-1}$ (see inset in Fig. 2) is observed as a result of the CH₂ symmetric and antisymmetric stretching vibrations [15].

3.2. Electrical properties

The prepared P3HT/n-Si hybrid heterojunctions possessed sharply defined rectifying properties within the measured temperature range (Fig. 3) that provides evidence in the formation of a high quality electric junction at the polymer/semiconductor interface.

Fig. 4 shows the forward branches of the I-V characteristics of the hybrid heterojunctions under investigation at different temperatures. The height of the potential barrier φ_0 of the P3HT/n-Si heterojunction can be estimated by means of the extrapolation of the linear segments of the forward I-V characteristics toward the interception with the voltage axis. The temperature dependence of the estimated height of the potential barrier of the P3HT/n-Si heterojunctions is well governed by the linear equation:



 $\textbf{Fig. 1.} \ \ \textbf{SEM} \ \ \textbf{images} \ \ \textbf{of the spin-coated} \ \ \textbf{P3HT} \ \ \textbf{thin film onto} \ \ \textbf{Si substrate}.$

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