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Electrical and optical properties of composite PEDOT:PSS-based thin films with NiO nanoparticles

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ABSTRACT

Due to the combination of low cost materials deposition and device fabrication methods as well as competitive efficiency compared to the other Si solar cell architectures, the hybrid organic-silicon solar cells have attracted attention of the scientific community. It has recently been demonstrated that spin-coated poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (hereafter PEDOT:PSS) on a silicon wafer is a promising material due to its good optical and electrical properties. However, degradation caused by atmospheric exposure and relatively poor passivation properties limits implementation of PEDOT:PSS–silicon devices. Functionalization of PEDOT:PSS by inorganic nanoparticles might provide a possible solution as was shown for TiO_2 and SnO_2 nanoparticles. In this contribution, we present our results on spin-coated PEDOT:PSS thin-films with NiO nanoparticles. We show that PEDOT:PSS mixed with Triton X-100 and dimethyl sulfoxide (DMSO) or ethylene glycol (EG) form a homogenous film and passivates the Si surface with charge carrier lifetimes of 300–400 μs with good reproducibility. Time-resolved measurements revealed continuous degradation of the passivation properties in air, however saturation of the degradation at approximately 150 μs was observed in N_2 atmosphere. The influence of the NiO nanoparticles on the optical properties of PEDOT:PSS is negligible, whereas the surface passivation properties are worsened due probably to the formation of large size agglomerates exceeding thickness of PEDOT:PSS film.

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1. Introduction

Although silicon based solar cells are the most prominent in the photovoltaic market, intensive research addresses alternative concepts for further enhancing the efficiency and lowering the fabrication cost. It was recently reported that the combination of silicon with organic materials reduces the fabrication cost owing to the possibility of room temperature and vacuum-free technological steps [1]. Some significant results have been demonstrated combining silicon with poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). This polymer is already widely used for many technological applications such as optoelectronics [2], thin-film transistors [3] and transparent electrodes [4] because of its high transparency in the visible spectrum, electrical conductivity and mechanical flexibility [5]. In Ref. [6], hybrid solar cells with an efficiency of ~20% were presented, using PEDOT:PSS on the rear side of both n-type and p-type silicon wafers. In order to solve stability issues, enhance electrical conductivity, and Si surface passivation, several attempts were made to functionalize PEDOT:PSS by nanoparticles. For instance, in Ref [7] incorporation of Au and Ag nanoparticles into PEDOT:PSS led to an 8% improvement in power conversion efficiency, which was attributed to the enlarged surface roughness. An increase of electrical conductivity with up to three orders of magnitude was observed by adding Ag nanoparticles [8]. M. Garcia-Tecedor et al. have demonstrated that functionalization by SnO_2 and TiO_2 nanoparticles can increase charge carrier lifetimes from 40 μs to 275 μs at low concentration of nanoparticles, however this effect vanished for heavily doped composites [9].

In this work we present our study of the optical and passivation properties of PEDOT:PSS mixed with Triton X-100 and DMSO or EG, as well as the effect of its functionalization by NiO nanoparticles on these properties and material durability.

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2. Experimental details

An aqueous PEDOT:PSS PH 1000 commercially available from Ossila was used in this work. The nonionic surfactant Triton X-100 (0.1 vol%) was utilized as a wetting agent in all samples to decrease the surface tension of the mixture thereby improving the homogeneity of the films. Samples prepared without Triton X-100 showed poor coverage of the substrate after spin-coating. It was also reported that non-ionic surfactants enhance the electrical conductivity of PEDOT:PSS [10]. To further increase conductivity and improve dispersion of nanoparticles 5 vol% of DMSO or EG were also added to the PEDOT:PSS (hereafter PEDOT:PSS (DMSO) and PEDOT:PSS (EG), respectively) [11]. The resulting mixtures were magnetically stirred for 2 h followed by filtering through a 0.45 μm polyethersulfone (PES) filter. Spin coating in the dynamic mode was employed to make coatings; parameters such as rotation speed, acceleration and time were optimized empirically to achieve good homogeneity and a thickness of the film around 100 nm, which was measured by a stylus surface profilometry. Single-crystalline float-zone Si wafers of n-type conductivity were chosen as substrates. Twins of the films applied for surface passivation experiments were coated onto glass substrate for optical characterization. After spin coating, the films were placed on the heating plate at a temperature of 120 °C for 15 min to evaporate residual moisture. Functionalization of PEDOT:PSS was done by dispersion of NiO nanoparticles into the mixture and ultrasonic homogenization has been performed before spin-coating. It was established that the time of ultrasonic homogenization should not exceed 2 min to avoid a rapid decrease of electrical conductivity. The nanoparticles were synthesized by the hydrothermal process, and their average size estimated using TEM and XRD was found to be 5–7 nm.

Optical characterization was performed using an Ocean Optics QE6500 spectrometer together with deuterium and halogen light sources used for probing. A combination of quasi-steady state photoconductance measurements (QSSPC) and photoluminescence imaging (PL-I) enabled us to obtain the charge carrier lifetime as a function of injection level and its distribution map in the film [12]. For this study a LIS-R1 PL imaging setup from BT Imaging equipped with an 808 nm laser was employed. Morphology was investigated by means of Hitachi S-4800 SEM using a 5 kV accelerating voltage. The diode behavior of the samples was confirmed from I to V curves obtained by applying voltage through samples on which Ag contacts were deposited on both sides by thermal evaporation.

3. Results and discussion

Considering PEDOT:PSS as a possible emitter layer, the optical properties of this material have to be addressed. Fig. 1 shows the measured transmittance and reflectance spectra for PEDOT:PSS (DMSO) and PEDOT:PSS (EG), and for the glass substrate. Both films demonstrate almost identical high transparency in the visible range, which is only 5–10% smaller than that of the glass substrate. The reflectance of the films is smaller than that of the glass substrate. However, PEDOT:PSS (DMSO) exhibits slightly smaller reflection. In general, it should be also possible to modify the transmittance of the film by changing its thickness, but for this study fixed thickness around 100 nm was used.

The surface passivation is another essential property for the emitter layer. As shown in Fig. 2a, both for PEDOT:PSS (DMSO) and PEDOT:PSS (EG) can be used to obtain a passivation resulting in a lifetime of 300–400 μs at the excess carrier density achieved by illumination of 1 Sun intensity (1 kW/m^2). Earlier reported life-

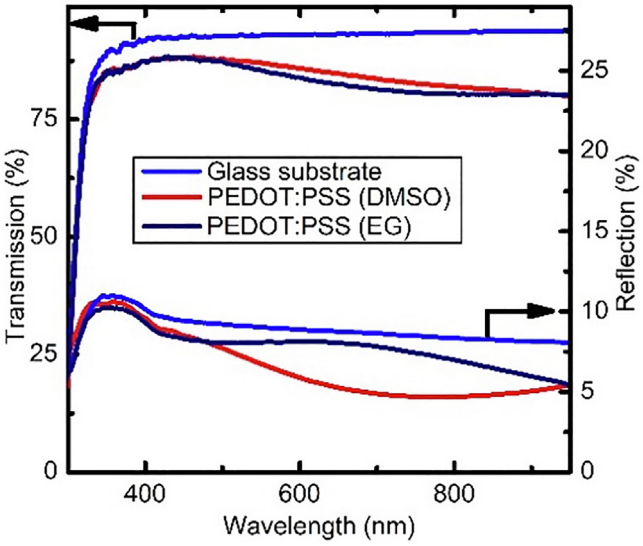

Fig. 1. Optical properties of PEDOT:PSS (DMSO) and PEDOT:PSS (EG). Optical properties from glass substrate is included as a reference.

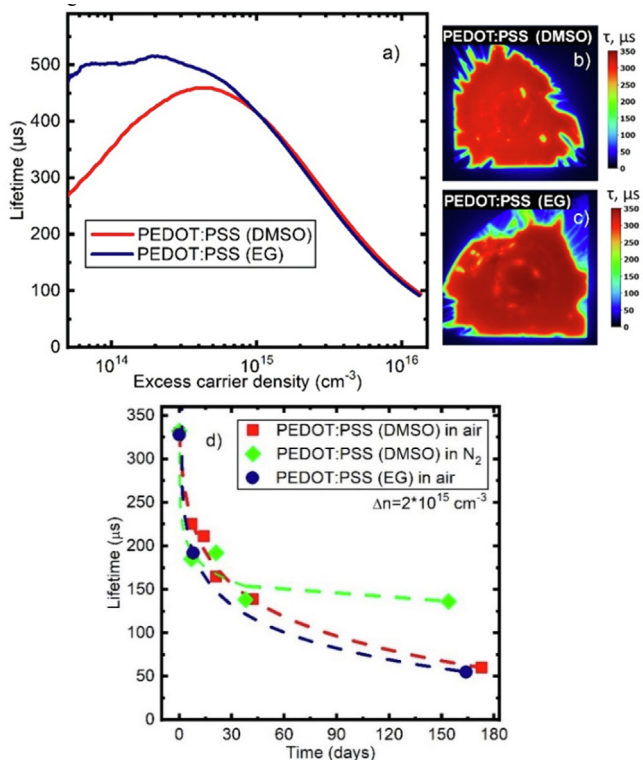

Fig. 2. Passivation properties of PEDOT:PSS (DMSO) and PEDOT:PSS (EG). a – charge carrier lifetime as a function of excess carrier density; b, c – PL images demonstrating lifetime at the injection level 1×10^{15} cm^{-3}; d – time-resolved measurements of the charge carriers lifetime vs. time.

times for PEDOT:PSS/c-Si are scattered in a broad range (from tens of μs to ms) depending on the substrate, film thickness and doping level [9,13,14]. Spatial distribution of charge carrier lifetime on Fig. 2b and c demonstrates homogeneous passivation of the area of several cm^2. The decrease of lifetime values at the edges can be attributed to the reduction of thickness of the PEDOT layer, whereas some variation observed in the middle reflects the inho-

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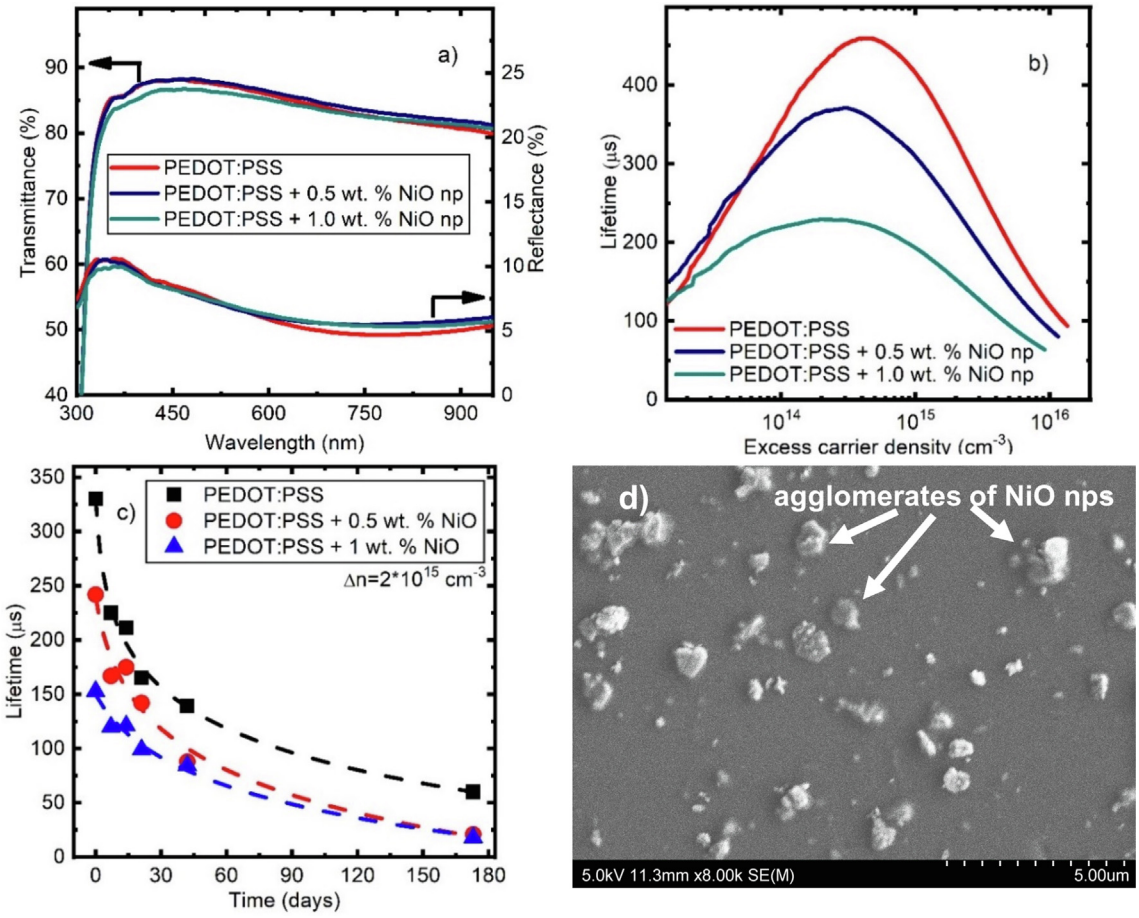

Fig. 3. Effect of functionalization by NiO nanoparticles on (a) transmittance and reflectance spectra, (b) injection level dependence of charge carrier lifetime and (c) its degradation with time. (d) SEM image of the PEDOT:PSS films functionalized by NiO nanoparticles.

mogeneity of the solution and can be eliminated by longer magnetic stirring and multiple filtering. Lifetime measurements were repeated to study degradation of passivation properties (Fig. 2d). A rapid decrease of lifetime from 330 μs down to 150 μs obeying logarithmic decay is observed within first month, reaching 50–60 μs after 6 months. A sample kept in N_2 atmosphere revealed similar trend. However, in this case the degradation stopped at 150 μs after 1 month. It is broadly agreed that moisture has a negative impact on the stability of PEDOT:PSS, as it causes irreversible changes in the polymer morphology which decrease charge carrier lifetime [15,16]. Apparently PEDOT:PSS placed in N_2 contained some moisture which remained after drying on the heating plate, but any degradation resulting from this stopped after 1 month in an oxygen-free atmosphere.

In an attempt to tune the Si surface passivation properties the PEDOT:PSS (DMSO) was functionalized by adding NiO nanoparticles at 2 different concentrations: 0.5 wt% and 1 wt%. As one can see from Fig. 3a, functionalization did not significantly change the optical properties. However, the charge carrier lifetime (Fig. 3b) has been reduced with increasing the NiO concentration. At 2×10^{15} cm^{-3}, a charge carrier lifetime decreased from 330 μs for PEDOT:PSS (DMSO) to 242 μs and to 153 μs for films with 0.5 wt% and 1 wt% of NiO, respectively. A logarithmic decay of charge carriers lifetime with time down to 20 μs is also observed for functionalized films after 6 months. A study of morphology by means of SEM (Fig. 3d) demonstrated that nanoparticles form μm size agglomerates which is approximately 10 times bigger than a thickness of the film. These inclusions break the continuity of the film increasing recombination rate on the surface.

4. Summary and outlook

In this work, the optical, electrical, and morphological properties of PEDOT:PSS-based hybrid materials were studied. PEDOT:PSS with Triton X-100 and DMSO or EG were spin-coated onto glass and FZ n-Si wafers. The films exhibited transmittance ≥80% and a charge carrier lifetime of 330 μs. Time-resolved measurements revealed degradation of the lifetime to 50–60 μs after 6 months due to humidity exposure, whereas a sample stored in N_2 atmosphere was more stable, showing 150 μs lifetime after the same time span. Functionalization of PEDOT:PSS by NiO nanoparticles did not significantly change the optical properties, whereas charge carrier lifetime decreased proportionally to the concentration of nanoparticles. As observed by SEM, the nanoparticles formed massive agglomerates breaking the continuity of the PEDOT:PSS film and thereby increasing the Si surface recombination rate. To further study functionalization by NiO, an improved method for dispersion of nanoparticles in PEDOT:PSS solution has to be developed. One of the possible approaches could be an ultrasonic homogenization of nanoparticles in DMSO or EG for a longer time or the usage of different surfactant.

CRediT authorship contribution statement

D. Moldarev: Investigation, Writing - original draft, Formal analysis. **M. Taeño:** Investigation, Writing - review & editing. **D. Maestre:** Supervision, Writing - review & editing. **A. Cremades:** Supervision, Funding acquisition. **S.Zh. Karazhanov:** Supervision,

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Writing - review & editing. **E. Marstein:** Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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