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Influence of Si-nanoparticles on PEDOT:PSS properties for hybrid solar cells

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ABSTRACT

Hole-conducting poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is a material receiving increasing interest for use in photovoltaic devices. In this work, we present the results of study of the degradation of the optical and electrical properties of pure PEDOT:PSS and PEDOT:PSS doped with Si-nanoparticles. The PEDOT:PSS has been deposited on top of Si wafers by spin coating. We found that incorporation of Si nanoparticles into PEDOT:PSS enhances the surface passivation of the surface of the Si wafer by increasing the carrier lifetime measured by the photoluminescence quasi-steady state photoconductance (PL QSS-PC) method from about 320 μs to 420 μs at a minority carrier injection level of $2 \cdot 10^{15} \text{ cm}^{-3}$. Analysis showed that incorporation of the Si nanoparticles does not change the kinetics of degradation of lifetime considerably.

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1. Introduction

Organic solar cells remain an interesting alternative to silicon solar cells due to their low cost, scalability and ability to be produced on flexible substrates. But despite of all the advantages, there are some issues related to stability and tuneability. In order to overcome them, combination with inorganic materials in hybrid solar cells was suggested [1,2]. This led to better control of electrical and optical properties [3]. The development of hybrid solar cell technologies led to the creation of novel solar cell architectures based on silicon wafers with competitive performance [4,5]. One of the most challenging issues remains the understanding of the surface passivation of the Si surface by the organic layer because of its crucial influence on minority carrier lifetime. In factories today, inorganic materials are commonly used for surface passivation, particularly Si nitride, amorphous Si (a-Si) [6], aluminum oxide (Al_2O_3) [7] and silicon oxide (SiO_2) [8] all of which provide high carrier lifetime. All of these processes add substantial cost to the solar cell production, among others due to requirements for vacuum systems, heating and gas infrastructure. Easy to apply conductive polymers are therefore interesting alternatives: they can play a double role in a solar cell and function as both a manda-

tory element for the p-n junction and a passivation layer for the silicon surface.

The most commonly used conductive polymer for hybrid solar cells is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Despite of its high p-type conductivity, there are stability issues mainly related to the breaking down of the ionic bonds between PEDOT cores and the nonconductive PSS matrix [9]. This effect is enhanced at high temperatures and leads to instability of both optical and electrical properties. In order to modify the properties of PEDOT:PSS, the functionalization of the polymer by inorganic nanostructure has been suggested [10,11]. It was found that tin oxide (SnO_2) and titanium oxide (TiO_2) nanoparticles can improve the effect of the organic layer on passivation of Si surface [12]. Functionalization also may increase the stability of PEDOT:PSS over time and reduce the reduction of the minor carrier lifetime [13].

In the present work, the effect of silicon nanoparticles on the surface passivation of Si substrates was studied. Kinetics curves for minority carrier lifetime over time were obtained and analyzed for different hold temperatures.

2. Experimental details

Two types of silicon nanoparticles (30–50 nm, US Research Nanomaterials, Inc (US-nano) and 300 nm, Institute for Energy

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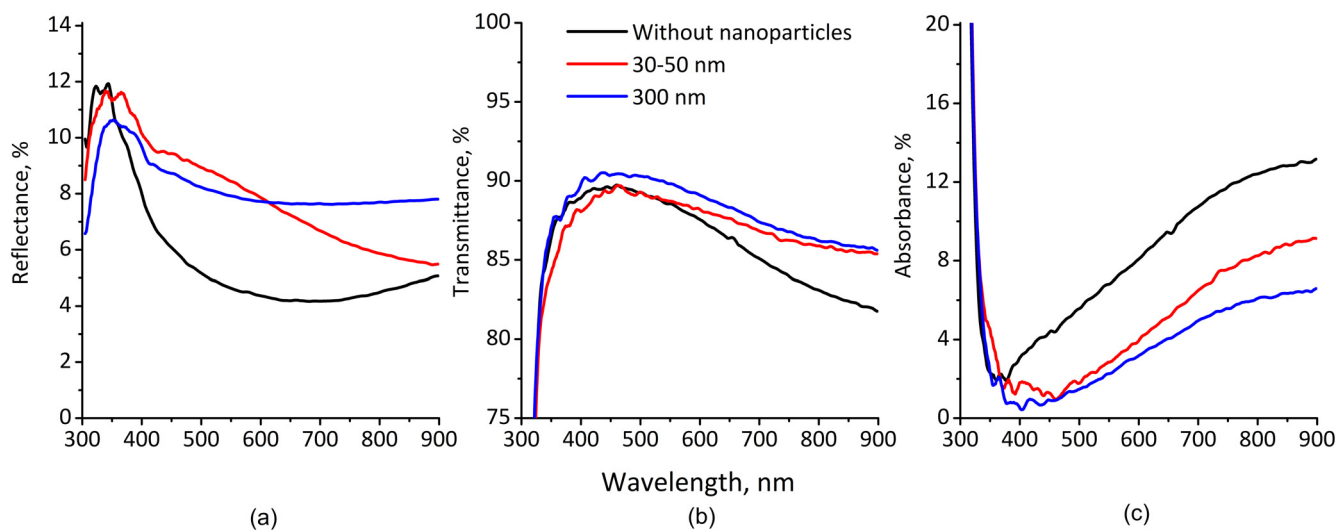


Fig. 1. Reflection, transmission and calculated absorption of PEDOT:PSS functionalized with Si nanoparticles at a concentration of 1%.

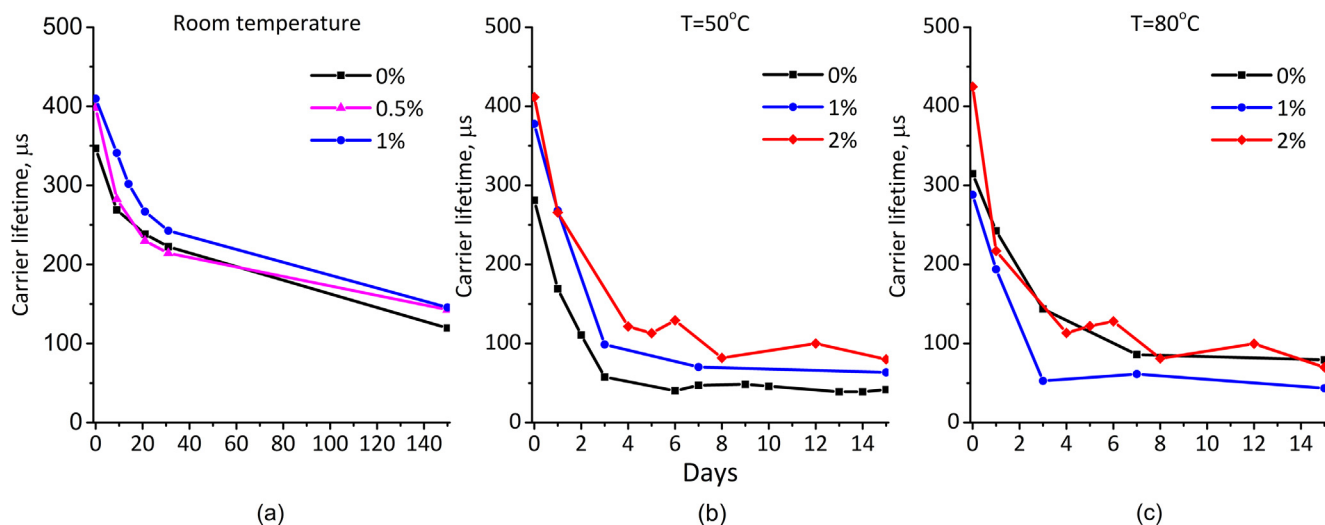


Fig. 2. Time dependence of carrier lifetime for Si-functionalized PEDOT:PSS held at different temperatures. Numbers show the nanoparticles concentration (in weight percent) for every curve.

Technology) were homogenized and mixed with conductive PEDOT:PSS (M122, Osilla), 5%(vol.) DMSO and 0.1% surfactant (Triton X-100, Alfa Aesar). After stirring and filtering with a 0.45 μm PES filter, the material was spin-coated using the dynamical mode onto Si and glass substrates for 50 s at 2000 rpm, then for 20 s at 6000 rpm. The layer was subsequently dried for 15 min at 120 $^{\circ}\text{C}$ on a hotplate.

The deposition quality via spin-coating is unstable even when applying a surfactant. Deposition was carried out on both sides of a quarter 4-inch n-type Si wafer produced with Czochralski method (Siegert Wafer, $\langle 1\ 0\ 0 \rangle$ orientation with 1–5 Ohm-cm resistivity). Carrier lifetime values were measured with the photoluminescence (PL) quasi-steady state photoconductance (QSS-PC) calibrated lifetime measurement method using a LIS-R1 PL imaging setup from BT imaging. The excitation energy for PL is 808 nm with an illumination intensity of $4.2 \cdot 10^{-2} \text{ W} \cdot \text{cm}^{-2}$. The carrier lifetime values were compared at an injection level of $\Delta n = 2 \cdot 10^{15} \text{ cm}^{-3}$. Optical characterization of functionalized PEDOT:PSS deposited

on glass substrate was performed with a UV-vis-NIR spectrophotometer (Ocean Optics QE65000).

3. Results and discussion

As the first step, the influence of Si nanoparticles on the optical properties of PEDOT:PSS was determined. As we see from Fig. 1, their presence in the solution leads to both reflectance and transmittance increasing, as well as absorbance decreasing, over the visible range. Reflectance, transmittance and absorbance curves for pure PEDOT:PSS and PEDOT:PSS functionalized using 300 nm nanoparticles exhibit a similar pattern with a reflectance minimum at $\sim 670 \text{ nm}$ and a transmittance maximum at $\sim 450 \text{ nm}$. The optical properties for PEDOT:PSS functionalized with the smaller 30–50 nm particles shows a different behavior with monotonously decreasing reflectance and transmittance over the visible range. Absorbance of the hybrid material, as it follows from Fig. 1, reveals to be considerably less than for pristine polymer. This behavior

appears as a combination of three different effects. Firstly, Si-nanoparticles incorporation modifies refractive index of the organic layer which leads to reflectance increasing. Secondly, nanoparticles influence on wettability of PEDOT:PSS and therefore slightly affect on thickness of the spin-coated thin film and its transmittance. Thirdly, Si possesses indirect band structure when the size of Si is of micrometer size, it absorbs sunlight worse than the polymer (Fig. 2).

In the current study, the carrier lifetime evolution of PEDOT:PSS functionalized by 30–50 nm Si-nanoparticles was studied at different annealing temperatures. Results obtained for different concentration shows correlation between the presence of nanoparticles and the degradation rate. The observed small differences between the lifetime for pure and functionalized PEDOT:PSS solutions at 80 °C might be caused by deposition quality and sample's position during PL lifetime measurement.

Analysis reveals the decrease of passivation properties of functionalized PEDOT:PSS over time, regardless of the presence of Si nanoparticles. Moreover, the degradation rate increases at higher temperatures: after 15 days the carrier lifetime decreases by approximately 30 percent at room temperature and by 4–6 times at 50 °C and 80 °C, which is in good agreement with the idea of thermally induced mechanism of degradation. Although the passivation level for higher temperatures seems to be stabilized after a relatively short period of time, the long-term degradation continues even after removing samples from the hot plate and leads to the gradual decreasing of the carrier lifetime down to zero.

One of the biggest challenges for functionalizing of PEDOT:PSS is agglomeration of nanoparticles, which might be formed just after splitting by homogenization and filtering. In case of spin-coating, the observed thickness equals 60–100 nm at 2000 rpm. That means that agglomerations may contact the silicon surface and simultaneously break through to the outer environment, resulting in incomplete coverage of PEDOT:PSS across the Si surface. However, even with only partial covering with polymer, the passivation level stays at the same level.

It should also be noticed that the spatial distribution of nanoparticles over the sample might be inhomogeneous after spin coating. During deposition, they tend to be concentrated at the edges of the spreading solution which can lead to the poor wettability and surface coverage.

4. Conclusion

PEDOT:PSS films functionalized by Si nanoparticles provide an increase of the measured surface passivation just after deposition compared to similar surfaces covered by pure PEDOT:PSS. Although only a substantial degradation of passivation is observed after storing at room temperature, the surface passivation is reduced after annealing at high temperatures. Si nanoparticles increase reflectance in visible range, but they also enhance the general transmittance, especially in the red part of the spectrum. Spin-coating could lead to an inhomogeneous density of nanoparticles which affect the variation of the resulting properties over the sample. Nanoparticle dispersion is crucial and needs more study.

CRedit authorship contribution statement

D. Mamedov - Data curation, Formal analysis, Investigation, Validation, Visualization, Writing - original draft, Writing - review & editing. **C.C. You** - Formal analysis, Methodology, Software, Writing - original draft, Writing - review & editing. **S.Zh. Karazhanov** - Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **E.S. Marstein** - Funding acquisition, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing.

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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