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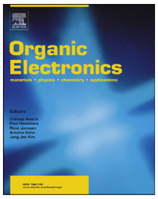

Enhanced photoresponsivity in organic field effect transistors by silver nanoparticles

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ABSTRACT

Organic semiconductors (OSC) such as thiophene-based oligomers exhibit useful electronic and optical properties making them applicable in photo-sensing devices. Generally, thiophene-based photodetectors exhibit a decent responsivity with a spectral sensitivity determined by the OSC's absorption properties. We present a simple, yet efficient method to enhance and spectrally tune the photoresponsivity of organic phototransistors (OPTs) utilizing the plasmonic properties of embedded metallic nanoparticles. The ability to fabricate and characterize nanostructures with high accuracy allows for tailoring of the optical properties of metal nanoparticles (NPs) and thereby tuning of the spectral range of enhanced photoresponsivity. In this work we have investigated OPTs based on the molecule 5,5″-bis(naphth-2-yl)-2,2':5′,2″-terthiophene (NaT3). We have fabricated OPTs with electron beam lithography-defined arrays of silver NPs under the organic thin-film. The photoconductivity of OPTs with and without NPs was characterized under spectrally resolved illumination. The OPTs exhibit significant responsivity at wavelengths below 500 nm essentially coinciding with the absorption spectrum of NaT3. Finite element simulations of the optical properties of the NPs reveal large electric field enhancement at the plasmon resonances. At these wavelengths (350→500 nm) the experimentally measured photoresponsivity of OPTs with NPs is significantly increased compared to the responsivity for OPTs without NPs. Due to a variation in particle size and shape of the fabricated silver NPs, a spectrally broad enhancement is predicted, which is in agreement with the experimental results. The results show that the photoresponsivity is dominantly enhanced in a spectral region of low OSC absorption coinciding with the localized surface plasmon resonances of the NPs. This work demonstrates that it is possible to improve and tailor the responsivity spectrum of photoactive organic devices by integration of metal nanoparticles.

1. Introduction

Organic semiconductors (OSCs) have seen a huge increase in interest due to their attractive device application potential within e.g. stretchable or flexible electronics [1,2] combined with beneficial characteristics such as low cost fabrication and relatively simple large area processing [3]. Considerable efforts have been invested in the improvement of the power conversion efficiency of opto-electronic devices such as organic light-emitting diodes for solid-state lighting as well as pixel lighting in flat-panel displays [4–8]. Furthermore, organic solar cell technology is under extensive research as a cost-effective and environmentally friendly sustainable energy source [9–14]. Organic photoactive media combine efficient light absorption from UV to NIR with good photogeneration yield and good charge transport properties, which can

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enable opto-electronic systems to be targeted in the field of imaging, optical communications or biomedical sensing [15,16].

A photosensitive OSC utilized in a field-effect transistor (FET) configuration provides a useful opto-electronic platform, which can be realized by simple large-scale fabrication methods. The organic FET-based photodetector is a type of optical transducer, in which light detection and signal amplification are combined in a single device. In an FET, the amount of current flowing from the source-to the drain-electrode in the accumulated channel is, for a given drain-source bias, controlled by the gate voltage. For an organic phototransistor (OPT) the conductance of the channel is further increased by absorption of light and the resulting generation of photocarriers [15]. The light-sensing properties are highly dependent on the light-trapping abilities of the device – a parameter tunable by nanostructural modifications of the device constituents [17].

The effect of metallic nanoparticles exhibiting localized surface plasmon resonances (LSPRs) has been exploited in a number of optoelectronic device applications. Localized surface plasmons are non-propagating excitations of the conduction electron plasma of metallic nanostructures coupled to an exciting electromagnetic field. The curved surface of a nanoparticle (NP) in an oscillating electromagnetic field leads to resonant field amplification in the near-field zone outside the particle [18]. The induced polarization of the nanoparticle by the oscillating electric field can either absorb (non-radiative decay) or scatter (radiative decay) the electromagnetic energy flux [17,19]. The optical properties of metallic nanoparticles are highly dependent on type of metal, size, shape and surrounding environment [20].

In inorganic solar cells the efficiency can be enhanced by scattering of the incident light [17]. Using nanoparticles on the front surface of the device, light is scattered in a forward direction (into the device) thus reducing reflection and increasing light-trapping [21]. Recently plasmonic metallic nanostructures have come into focus as a new scheme for the conversion of solar into chemical energy in the field of photocatalysis [22,23]. Plasmonic absorbers have also been used to increase hot electron generation and injection into semiconductors, demonstrated in a Schottky diode structure [24,25]. In such devices a Schottky barrier is formed at the metal-semiconductor interface and the energy needed for hot electrons to overcome the Schottky barrier is considerably smaller than the bandgap of the semiconductor [23]. Recent work has demonstrated enhanced photo-response in a photoconductor device based on a polymer nanowire with embedded gold nanoparticles [26].

Here we demonstrate an approach to enhance and spectrally tune the photoresponsivity of an OPT by incorporating silver (Ag) NPs with LSPR within the absorption band of the OSC. Ag nanoparticles demonstrate significant LSPR in the UV-VIS region [27]. We have fabricated p-type organic FETs using the thiophene-based molecule 5,5″-bis(naphth-2-yl)-2,2':5′,2″-terthiophene (NaT3) to form the active layer (Fig. 1a). The naphthyl end-capping reduces the likelihood of polymerization and thereby ensures a stable optoelectronic performance [28].

The photo responsive mechanism of the OPTs is based on exciton formation and dissociation. If the photon energy of the incident radiation is larger than the bandgap of the OSC, the photon can be absorbed in the OSC leading to the formation of an exciton. An applied bias voltage entails a finite probability to dissociate the exciton to free carriers and thereby increase the transistor current [15].

The Ag NPs are embedded in the transistor channel as localized surface plasmon resonators, which can be excited optically. This article investigates the resulting photon-to-current conversion and enhancement of responsivity by NPs through a series of photoresponsivity measurements. The results show that the LSPR increase the electron-hole pair (EHP) generation in the organic semiconductor by light scattering and locally enhancing the electric field near the particles, both effects leading to an increased photoresponsivity.

2. Experimental

2.1. Device layout and fabrication

The device layout (Fig. 1b) is based on a simple structure, consisting of a highly n-doped Si carrier substrate as back gate electrode and a 200 nm thick thermally grown SiO_2 layer as the gate dielectric. On top, interdigitated source and drain electrodes were fabricated by E-beam evaporation of Ti/Au (3 nm/30 nm), structured by photolithography and lift-off. The dimensions of the interdigitated electrodes define the width and length of the transistor channel: 2 mm and 10 μm, respectively, resulting in a width/length (W/L) ratio of 200. Ag NPs were fabricated by electron beam lithography (EBL) in PMMA, thermal evaporation of a 40 nm layer of Ag on top of a 3 nm Ti adhesion layer, and lift-off in acetone. Finally, a 55 nm thick NaT3 layer [29] was deposited by vacuum sublimation (deposition pressure $\sim 10^{-8}$ mbar, deposition rate ~ 0.2 nm/s) on top of the transistor substrates.

2.2. Characterization methods

The OPTs were investigated in the wavelength range 350 nm – 500 nm, in which the OSC is photoactive. The light absorption of NaT3 is, as most OSCs, dominated by the π, π^* molecular orbitals [28]. The optical constants (complex refractive index), $n' = n + ik$, have been measured using spectroscopic ellipsometry on a ~ 46 nm thick NaT3 film deposited on a Si substrate. Additionally, the absorbance (A) of a ~ 46 nm thick NaT3 film deposited on BK7 glass was determined by spectrophotometry, using a volume scattering integration sphere, as $A = -\log_{10}(T)$, where T is the diffuse transmittance of the NaT3 film (Fig. S1, Supporting Information).

2.2.1. Optoelectronic device characterization

The electrical characteristics of the OPTs were measured using a custom-made characterization set-up based on a LabVIEW-controlled data acquisition card connected to voltage and current amplifiers providing the input and a probe station measuring the output signal from the OPT. White light was passed through a monochromator to select a narrow wavelength band and focused on the sample surface with a 20× objective lens. Based on consecutive measurements of the electrical characteristics at different illumination wavelengths, the wavelength (λ) dependent photoresponsivity spectrum was determined according to the definition:

$$R(\lambda) = \frac{I_{DS,light}(\lambda) - I^{(\lambda)}_{DS,dark}}{E_e \cdot S}$$

E_e being the irradiance in W/m^2 onto the OPTs active area S and the drain-source currents $I_{DS,light}$ and $I_{DS,dark}$ representing the measured values with and without light, respectively. Since the photocurrent in an OPT has a non-linear dependency on the illumination power [30], the output intensity of the monochromator was adjusted by varying the monochromator input slit width at each wavelength to ensure that a constant power (0.6 μW) was illuminating the active area. With a constant gate voltage $V_G = -10$ V applied, the drain-source voltage (V_{DS}) was swept from