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Optical characterization of organic blend films integrating metallic nanoparticles

Sylvain Vedraine [a], Philippe Torchio [a,*], Alexandre Merlen [b], Joanna Bagierek [b], François Flory [c], Alexandre Sangar [b], Ludovic Escoubas [a]

[a] Aix-Marseille University, Institut Matériaux Microélectronique Nanosciences de Provence-IM2NP, CNRS-UMR 6242, Domaine Universitaire de Saint-Jérôme, Service 231, 13 397 Marseille Cedex 20, France
[b] Université du Sud Toulon-Var, IM2NP CNRS-UMR 6242, Bâtiment R, BP 132, 83 957 La Garde Cedex, France
[c] Ecole Centrale Marseille, IM2NP CNRS-UMR 6242, Technopôle de Château-Gombert, 38 rue Frédéric Joliot Curie, 13 451 Marseille Cedex 20, France

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ABSTRACT

A study of plasmonic phenomena produced by silver nanoparticles embedded in a photoactive (poly-3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction is performed via spectrophotometric and Raman characterizations. An enhanced absorption of light is experimentally obtained in a 90 nm-thick P3HT:PCBM interpenetrated blend layer incorporating evaporated 5 nm-thick silver nanoparticles on glass/ITO substrate. An increase of Raman signal is observed and correlated to an increase of the electromagnetic field close to metallic nanoparticles. This is confirmed by Finite-Difference Time-Domain (FDTD) modeling considering an organized 2D-grating of ellipsoidal domes.

This paper shows also that the use of relatively thick organic blend films as probe molecules upon plasmonic structures does not obscure the Raman response.

1. Introduction

Solar energy conversion is receiving increasing interest as a serious solution to energy production. New thin-film technologies have a strong potential to reduce the cost of photovoltaics using Organic Solar Cells (OSCs). OSCs are also promising because of their compatibility with flexible substrates. But the efficiency of this technology is limited because of the short lifetime of electrical carriers and the short exciton diffusion length, restricting the thickness of the active layer. Bulk heterojunction can be used to solve the diffusion length problem, but the active layer thickness should be thin enough for limiting charge recombination. We employed here a (poly-3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butiryc acid methyl ester (PCBM) bulk heterojunction as organic active layer, which is the most commonly used organic material for manufacturing OSCs.

One solution to increase the efficiency in thin photoactive films consists in improving photonic absorption by harvesting and trapping incident light, in particular in the spectral range where materials absorb weakly. Several photonic concepts are currently being developed by many researchers such as optimization of the electromagnetic field distribution [1–3], photonic crystals which allow coupling of light into "Bloch mode" [4], or plasmonic structures which excite localized surface plasmons on metallic nanoparticles (MNPs) [5–11]. A surface plasmon is an interaction between an incident electromagnetic wave and the conduction electrons of these MNPs at a dielectric/metal interface. This can lead to an enhanced electromagnetic field near this interface which makes it possible to increase light absorption in the active layer. Moreover, the MNPS can scatter light which would increase the lifetime of light into the active layer. However, MNPs can also lead to a harmful electrical effect due to possible shunt currents or can introduce carrier recombination centers in the energy bandgap.

We investigate here the experimental behavior of organic photoactive material incorporating MNPs via spectrophotometry and Raman spectroscopy. The presence of MNPs can increase sensitivity of measurement via an electromagnetic enhancement [12] or a charge-transfer effect [13]. This plasmon-enhanced spectroscopy is called Surface Enhanced Raman Scattering (SERS). SERS spectroscopy is a powerful analytical technique for ultra-sensitive chemical analysis [14–16]. This can allow us to highlight the near-field enhancement of MNPs into adjacent layers and allow new optical investigation.

Optical properties of MNPs depend on their composition, size, periodicity, shape and surrounding medium [11,17]. In the

* Corresponding author.
E-mail addresses: philippe.torchio@univ-cezanne.fr (P. Torchio), alexandre.merlen@im2np.fr (A. Merlen).

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particular case of gold or silver, surface plasmon resonance frequencies are situated in the visible spectrum, a key parameter for organic photovoltaic applications. Silver was chosen in this study in so far as its resonance is closer to the absorption of organic molecules studied in this paper, i.e. P3HT:PCBM. MNPs can be prepared by evaporation [6], sputtering [18], pulsed laser deposition [19], nanospheres lithography [20], electrodeposition [7], self-assembly [9], etc… The size, distribution and shape of MNPs depend on the deposition method. For its simplicity and efficiency, thermal evaporation followed or not by an annealing process was chosen.

2. Results and discussion

2.1. Experimental

MNPs were realized via Electron Beam Evaporation. Once the vacuum chamber was evacuated to 1.10^{-6} mbar, the deposition of silver was performed at a rate of 0.2 Å/s while the total chamber pressure rising no higher than 5.10^{-6} mbar. MNPs were deposited on a glass/Indium Tin Oxide (ITO) substrates bought from Luminescence Technology Corp.® (LumTec). The ITO layers, which act as transparent conducting oxide anodes, had a thickness of about 180 nm. The thicknesses of the silver layer were close to 5 nm. They were chosen to be sufficiently thin to limit the amount of light absorbed before reaching the active layer. A Scanning Electron Microscope (SEM) image of typical obtained silver layer is shown in Fig. 1(a). The resulting nanoparticles have an average diameter of 18 nm, with a minimum of 9 nm, and a maximum of 27 nm. Some of these samples were annealed in an oven at 200 °C for 10 min in order to improve the silver particles aggregation on the top of ITO (Fig. 1(b)). Coalescent particles aggregate around an average diameter of 26 nm, with a minimum of 11 nm, and a maximum of 39 nm.

The P3HT material was purchased from Rieke Metals, Inc® and PCBM material from SES Research Company®A solution of 10 mg-P3HT and 10 mg-PCBM in 1 ml of chlorobenzene was spin-coated in a glove box on the top of glass/ITO/silver samples, forming the expected (1:1) organic blend active layer. The spin-coating process was carried out in two steps: a first step at 700 rpm for 10 s followed by a second step at 900 rpm for 40 s. The thickness of such coating was fixed about $\approx$ 90 nm (estimated by AFM and mechanical profilometry). Similar samples without any silver nanoparticles on the ITO were also fabricated, under identical experimental procedures, and compared with those including silver nanoparticles.

The previous samples are first optically characterized by spectrophotometry. Fig. 2 shows the absorption spectra of $A=1-T-R$, deduced from measurements of reflection R and transmission T, by a CARY 5000 spectrophotometer from Varian® equipped with an integrative sphere. A significant increase in absorption is observed in the visible spectral range higher than $\lambda=340$ nm for samples including MNPs by comparison to samples without MNPs. Above $\lambda=650$ nm, the absorption gain can be essentially due to the MNPs absorption because the optical gap of P3HT:PCBM is around 650 nm. In the 340–650 nm spectral domain, the absorption can be mainly attributed to a plasmonic effect occurring inside the P3HT:PCBM heterojunction. Previous investigations have shown that this increased absorption is not completely due to the absorption inside silver, but can occur inside the adjacent dielectric layer [11,21]. The absorption enhancement inside the embedded dielectric material can be controlled via the geometrical parameters of the plasmonic structure [11].

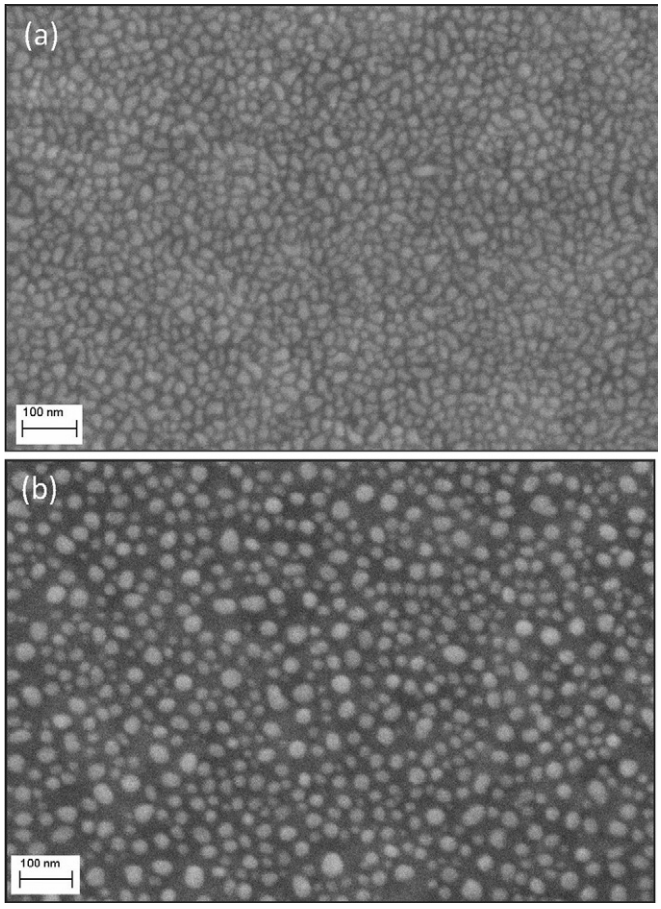

Fig. 1. SEM images of silver structures obtained via Electron Beam Deposition of a 5 nm-thick layer upon an ITO-coated substrate (a) before annealing and (b) after annealing at 200 °C during 10 min.

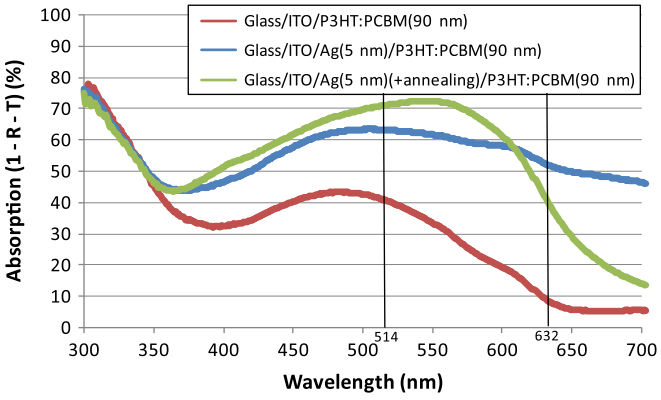

Fig. 2. Measured absorption spectra of A (deduced from spectrophotometric measurements of R and T, and $A=1-R-T$) for the following devices: glass/ITO/P3HT:PCBM (red), glass/ITO/Ag (without annealing)/P3HT:PCBM (blue) and glass/ITO/Ag (with annealing)/P3HT:PCBM (green) devices.

Moreover, it is shown that absorption of annealed structure is higher than absorption of non-annealed structure in the wavelength range of 360–607 nm, and the contrary for wavelengths higher than 607 nm. As size and shape dispersions are different in both structures (Fig. 1), the annealing can modify the size range which becomes adequate to an increased absorption in the P3HT:PCBM absorption range.

To investigate if the absorption increase can be attributed to the enhancement of the near electromagnetic field, we performed