



# Annealed silver-islands for enhanced optical absorption in organic solar cell



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## ABSTRACT

Silver nano-islands are explored for enhancing optical absorption and photo-conversion efficiency in organic solar cells (OSCs) based on the surface plasmon resonance effect under diverse annealing conditions. Ag nano-islands have been deposited by RF magnetron sputtering at 15 W for 10 s and subsequently annealed between 100 °C–250 °C in air and Argon ambient. The optical properties of the reconstructed Ag islands demonstrate an increase and a blue shift in the absorption bands with increasing annealing temperature. This is the localized surface plasmon effect due to the Ag islands of diverse sizes, shapes and coverages. The increase in optical absorption with temperature is attributed to changes in island shape and density as collaborated by atomic force microscopy and TEM.

As a proof of concept, an organic solar cell was characterized for current–voltage (I–V) measurements under dark and under solar simulated white light. Incorporation of annealed Ag islands has yielded an efficiency increment of between 4–24%.

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## 1. Introduction

Increasing global demand for inexhaustible, clean and affordable energy continues to drive intensive research for low cost and highly efficient organic photovoltaic devices (OPVs). These devices are made of conjugated polymers that have the base property required for photoconduction [1–3]. However, their commercialization is constrained by their low photo-conversion efficiency and limited device stability. These two parameters are being intensively investigated to enable OPVs become promising commercially viable alternatives. The organic polymers exhibit a thickness dependent absorption coefficient ( $>10^5 \text{ cm}^{-1}$ ) within the visible spectrum [4]. Their short exciton diffusion lengths (10–20 nm) and low charge-carrier mobilities ( $\sim 10^{-5} \text{ cm}^2/\text{Vs}$ ) limit the optimal active layer thickness to few hundreds of nm and this in turn trades off optical absorption. The reduced light absorption efficiency, charge-carrier generation and collection densities impact negatively on the power conversion efficiency (PCE) [5,6]. One strategy to circumvent the low absorption efficiency is the application of the surface plasmon resonance effect in OPV devices.

In this respect surface plasmons continue to generate intense research interest in nano optic devices [7]. The surface plasmon polariton

(SPP) is a transverse electromagnetic excitation that is confined to propagate along the metal–dielectric interface to produce an evanescent field that enhances light–matter interaction [8]. Several material systems ranging from bulk noble metal films to nanoparticles/nano-islands have exhibited this excitation. Thus, metallic nanoparticles can be used as sub-wavelength scattering elements to couple and trap propagating plane waves into an absorbing inorganic-polymer thin film. Furthermore as sub-wavelength antennas, they have coupled the plasmonic near-field to a semiconductor for increased effective absorption cross-section [7]. The nature and magnitude of the absorption coefficient is determined essentially by the morphology, size, shape and the coverage of the noble metal nanoparticles [9]. In this work, Ag nano-islands have been sputtered on ITO coated glass substrates in Argon ambient and at room temperature. The islands were later annealed in air and in Argon ambient to tailor the temperature dependence of their optical properties. The size and distribution of the Ag nanoparticles, which affect plasmon resonance absorption and width were studied. The effect of optical absorption enhancement through the SPR effect under both annealing conditions on the photo-conversion efficiency of an organic solar cell device was studied as a proof of concept.

## 2. Experimental details

In this study ITO (surface resistivity: 30–60  $\Omega/\text{sq.}$ ), PEDOT:PSS (1.3 wt% dispersion in  $\text{H}_2\text{O}$ ), P3HT (purity: 99.995%) and PCBM (purity:

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99.5%) were purchased from Sigma Aldrich while Ag target (purity: 99.99%) was obtained from Semiconductor Wafer, Inc. (SWI).

Ag nanoparticles have been deposited using RF magnetron sputtering onto ITO coated glass substrates at room temperature. The chamber was evacuated to a base pressure of about  $2 \times 10^{-5}$  mbar while sputtering was performed under Argon with a working gas pressure of  $2.3 \times 10^{-3}$  mbar. A 76 mm diameter Ag disk (99.99% purity) was used as the cathode for sputtering at an RF power of 15 W for 10 s. The 'as deposited' Ag nano-islands of 10 nm thicknesses were annealed at 100 °C–250 °C in air and in Argon ambient for 15 min. Optical absorption measurements of the 'as deposited' and annealed samples were made using a Cary 500 UV–Visible Spectrometer. The topography and nano-particle morphology of the films were studied using a Veeco Di-3100 atomic force microscopy (AFM) in tapping mode. The Ag islands annealed in Argon ambient at 100 °C and 250 °C were subsequently used in the assembly of the OPV device. The procedures for device assembly entailed a spin coating of Poly(3,4-ylenedioxythiophene)/Poly(styrenesulfonate)(PEDOT:PSS) at 2000 rpm for 60 s. The resulting film was annealed over a hot plate at 100 °C for 15 min to remove any residual water.

The active layer constituting of a P3HT:PCBM blend (Sigma-Aldrich) was dispersed in dichlorobenzene at a ratio of 1:1 spun at 2000 rpm to yield a homogeneous film of 215 nm. The cathode was metalized through thermal evaporation of aluminum. Annealing of the reference and Ag nanoparticles based devices was carried out at 80 °C for 15 min under Argon ambient to remove organic polymer solvent and any residual water. The thicknesses of the PEDOT:PSS layer and P3HT:PCBM blend was measured by a Surface profilometer. The current density–voltage (J–V) characteristics were obtained using the solar simulator (150 W Xe lamp) with 1.5 air mass filters and a source/measure unit (HP 4141B DC) unit under 70 mW/cm<sup>2</sup> illumination. All the measurements were carried out at room temperature under standard conditions. The device geometries used for this study are presented in Fig.1 [10].

### 3. Results and discussion

#### 3.1. Morphology studies by AFM

Fig. 2 (a)–(e) depict the surface topography images of plasmonic Ag nanoparticles for the pristine and for samples after annealing in an argon ambient at 100 °C, 150 °C, 200 °C and 250 °C, respectively. The corresponding size distribution is presented in Fig. 3 (a–e).

The AFM images show that an increasing annealing temperature leads to the formation of large Ag nanoparticles coupled with reduced coverage (Figs. 2 & 3). This is seen by the increase in the inter-island spacing with annealing as well as a gradual increase in surface roughness as corroborated by the values in Table 1. The Ag nanoparticles reconstruct to assume a "spherical" like shape with increasing temperature [11–18]. During Ag film growth the ad atoms initially form islands with irregular shapes. This conforms to the Volmer–Weber film growth mode. The shapes and sizes of these nano-islands are reconstructed by annealing due to increased diffusion of ad atoms

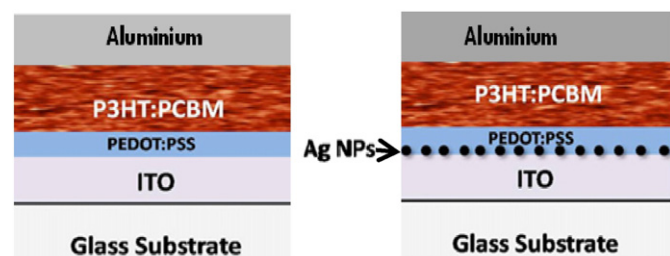


Fig. 1. Device architecture: (a) normal, used as reference, (b) device with silver nanoparticles [10].

at high temperature. Further annealing modifies the surface energy approximated to be in the range of 0.97–2.17 J/m<sup>2</sup>, inducing surface migration and reconstruction of the Ag nanoparticles to more hemispherical like shapes relative to their 'as deposited' counterparts [19]. This corroborates the decrease in surface coverage with increasing annealing temperature (Table 1). The AFM images of Fig 3 show that the surface coverage decreases from 79% as-deposited to 38% after annealing at 250 °C. Since these temperatures, are far below the melting temperature of Ag ( $T_M = 1235$  K), the reduction in surface coverage can be attributed to the migration of Ag atoms at the surface which leads to an increase in Ag nano-island diameter after coalescence [20]. (See Table 2.)

The annealed films contain a broad distribution of nanoparticles, all of which are less than 100 nm with the mean particle diameter varying from 39 nm as-deposited to 71 nm at 250 °C. At 250 °C Ag atoms begin to aggregate in the film to form bigger Ag nanoparticles.

These morphological changes are seen indirectly in the absorption spectra for the nanoparticles formed on ITO coated glass substrates. To determine the energy needed to reconstruct the surface of the Ag nano-islands, the activation energy has been extracted to be  $50 \pm 13$  meV using an Arrhenius relation for the surface coverage as shown in Fig. 4. This value corroborates that determined from the Ag island size and it is consistent with the values obtained for Ag diffusion in a monolayer of Ag [12].

Annealing in air ambience did not show significant morphological changes when viewed in the AFM.

#### 3.2. The optical absorption spectra of annealed Ag islands

Fig. 5 presents the optical absorption spectra of Ag island films on ITO coated glass annealed at temperature ranging from 100 °C to 250 °C in Argon ambient compared to that of annealed in air. (See Fig. 6.)

The Ag nano-islands are longer and asymmetrical in shape in the as deposited state. Thus the broadening in the LSP resonance band is attributed to LSP multi-pole effects as elaborated by Mie scattering theory [21]. It can be seen that as for as-sputtered Ag island, the LSP resonance band is at about 592 nm. This is shifted sharply to about 510 nm upon thermal treatment at 100 °C in both air and Argon ambience. Further increase in temperature resulted in smaller shifts in absorption bands. The shift in absorption band is also accompanied with narrowing of the bands. Annealing in argon ambient initially leads to a blue shift in plasmon band and sharper peaks with small full width at half maximum changing from  $\lambda_{FWHM} \sim 350$  nm to  $\lambda_{FWHM} \sim 180$  nm which further reduces to  $\lambda_{FWHM} \sim 170$  nm upon annealing at 250 °C coupled with a slight red shift in plasmon band. The surface plasmon absorption of Ag nanoparticles is exhibited in the optical absorption spectra of all the samples (Fig. 5).

Thermal treatment resulting in particulate modification may also be used to increase the scattering cross section when an enhanced local field interferes with the incident and reflected light [8,22]. The overall effect is a shift in the position of the enhancement peaks. The blue shift in plasmon absorption corresponds to changes in Ag nano-island size, shape and inter-island spacing as evidenced by AFM. Although it is expected that an increase in particle size leads to a red shift in plasmon absorption maximum, the decreased interaction of neighboring nanoparticles dominate due to increased particle separation since mass is conserved on the surface during annealing [23,24]. Hence as nanoparticles become more spherical, larger and more spaced, the width of the absorption band is determined by the inter-particle dipole–dipole interactions [10]. P Cheng also reported that although heating induced coalescence of small particles, surface strain during heating induced a decrease in the size of the Ag nano-islands leading to a blue shift of SP resonance [25].

At 250 °C slight behavior is observed, whereby the Ag nanoparticles absorption eventually is red shifted due to an increase in Ag nano-island size after coalescence ( $\phi = 71$  nm) as well as widely spaced islands with weak dipole–dipole interaction [10]. The decrease in the dipole–dipole

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