Enhancing light absorption and lifetime stability of organic solar cells using pentacene encapsulation

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ABSTRACT. In the present work we compare the performance of a pristine P3HT:PCBM based bulk heterojunction solar cell with a device incorporated with pentacene encapsulated Ag nanoparticles. Encapsulation has been achieved through thermal evaporation of a 22 nm pentacene thin film. Introduction of pristine Ag nanoparticles revealed better overall performance with a 22% increase in photo-conversion efficiency. This is attributed to the localized surface Plasmon effect by Ag nano-islands. A study of device lifetime showed that despite the efficiency enhancement, the device drastically degraded upon exposure to air. Encapsulating Ag nanoparticles with pentacene increased light absorption and device stability but traded off photo-conversion efficiency. This long lifetime could be as a result of silver passivation by pentacene which minimizes oxidation of Silver nanoparticles and etching of the ITO electrode by the acidic PEDOT:PSS.

1. Introduction

The increasing demand for energy in this era of escalating energy prices as well as global warming resulting from the extensive use of fossil fuels has prompted intensive research on green energy as potential remedies to providing clean, cheap and inexhaustible energy. Photovoltaic offers a promising alternative due to the intrinsic characteristics of the energy source since solar energy is abundant, free and green [1-2].

Among the numerous photovoltaic options, organic solar cells made from conjugated polymers and hybrid materials continue to attract a lot of attention. This is driven by the low cost of high volume production of polymers, their ultrafast optoelectronic response and generation of charge carriers at the donor – acceptor interface. In addition, these materials can be fabricated on flexible substrates and their band gaps can be tuned depending on the length and functional group of polymers used for synthesis [3].

Despite these attractive properties their low photo-conversion efficiency (10-12%) and instability to air remain their greatest drawbacks to making them competitive with grid parity. Furthermore the tradeoff between their short exciton diffusion lengths (10-20 nm) and the high thickness dependent absorption (> 10^5 cm^{-1} within the visible spectrum) constrain the optimal thickness of the active layer to a few nanometers [4]. Traditionally, polymer based solar cells have a short life expectancy compared to their inorganic counterparts [5]. Degradation of organic solar cells is attributed to the oxidative damage of the photoactive layer associated with device illumination in the presence of oxygen. Furthermore, the chemical interactions at the ITO electrode/organic interface have also caused device degradation. This mechanism of degradation is attributed to the hygroscopic and acidic nature of PEDOT:PSS which etches out the ITO layer. Concerted research efforts continue to be employed to curb device degradation [6-8].

Incorporating Ag nanoparticles in the device as sub-wavelength scattering elements can 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 the semiconductor for increased effective absorption cross-section [9]. Silver shows stronger plasmonic properties in the visible optical spectrum with optical cross-section [10]. In this work we explore the effect of encapsulating Ag nanoparticles with a high mobility conjugated polymer on the optical, plasmonic characteristics and the electrical properties of the device. Ag nano-islands have been sputtered on ITO coated glass substrates in Argon ambient and at room temperature. The islands were later annealed in Argon to modify nanoparticles geometry and distribution. Pentacene was then thermally evaporated on the Ag surface. Our results show an intriguing but unexplored finding that apart from enhanced absorption, pentacene encapsulated devices showed a slowed degradation of the solar cell device in which they are incorporated into.

2. Experimental details

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 2×10^{-5} mbar while sputtering was performed under Argon with a working gas pressure of 2.3×10^{-3} mbar. A 76 mm diameter Ag disk (99.99% purity) was used as the cathode for sputtering at an RF power of 15W for 10 seconds. The 'as deposited' Ag nano-islands of 10 nm thickness were annealed at 250 °C in Argon ambient for 15 mins. The sputtered Ag islands were loaded to a thermal evaporator evacuated to a base pressure of 1.5×10^{-5} mbar for pentacene deposition. Pentacene was heated to 170 - 200 °C to yield a deposition rate of 1.6-2.1 $\text{Å}s^{-1}$. The nanoparticles on ITO acting as the substrate were kept at room temperature during the evaporation of pentacene. The deposition rate was monitored using the quartz crystal monitor that showed the film thickness of 22 nm.

Optical absorption measurements of the encapsulated annealed Ag islands were made using a Cary 500 UV–Visible Spectrometer. The topography and nano-particle morphology of the films were studied using atomic force microscopy (AFM) in tapping mode. These nanoparticles were then incorporated in solar cell device. The procedures for device assembly have been explained in detail elsewhere [11]. Annealing of the reference and surface Plasmon based devices was carried out at 80°C for 15 mins 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 Surface profilometer. The current density–voltage (J–V) characteristics were obtained using HP 4141B source measure unit under 70 mW/cm^2 illumination (AM 1.5G) over time period of 166 hours of exposure to air ambient.

3. Results and discussion

3.1 Morphology studies by AFM

Figure 1 (a)-(b) and (c) - (d) depict the surface topography AFM image of annealed Ag nanoparticles before and after encapsulation using thermally evaporated pentacene, respectively.

From the morphology studies using Veeco Di 300 AFM, pentacene thin film on Ag nanoparticles shows rough surface with voids. The rms of the nanoparticles annealed at 250^{o}C increased by 6 nm This molecular voids may trap or scatter charge carriers. Craig et al. reported that the environment with relaxed molecules surrounding a void is energetically more stable than that in a perfect crystal [12].

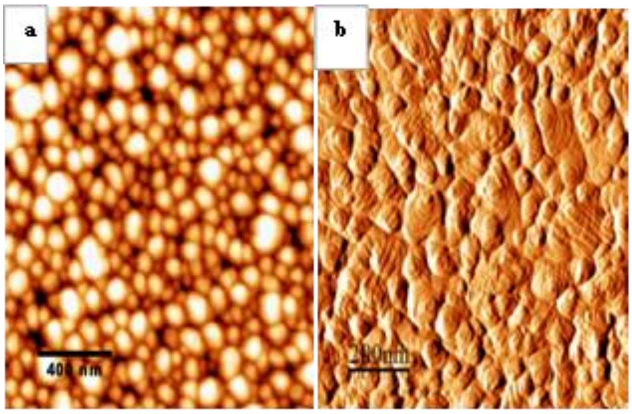

Figure 1(a). AFM image of RF sputtered Ag nanoparticles annealed at 250°C in Argon ambience (b) 22.2 nm evaporated pentacene on the annealed nanoparticles.

However, the deformed lattice near a void may change the molecular electronic states in the defect region. Such distortion in the crystalline lattice may lead to formation of traps for holes or electrons [13]. These might be the cause of reduced current density of the device despite the enhanced optical absorption resulting from coupling of surface plasmons with pentacene shown in Figure 2.

3.2 Absorption spectra

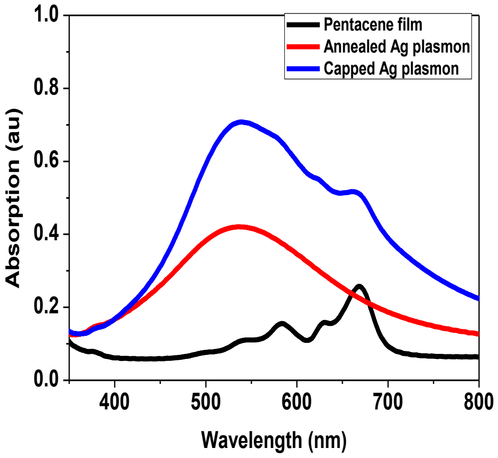

Figure 2. Optical absorption spectra of annealed Ag nanoparticles, pentacene, and pentacene encapsulated Ag nanoparticles (T_{ann} = 250 °C).

Pentacene thin films experience ultra-fast singlet and triplet exciton excitations due to polymorphism. Furthermore singlet fission into two triplets can occur within the visible region.

From the UV-Vis measurements shown in figure 2, pentacene thin film has four main different absorption peaks with energies of 1.85 eV (λ = 671 nm) , 1.97 eV (λ = 630 nm), 2.12 eV (λ = 585 nm), and 2.27 eV (λ= 545 nm). Since the excited states in pentacene thin film are singlet states, the excitation at λ = 671 nm is assigned to the S_1 state while that at λ = 630 nm corresponds to the second level of the Davydov doublet after Davydov splitting [14]. The absorption bands at λ = 545 nm (2.27 eV) correspond to an electron-hole pair, situated on two neighboring molecules of adjacent unit cells. The absorption band at λ = 585 nm is a charge transfer state at the sites of the two molecules within a unit cell [15]. The coupling of pentacene with Ag nanoparticles produced the enhanced absorption.

This enhancement is essential in the performance of the organic solar cell device. Spin coating of P3HT:PCBM blend on pentacene creates a different dielectric environment with enhanced optical absorption (fig. 3).

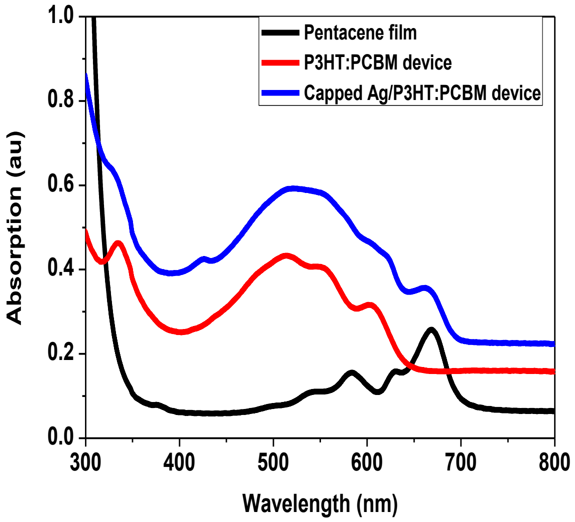

Figure 3. Absorption spectra of PEDOT:PSS, P3HT:PCBM on top of annealed Ag nanoparticles encapsulated with pentacene thin film.

The enhanced absorption at a wavelength of 670 nm extends the absorption spectrum of the active layer to a higher wavelength to provide multiple absorption peaks. However, the conductivity of the encapsulated layer remains a fundamental parameter in the determination in charge transport within the device. From figure 3, pentacene introduces a contact barrier of ~0.8 eV. This could cause hole trapping at the PEDOT:PSS-pentacene interface leading to reduced Jsc as observed in the J-V characteristic curve in figure 4.

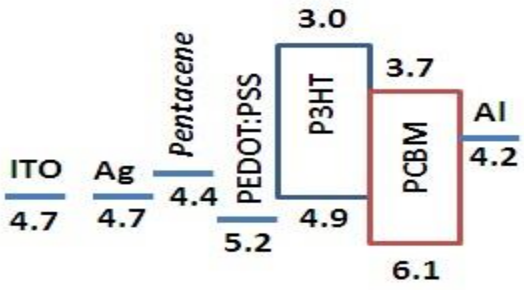

Figure 4. Band energy diagram for ITO/Ag nanoparticles /Pentacene/PEDOT:PSS/P3HT:PCBM/Al device.

3.3 J-V Characteristics curve

Despite the clear absorption enhancement upon encapsulation of Ag nanoparticles using pentacene, the Jsc, and Voc reduced by 55% and 5%, respectively. The reduction in Voc and Jsc lowers the PCE but improves device stability when exposed to air ambience as shown figure 6. The degradation rate in Jsc reduces upon encapsulation from 28.27 to 9.22 μA/cm^{2}min while Voc degrades slowly from 2.4 to 1.8 to mV/ min.

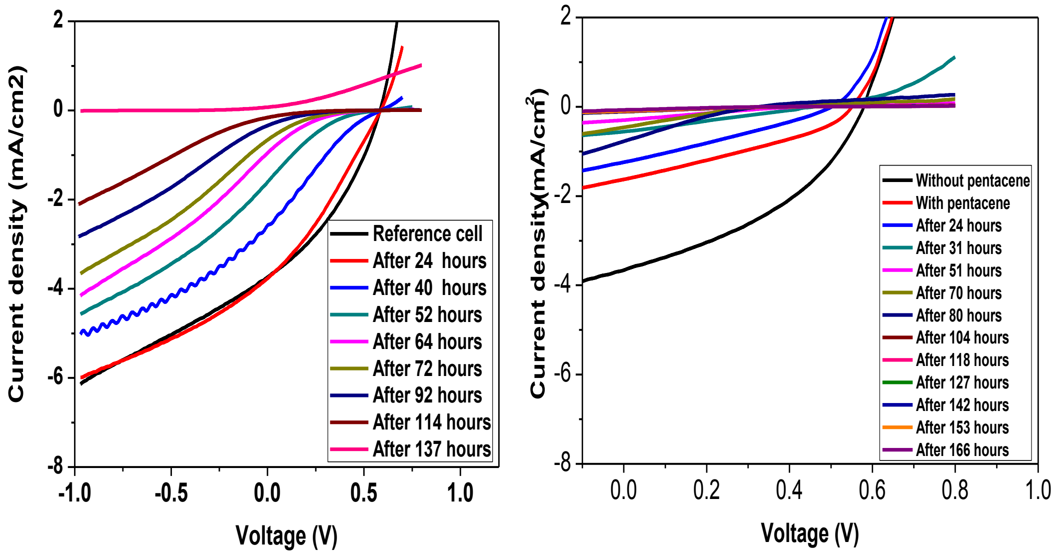

Figure 5. J-V characteristics for ITO/PEDOT:PSS/P3HT:PCBM/Al solar device degrading with time in air under AM 1.5 G filtered spectral illumination at incident intensity, 70 mW/cm^2.

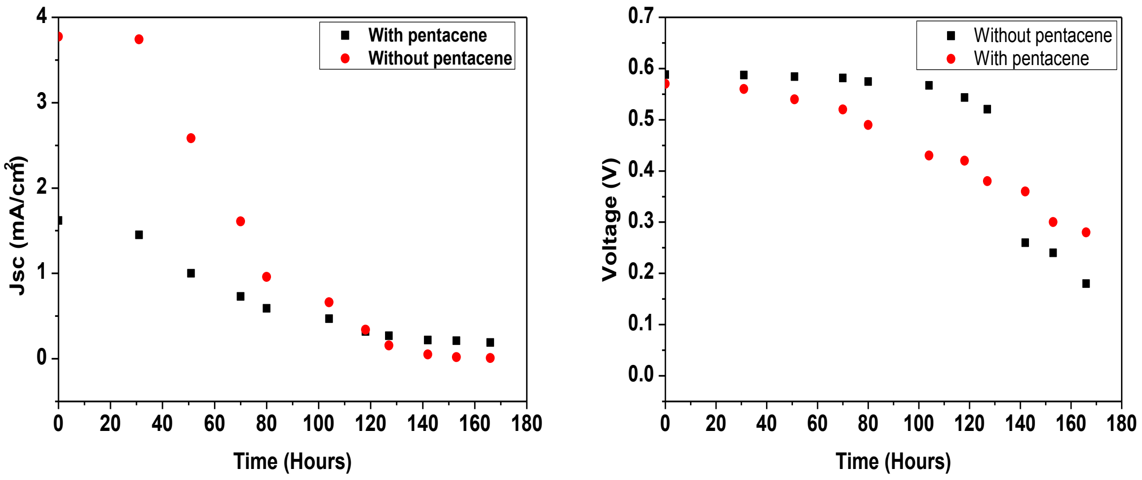

Figure 6. Performance of encapsulated device as a function of exposure time to ambient air.

Analysis of Jsc shows that devices without pentacene encapsulation acquired same value as the one with encapsulation after 118 hours despite its high original Jsc upon fabrication, thus encapsulation reduces the degradation rate of Jsc and Voc by 67% and 25%, respectively (fig. 6). Beyond this time, the encapsulated plasmonic device showed a greater Jsc. A similar trend was seen with the Voc where after 140 hours, encapsulated plasmonic device recorded a higher Voc compared to the device without encapsulation. The long electrical activity upon encapsulation could be as a result of pentacene forming a thin layer separating PEDOT:PSS from ITO Pentacene preventing etching of ITO layer by the PEDOT:PSS. The encapsulation of nanoparticles could also be used for passivation of the silver surface hence reducing the rate of oxidation of the nanoparticles that could lead to reduced plasmonic absorption. However, such passivation only requires a very thin layer in order not reduce the field around the nanoparticles as well as molecular self-assembly to enhance charge transport due to better π orbital alignment [10].

The reduced Jsc compared to plasmonic devices without encapsulation can be attributed to formation of a Schottky barrier between pentacene and Ag nanoparticles resulting in a large contact resistance between the ITO electrode and the active layer due to mismatch of their Fermi (HOMO) energy level.

4. Conclusion

ITO/Ag/PEDOT:PSS/P3HT:PCBM/Al bulk heterojunction solar cells was prepared with encapsulated Ag nanoparticles compared to that without encapsulation. The device performance was monitored in air ambient. The UV-Vis measurement has shown an enhanced optical absorbance of the device upon encapsulation of the Ag nanoparticles. The device performance was evident over a long period of time (166 hours) while the un-encapsulated showed no performance beyond 114 hours. However, the Jsc reduced upon Ag encapsulation. This could have been as a result of the HOMO mismatch of Pentacene and the PEDOT:PSS which is likely to cause charge recombination due to hole trapping at this interface. The low values of photocurrent in an encapsulated polymer cells despite the presence multiple absorption peaks and prolonged lifetime call for the device architecture modification to reduce the contact barrier to charge transport.

Acknowledgement

The authors would like to thank the University of the Witwatersrand, Material Physics Research Institute, School of Physics; the MMU facilities; Wits and Material Energy Research Group (MERG) for funding and NRF for funding of the research facilities.

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