LOW COST NANO IMPRINTING FOR ORGANIC SOLAR CELLS APPLICATIONS

EMAH, J. B.

Department of Physics,
Akwa Ibom State University, Ikot Akpaden,
Mkpat Enin L.G.A., P.M.B. 1167, Uyo,
Akwa Ibom State, Nigeria.
joemah73@gmail.com.

ABSTRACT: Regular ridge-like patterns were imprinted on poly (3, 4-ethylenedioxythiophene) poly (styrene sulfonate), (PEDOT:PSS) buffer layer for organic solar cell applications using soft lithography. Poly (dimethylsiloxane), (PDMS) was used to make the stamps for the imprinting. Two approaches of soft lithography: the "lift-up" and "put-down" processes were used. A DVD plate was used as the master stamp to make PDMS stamps which contained regular radial ridge-like features with depth ~27 nm and period ~700 nm as revealed by the Atomic Force Microscopy (AFM) measurements. These features were replicated in the PEDOT:PSS film with imprinted period of 700 nm and a reduced depth of ~10 nm using the lift-up process. It is suggested that the direct patterning of the surface of PEDOT:PSS layer using this process increased its surface area by ~0.04%. The alternative stamping procedure, the put-down process, gave an imprint depth of ~42 nm with a period of ~727 nm and an increase in surface area up to ~0.7%. This is capable of pushing device performance, especially the short circuit current, a bit further besides other considerations.

INTRODUCTION

Harnessing electrical energy from solar radiation using Photovoltaic (PV) technology promises to be an essential component of future global energy production. For PV devices to become a sustainable energy source that can supply our daily energy needs, it must be made economically competitive with fossil fuels and other emerging renewable energy technologies. Sadly, fabrication of inorganic semiconductor based solar cells demand expensive technologies at present, which result in very expensive Photovoltaic Devices (PVDs) and makes it difficult to compete with other conventional energy sources. A possible reason is associated with current industrial process of production from quartz to Si wafers which requires temperatures up to $1900^{o}C$, (Markvart, 2000).

Semiconducting polymers and small molecule organic materials offer an alternative means of fabricating low cost Organic Solar Cells (OSC). But these photoactive organic materials are characterised by large optical band gaps (1.5eV–3.0eV), low photo absorption/light penetration depth (in the range of 10–100nm) (Roman, *et al* 2000) even at maximum absorption, low charge carrier mobility (μ), (Carter, *et al.,* 1997a & b), coupled with short exciton diffusion length, typically in the range of 5 – 20nm, (Theander, *et al;* 2000). These imply low radiation to electrical power conversion efficiencies (η) in such devices.

To circumvent the above limitations on the efficiency of OSC while keeping the geometrical length (i.e. the cell thickness) minimal (<200nm), it becomes necessary to resort to "light trapping" schemes by diffraction into guided modes in the thin polymer films. Such techniques would allow for increase in surface area, interfacial absorption, as well as effectively increasing the optical path length through multiple internal reflections at the top and bottom of the cell. This approach has already been used to enhance light trapping and absorption in silicon solar

cells, (Morf and Kiess, 1989), particularly in the energy range where optical absorption in silicon is low, thus increasing the power conversion efficiency, (Delley and Kiess, 1994).

Enhancing the absorption by an appropriate light-trapping scheme such as regular patterns would result in an increased short circuit current density, J_{SC} of a solar cell. This implies that the cells could be made with a thinner photoactive layer and would still provide the same J_{SC}. In such a configuration, the advantage is a lower bulk recombination that will lead to a higher open circuit voltage, V_{OC}. Any increase in either J_{SC} or V_{OC} will ultimately enhance the power conversion efficiency of the solar cell.

The term "light-trapping" is used to refer to the redistribution of the incoming light into new directions within the solar cell. Ideally, total internal reflection will then prevent this redirected light from escaping from the solar cell, (Redfield, 1974). One of such schemes achieved for inorganic solar cell is the Lambertian light distribution coupled with a perfect back reflector (Fahr, *et al,* 2008). The Lambertian light distribution is achieved by incorporating an appropriately structured surface, whose nature can be either statistical (rough surfaces) or deterministic (periodic arrangements).

In this work, rather than using a special material as the Lambertian scatterer, the surface of the PEDOT:PSS interlayer between the active material and the ITO anode was modified to achieve the same scattering effect through geometrical schemes. The idea is that light, incident normally to the glass substrate, will enter the photoactive layer obliquely at different angles at the PEDOT:PSS/active layer interface (Fig. 1). The photoactive material chosen for the study is a bulk hetero-junction blend of Poly (3-hexylthiophene-2,5-diyl) (P3HT) with [6,6]-Phenyl-C_{61}-butyric acid ester (PCBM), usually presented as P3HT:PCBM.
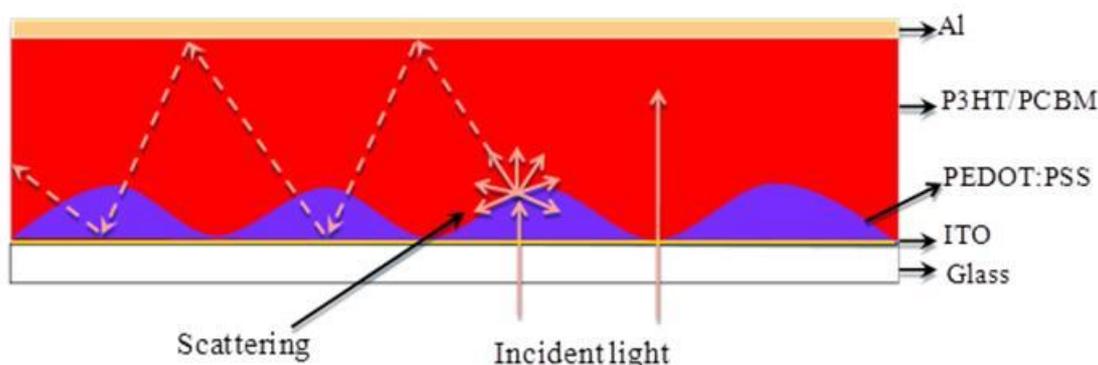

Figure 1: Light-trapping using patterned PEDOT:PSS as geometrical light scheme

Thus, light of wavelength less than the dimensions of the features will be scattered by Raleigh scattering in different directions and those features comparable to the wavelength of the incoming light will be scattered by Mie scattering. Some of the redistributed light gets reflected into the device at the Al back electrode by total internal reflection and thus travels longer within the photoactive layer. Although the size of the features may be small, there is bound to be refraction effect at the interface between the PEDOT:PSS and the photoactive layer where the incident light meets the interface at an angle other than normal. This should naturally occur due to the different refractive indices of P3HT:PCBM and PEDOT:PSS estimated at ~1.55 and 1.85 respectively, (Ng, *et al,* 2008, Hope and Meissner, 2002).

MATERIALS AND METHODS
The PDMS stamp was prepared and made ready for use as outlined elsewhere by Emah, *et al* (2008). The features of the stamp were replicated in the PEDOT:PSS film by placing the plasma treated PDMS stamp over the polymer without any pressure other than the weight of the stamp, and annealed at $150^{o}C$. This describes the 'lift-up' process of stamping the PEDOT:PSS.

To improve on the above-mentioned gains, an alternative stamping procedure have been chosen in order to increase the imprint peak height beyond the 10 nm already achieved through the lift-up process. The alternative procedure, the "put-down" process, is described schematically in Fig. 2. The main difference in this procedure is that the PEDOT:PSS was spin-cast directly on the PDMS stamp instead of the substrate. To increase the imprint depth, the spinner was set to 2500 rpm for 40 seconds as opposed to 3000 rpm (60 seconds) used in the previous process. The set up was annealed at 100°C for 10 min and allowed to cool before the stamp was removed, maintaining a lifting angle of ~30° between the stamp and the substrate to avoid "snapping" of the stamp.
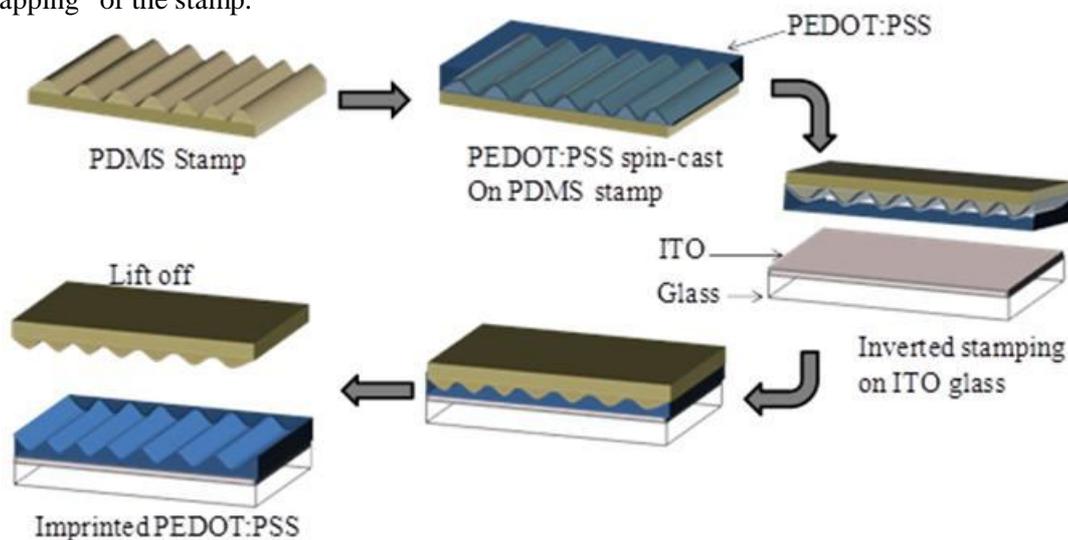

Figure 2: Schematics showing the put-down process of stamping PEDOT:PSS.

RESULTS AND DISCUSSION

AFM images and the corresponding surface profiles of the PDMS stamp and an imprinted PEDOT:PSS thin film on ITO using the 'lift-up' process are shown in Fig. 3. The period of the imprinted features remained the same at 700 nm, subsequent to annealing, with a reduced depth of ~10 nm as shown in Fig. 3 (c and d). This demonstrates that the simple procedure described may be used to pattern the polymer film with nanometre scale features. Another look at the depth profile of the stamped PEDOT:PSS in Fig. 3 (c) shows smaller features on the crest of each regular pattern which will bring about significant scattering as their periodicity (which is variable, ranging from 230 to 400 nm) will be much less than the wavelength of the incoming light resulting in Raleigh scattering.

AFM image (3D) of the stamped PEDOT:PSS using the put-down process and its corresponding profile is shown in Fig. 4 (a) and (b) respectively. The depth profile indicates that the imprint peak height was increased to ~42 nm with a period of ~727 nm. This represents a significant improvement in the quality of these structures using this low-cost approach of nanoscale patterning over what was previously reported, (Emah, *et al,* 2008). It should be noted that there are less sub-features on the patterns as compared to that observed in the stamped PEDOT:PSS using the 'lift-up' process.

The direct patterning of PEDOT:PSS layer using the 'lift-up' process increased its surface area by ~0.04% (assuming an imprint peak height of 10 nm every 700 nm). The second approach utilising the 'put-down' process yielded a further boost in the imprinting depth up to 42 nm and a period of 727 nm. This marked a significant improvement of 320% and 3.9% in depth and period respectively over the lift-up process.

While the 'lift-up' process increased the surface area of the patterned PEDOT:PSS surface by ~0.04%, the 'put-down' process increased it further to ~0.7%, which is a significant

improvement in the quality of the structures and is capable of pushing device performance a bit further besides other considerations.
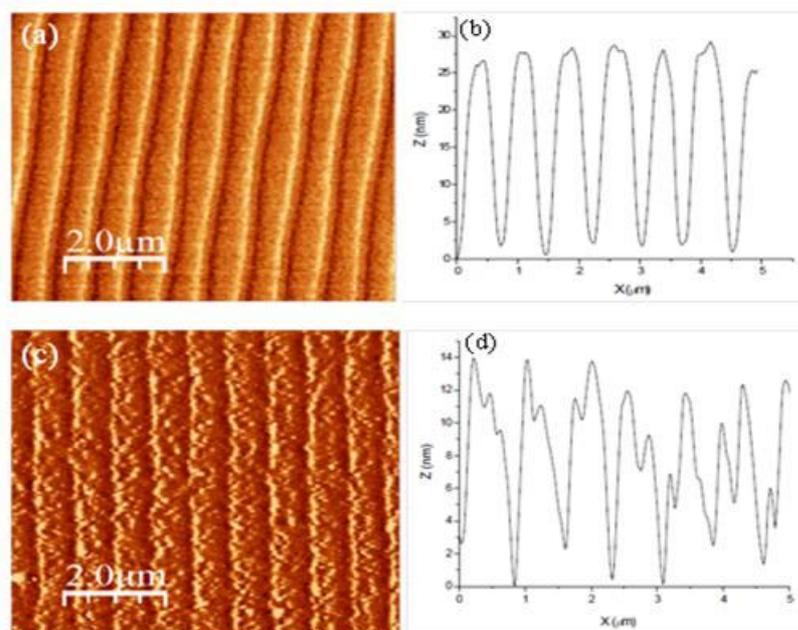

Figure 3: (a) AFM image of PDMS stamp and (b) its corresponding profile (depth ~27nm, period ~700nm); (c) AFM image of stamped PEDOT:PSS film annealed at 150°C and (d) its corresponding profile (depth ~10nm, period ~700nm).
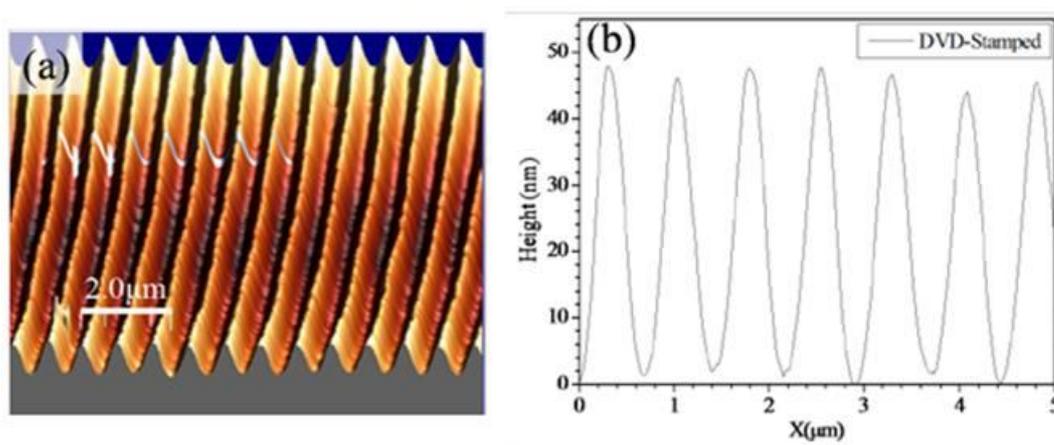

Figure 2: AFM image of (a) DVD-patterned PEDOT:PSS and (b) corresponding profile (depth ~42 nm, period ~727 nm).

The increase in the surface area from analysis should directly lead to increase in the number of charge carriers being extracted from the photoactive layer. With the photoactive layer having different refractive index from the PEDOT:PSS, it is apparent that most of the incident photons will pass into the device through the periodic patterns at certain angles different from the normal (Fig. 1). This should culminate into the elongation of the optical path length within the solar device and ultimately lead to enhancement of photo absorption by the active layer of the device. This in turn should directly enhance the short circuit current of the solar cell and the power conversion efficiency.

CONCLUSION

A single step soft lithographic technique have been used to pattern the surface of PEDOT:PSS. The 'put-down' procedure have demonstrated a better feature quality in the regular structures formed and less sub-features as compared to the earlier reported 'lift-up' process. Specifically, significant improvements in feature sizes from ~10 nm depth and ~ 700 nm periods to ~42 nm and 727 nm respectively have been achieved. This is a 320% and 3.9% increment in depth and period respectively. This can provide an important step towards further optimization of organic PV cell performance by patterning the polymer layer to increase light absorption.

ACKNOWLEDGEMENT

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