Metallic nanomesh electrodes with controllable optical properties for organic solar cells

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We have fabricated a metallic nanomesh using nanosphere lithography and metal evaporation. The metallic nanomesh has a precisely controlled nanostructure showing excellent uniformity with hexagonally arrayed periodic circular holes. A P3HT:PCBM organic solar cell, with the gold nanomesh electrode, demonstrates a high fill factor of 61% and a considerable power conversion efficiency of 3.12%. Electromagnetic simulation indicates that the optical properties of the metallic nanomesh can be optimized for organic photovoltaic devices by tuning the film thickness, hole diameter, and periodicity. These results show the promising potential of using a metallic nanomesh as the transparent electrode in organic solar cells. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3701582]

Organic solar cells (OSCs) are a promising alternative to conventional photovoltaic devices due to their flexibility, light weight, low cost, and convenient fabrication.1 Indium tin oxide (ITO) is the most widely used material for transparent electrodes in OSCs because of its electrical conductivity and optical transparency. However, due to the scarcity of indium, it is a relatively expensive material, which directly raises the manufacturing costs of OSCs.2 The brittleness of ITO also further obstructs its application as a transparent electrode in flexible optoelectronic devices. In the past few years, researchers have been seeking alternatives to ITO, such as: carbon nanotubes,3 graphene,4 and metal thin films.5 Very recently, transparent electrodes based on metallic nanostructures have attracted a great deal of attention due to their flexibility, high transparency, and high conductivity.6,7 In contrast with carbon nanotubes and graphene, the metallic nanostructures can also have plasmonic effects which could improve the optoelectronic performance of devices.8,9

Since the momentous research by Ebbesen et al.,10 the extraordinary optical transmission of metal films with subwavelength holes has attracted a surge of interest.11 Reilly et al. found that a metal film with nanoholes demonstrated a promising route to replacing the ITO transparent electrode.12 Despite the advantages of nanohole metal films, there are still numerous technical difficulties when integrating them with OSCs as the transparent electrodes. The difficulties arise from the changes of surface roughness and material work function. In this research, we investigate the use of a metallic nanomesh electrode in OSCs by employing a polymer bulk heterojunction blend. The nanomesh is made out of gold to match the work function of the anode to the active layer.13 The gold nanomesh is fabricated by using nanosphere lithography. This fabrication method is versatile and can be applied to other common metals including aluminum, copper, silver, and their alloys. The active layer of the OSC is a popular polymer bulk heterojunction of poly(3-hexylthiophene) and [6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM, 1:1 in weight). The device with the gold nanomesh shows a high fill factor, short circuit current, and power conversion efficiency (PCE). We also demonstrate, using finite-difference time-domain (FDTD) simulations, that the optical properties of the nanomesh can be manipulated by controlling the geometric size of the nanostructure.

The gold nanomesh with a hexagonal array of periodic circular holes is fabricated using a polystyrene (PS) nanosphere template.14 First, a commercial suspension of PS nanospheres, with a weight concentration of 10%, is diluted with an equal volume of ethanol. The PS nanospheres have a diameter of 430 nm with a size deviation of less than 3%. The PS nanospheres are then spread onto a silicon wafer and a silicon wafer with a negative photoresist template is placed on top of the PS nanospheres. A parallel two-step wet etching process is used to form the nanosphere template.14 First, a commercial suspension of PS nanospheres is spin-coated onto a silicon wafer and then a silicon wafer with a negative photoresist template is placed on top of the PS nanospheres. A parallel two-step wet etching process is used to form the nanosphere template.14 Then, the PS nanospheres are removed by a piranha solution etching process.14

We have fabricated a metallic nanomesh using nanosphere lithography and metal evaporation. The metallic nanomesh has a precisely controlled nanostructure showing excellent uniformity with hexagonally arrayed periodic circular holes. A P3HT:PCBM organic solar cell, with the gold nanomesh electrode, demonstrates a high fill factor of 61% and a considerable power conversion efficiency of 3.12%. Electromagnetic simulation indicates that the optical properties of the metallic nanomesh can be optimized for organic photovoltaic devices by tuning the film thickness, hole diameter, and periodicity. These results show the promising potential of using a metallic nanomesh as the transparent electrode in organic solar cells. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3701582]

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FIG. 1. (a) SEM image of close-packed PS nanospheres without oxygen RIE. SEM images using a RIE power of 50 W and an oxygen flow rate of 50 sccm, (b) PS nanospheres etched for 60 s and (c) PS nanospheres etched for 120 s. (d) Diameter of PS nanosphere as a function of RIE time T.
nanospheres are self-assembled onto a surface of deionized water in a vessel to form a monolayer of nanospheres. The monolayer is then transferred onto a clean glass substrate and the substrate is dried in air. The substrate is then baked on a hot plate at 100°C for 25 min to remove any water residue. The PS nanospheres form a close-packed periodic hexagonal array on the substrate, as characterized by scanning electron microscope (SEM) in Fig. 1(a). Oxygen reactive-ion etching (RIE) is then used to etch the edge of the PS nanospheres and reduce their size, as shown in Figs. 1(b) and 1(c). The size of the etched PS nanospheres can be tuned by changing the oxygen flow rate, RIE power, and time, as shown in Fig. 1(d). Electron beam evaporation is used to deposit metals on the substrate. In this work, a 2 nm chromium film followed by an 18 nm gold film is vertically deposited on the substrate. Chromium is used to improve adhesion between the gold layer and the glass substrate. Finally, the etched PS spheres are removed by ultrasonication in chloroform. The gold remains on the substrate forming the nanomesh and can be seen in Fig. 2(a). The metallic nanomesh can also be fabricated on a flexible transparent substrate of polyethylene terephthalate (PET) instead of glass, as shown in Fig. 2(b). The hole periodicity is determined by the original diameter of the PS nanospheres.

The OSCs are prepared on the glass/Au nanomesh substrates. The schematic structure of the solar cell using gold nanomesh as the anodic electrode is illustrated in Fig. 3(a). The nanomesh substrates are thoroughly cleaned in an ultrasonic bath with deionized water, acetone, and isopropyl alcohol successively for 10 min each and dried in a vacuum oven for 20 min at 60°C. Subsequently, the substrates are processed by oxygen plasma at a power of 200 W for 1 min to remove any organic residue and smooth the surface. An electron blocking layer of aqueous poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) (PEDOT:PSS) is spun on top of the nanomesh at 4500 rpm for 1 min and baked in air at 130°C for 35 min. The surface is uniform with hexagonally periodic circular pits less than 8 nm deep, as determined by atomic force microscope (AFM) seen in Fig. 3(b). PEDOT:PSS acts as a buffer layer and allows for proper wetting between the gold nanomesh and the active layer. The substrates are transferred into a nitrogen glove box where the active layer is deposited by spin coating as described in our previous research. The samples are solvent annealed in covered Petri dishes for about 16 min and then baked at 140°C for 5 min. Finally, a Ca/Al (20 nm/100 nm) layer is deposited as the back electrode.

The photovoltaic performance of OSCs under AM 1.5 G illumination is investigated and shown in Fig. 4. The open circuit voltage is minimally changed when the ITO electrode is replaced by gold nanomesh, since the work functions of gold and ITO are so similar. The device with the gold nanomesh demonstrates lower photocurrent density than the ITO reference device. The short-circuit current density (Jsc) of the nanomesh device is 9.6 mA/cm² while the Jsc of the ITO device is 10.8 mA/cm². It has been suggested that the incorporation of gold nanomesh could induce surface plasmon enhanced optical absorption of the OSC. However, the near-field enhancement effect should be mostly limited within the PEDOT:PSS layer in the gold nanomesh device.
that we fabricated. The reduction of $J_{sc}$ mainly corresponds to the decrease of optical transparency of gold nanomesh versus ITO. The optical transmission of ITO is about 85%, which is higher than the optical transmission of gold nanomesh fabricated in this work, seen in Fig. 5. Even though the nanomesh device has a lower $J_{sc}$ than ITO, it maintains a high fill factor of 61% and a considerable PCE of 3.12%, versus the result of 1.22% PCE when using a silver nanohole film electrode as reported by Reilly et al. in Ref. 12.

The photocurrent density depends on the optical absorption in the active layer and is partially determined by the optical transmission of the front transparent electrodes. We perform an electromagnetic simulation using the 3-dimensional FDTD method to illuminate the optical properties of the metallic nanomesh. This modeling method is validated by experimental measurement as shown in Fig. 5(a). The optical transmission of the metallic nanomesh can be manipulated by tuning the film thickness ($t$), hole diameter ($D$) and periodicity ($P$), as shown in Figs. 5(b)–5(d). The suppression of optical transmission in a certain wavelength range is attributed to the excitation of a short range surface plasmon.\(^{17}\) The near-field enhancement induced by the short range surface plasmon is confined within the PEDOT:PSS layer and likely cannot effectively enhance the optical absorption in P3HT:PCBM. The transmission suppression due to the plasmon resonance should be tuned below the energy band gap of the OSC to allow more useful light to enter the active layer. The simulation indicates that the optical transmission of the nanomesh could approach nearly 80% with a weak suppression around the plasmon resonance frequency. Further work could be done to decrease the plasmon resonance energy below the band gap of P3HT and raise the performance of the cell. The electrical resistance of the nanomesh as a function of film thickness, hole diameter and periodicity can also influence the device performance.\(^{18}\) Future research could be carried out to quantify the trade-off between the optical properties and the conductivity of the metallic nanomesh.

In summary, a gold nanomesh was fabricated using a versatile and convenient method. The design and fabrication of polymer bulk heterojunction solar cells using gold nanomesh was demonstrated. OSCs using the gold nanomesh showed a high fill factor and considerable PCE. The optical and electrical properties of the metallic nanomesh could be further optimized by tuning the film thickness, hole diameter and periodicity. These results demonstrate that the metallic nanomesh should have great potential to replace ITO electrodes in the organic photovoltaic industry.

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