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Research paper

# Contact-printed ultrathin siloxane passivation layer for high-performance Si-PEDOT:PSS hybrid solar cells

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ABSTRACT

A simple way for high-performance planar Si-PEDOT:PSS hybrid solar cells have been demonstrated in this work. Contact-printed, hydrophobically-recovered ultrathin siloxane layer has been employed as insertion layers at interfaces in Si-PEDOT:PSS hybrid solar cells. The printing has been done at room ambient in dry state for 5– 10 min, which has led to <0.5 nm thin siloxane layer at interfaces. The printed ultrathin siloxane plays the role of passivation layer and significantly increases the photocurrent by suppressing charge carrier recombination at interfaces, leading to >13% cell efficiency with non-textured planar Si substrate. Interestingly, the layer has been found to be equally effective at both interfaces ('top' interface between Si and PEDOT:PSS, and 'bottom' interface between Si and bottom electrode), while other insertion layers suggested in literature works at one interface only. Furthermore, the sheet resistance of PEDOT:PSS layer, rather than resistivity or conductivity, has been found to be the relevant characteristics in the hybrid solar cells, because the carrier conduction in 2-dimension is utmost importance in such devices. The suggested method can be a valuable help for low-cost, high-performance Si-PEDOT:PSS hybrid solar cells and can expedite the commercialization of the hybrid photovoltaics in near future.



## 1. Introduction

Many interests on renewable energy sources have been paid recently due to climate change induced mainly by combustion of traditional fossil fuels such as coal and oil. Among them, photovoltaics, which directly convert sun light into electricity, is one of very attractive choices thanks to virtually unlimited supply of sun light. Photovoltaic cells based on crystalline inorganic materials such as Si and GaAs have long history of research and development, and thus they are the dominant players in the market. Although their high performance and stability, the high fabrication cost hinders them to be competitive enough when compared to other traditional energy sources. Inorganic-based photovoltaic devices usually require high (up to 1000 °C) temperature and expensive vacuum equipment. On the other hand, organic-based ones have the advantage of low temperature solution processability, but suffers from poorer performance and stability compared to inorganic counterparts [1].

Therefore, it seems quite natural to combine the advantages of inorganic and organic photovoltaic materials. One of such approaches is the hybrid combination of crystalline Si and organic conducting polymer, poly(3,4-ethoxydioxythiophene):polystyrene sulfonate (PEDOT:PSS). The Si plays the role of photoactive material, that is, generate charge carriers by absorbing the incident light, while the PEDOT:PSS layer forms metal-like Schottky contact with Si and selectively extract holes ($h^+$). The Si-PEDOT:PSS hybrid solar cells do not involve any high temperature process and can be fabricated by solution processing of PEDOT:PSS layer. Also, the photovoltaic efficiency has already reached >14% in literature [2,3], which makes this type of photovoltaic device be a promising candidate for cost-effective renewable energy source.

Various approaches have been suggested in literature to enhance the performance of Si-PEDOT:PSS hybrid solar cells. One way to enhance the efficiency of the cell is to manage the incident light effectively. Considering the fact that polished Si surface has very high reflectance, texturing of the Si, such as pyramidal structure by anisotropic chemical etching [4–6], nanowires by the metal-assisted chemical etching (MaCE) [7–15], and hierarchical micro/nano-structuring by combining the both [16,17], has led to the enhanced performance of solar cell devices compared to those fabricated on flat Si thanks to the increased light trapping by such surface textures. Another is the materials engineering of the conductive PEDOT:PSS layer. The enhanced conductivity of PEDOT:PSS by additives, called as secondary doping, has been found to be effective to increase the cell efficiency [18–22]. Efficient collection of charge carriers to the right electrodes, $h^+$ to the top electrode via PEDOT:PSS and $e^-$ to the bottom electrode, respectively, is another key approach for high-performance Si-PEDOT:PSS hybrid solar cells. For this, there should be some mechanisms that prevents charge carriers to reach the wrong electrodes, otherwise they would recombine

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with opposite type of charge carriers there and thus reduce the photocurrent. This usually requires insertion of thin layer of materials having the desired characteristics or special interfacial treatment, which has long been studied in other fields such as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs) [23].

Insertion layers have to meet specific requirements at each interface. At one interface where the $h^+$ is the right carrier to be collected there, insertion layer should be able to block the flow of $e^-$. The opposite is true for the other interface. These selective carrier blockings have usually been achieved by inserting a thin layer having aligned energy level with materials at each interface. That is, the insertion layer should have proper energy band structure to meet this requirement. For example, insertion material for the top interface (between Si and PEDOT:PSS) should have similar highest occupied molecular orbital (HOMO) energy level compared to PEDOT:PSS to easily pass $h^+$ to PEDOT:PSS, and at the same time it should have very high lowest unoccupied molecular orbital (LUMO) level compared to PEDOT:PSS to block the $e^-$ [24,25]. For the bottom interface (between Si and bottom electrode), however, the situation is opposite. The layer should be able to selectively block the flow of $h^+$ while passing $e^-$ freely [26–28]. Therefore, any material that can be used as an insertion layer on one interface cannot be used for the other interface, and thus two different insertion layers, one for the top interface and the other for the bottom interface, have to be used for high-performance hybrid solar cells [3,29,30]. Ultrathin insulating layer have also been applied as an insertion layer in literature [8,14,31], but they were limited in one interface only or need expensive, vacuum process.

In this work, we demonstrate high-performance Si-PEDOT:PSS hybrid solar cells based on planar Si. To achieve ~13% cell efficiency without texturing of the Si surface, we have employed ultrathin siloxane insulating passivation layers at *both* interfaces, i.e., Si-PEDOT:PSS (called 'top' interface hereafter) and Si-bottom electrode ('bottom' interface), by exploiting the well-known 'hydrophobic recovery' phenomenon of elastomeric polydimethylsiloxane (PDMS) stamp [32–35]. The contact printing of siloxane passivation layer has been carried out by the simple conformal contact of patterned PDMS stamp onto Si surfaces for 5– 10 min at room ambient. The printed ultrathin (≤0.5 nm) siloxane passivation layer has been found to enhance the cell performance, especially short-circuit current density ($J_{sc}$) and fill factor (*FF*) by suppressing recombination current. The siloxane layer can be applied for both interfaces, which is quite contrast to other insertion layers suggested in literature. And the contact printing process can be done at room ambient without involving any complex and expensive vacuum-based equipment or wet solution. Also, the sheet resistance, rather than conductivity, of PEDOT:PSS layer has been found to be the proper parameter in characterizing Si-PEDOT:PSS hybrid solar cells.

## 2. Materials and methods

### 2.1. Siloxane contact-printing

For the contact printing of siloxane oligomers, the well-known hydrophobic recovery phenomenon has been exploited. An elastomeric PDMS stamp of has been replicated from commercial blank compact disc (CD) as a master mold. Mixture of base resin and curing agent (10:1 by weight) from Sylgard 184 kit (Dow) has been poured, de-aired, cured at 70 °C for >4 h. The replicated PDMS stamp has been made in conformal contact onto Si (top or bottom surfaces) for specific time duration at room ambient. Gentle removal of PDMS stamp leaves ultrathin (~1 nm or less) siloxane oligomer on the Si surface. Note here that the patterned PDMS stamp can greatly enhance the out-diffusion of siloxane oligomers, leading to very short (5– 10 min) contact printing time compared to non-patterned flat one [35].

### 2.2. Device fabrication

n-Type Si (1– 10 Ω cm) was cut into ~2 cm * 2 cm. The Si substrate was cleaned in deionized (DI) water with ultrasonication, followed by cleaning in piranha solution at ~90 °C for 20 min. Final dipping in diluted HF (10% in DI water) solution for 10 min makes the Si surface to be H-terminated. In certain case, the H-terminated Si substrate was simply exposed to room ambient for 3 h to regrow native oxide layer.

As a conducting organic layer, highly conductive PEDOT:PSS (Clevios PH-1000, Heraeus) has been used. To enhance the electrical conductivity of PEDOT:PSS, nonionic surfactant (Triton X-100, Aldrich) has been added into the PEDOT:PSS dispersion in various contents, ranging from 0.2 wt% to 8 wt%. Without the addition of surfactant (i.e., pure PEDOT:PSS/DI dispersion), it was impossible to coat the layer onto highly hydrophobic, H-terminated Si surface. Then, the PEDOT:PSS solution with added surfactant has been spun on the cleaned Si substrate at various spin speed (300 rpm–2000 rpm) for 120 s. Note here that the Si substrate surface was HF-stripped again right before the spinning of PEDOT:PSS solution, to completely remove any re-grown native oxide layer. Then, the sample was annealed at 120 °C for 15 min. After cooling down the sample to room temperature for 5 min, the PEDOT:PSS layer was washed with methanol drops while spinning at 8000 rpm for 60 s.

The back surface of the sample was then HF-stripped by dropping diluted HF solution while spinning, which ensures the H-terminated surface on the back side of Si. Ti(100 nm)/Ag(100 nm) was deposited as a bottom electrode on the back surface of Si by e-beam evaporation, at deposition rates of 3 Å/s for Ti and 5 Å/s for Ag, respectively. Ag(200 nm) was shadow evaporated on the top surface of the sample using stainless steel shadow mask. The grid pattern on the shadow mask has linewidth of 0.2 mm with spacing of 1 mm or 2 mm, leading to shadow ratio of 20% and 10%, respectively. All the devices in this work have been fabricated using shadow mask having 1 mm spacing, except the device shown in Fig. 2f. Finally, the non-active area of the sample was cut [38], leaving device of size ~1 cm * 0.9 cm. For those devices with contact-printed siloxane layer, the contact printing has been performed right before the spinning of PEDOT:PSS/surfactant solution (top interface) or the deposition of bottom electrode.

### 2.3. Characterization

Scanning electron microscopy (SEM; JEOL), and atomic force microscopy (AFM; MFP-3D, Asylum) have been used for sample imaging. The thickness of PEDOT:PSS layer was measured from cross-sectional SEM images, and cross-checked with surface profiler (Dektak XT, Bruker). The sheet resistance of PEDOT:PSS layer was measured by four points probe (Laresta-GP, Mitsubishi Chemical Analytech); for these measurements, the PEDOT:PSS layer was prepared on insulating glass substrate by spin coating with the same formulation mentioned above. For the optical characterization, organic layer on glass (for transmittance) or on Si (for reflectance) has been used and measured by UV–vis spectrophotometer (V630, Jasco). Solar simulator (Oriel Sol3A, Newport) was used to characterize the solar cell performance. The current density was obtained from the measured current divided by the sample area (thus, all the reported solar cell parameters are based on the sample size of ~1 cm * 0.9 cm, including the shaded area by opaque, thick top electrode).

## 3. Results and discussion

To find the optimum processing conditions, we first have carried out some control experiments and the results are shown in Fig. 1. First of all, the characteristics of organic PEDOT:PSS layer, such as conductivity and optical transparency, is very important for high-performance Si-organic hybrid solar cells. Fig. 1(a) shows the current density (*J*) vs. voltage (*V*) plot as a function of the content of surfactant, Triton X-100. Recently, the addition of Triton X-100 into PEDOT:PSS/water dispersion can lead