

Unveiling the Hybrid n-Si/PEDOT:PSS Interface

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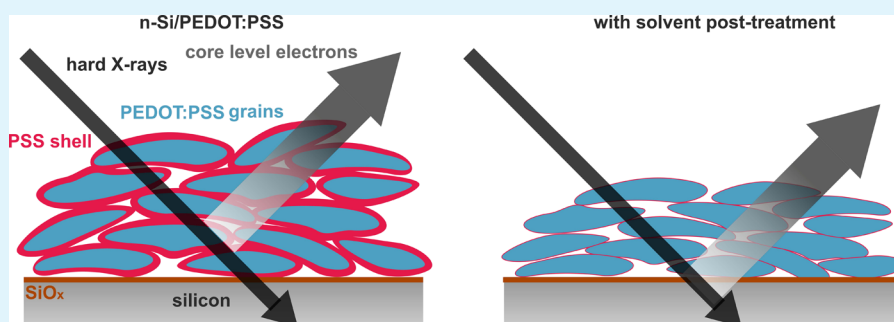
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Supporting Information



ABSTRACT: We investigated the *buried* interface between monocrystalline n-type silicon (n-Si) and the highly conductive polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), which is successfully applied as a hole selective contact in hybrid solar cells. We show that a post-treatment of the polymer films by immersion in a suitable solvent reduces the layer thickness by removal of excess material. We prove that this post-treatment does not affect the functionality of the hybrid solar cells. Through the thin layer we are probing the chemical structure at the n-Si/PEDOT:PSS interface with synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES). From the HAXPES data we conclude that the Si substrate of a freshly prepared hybrid solar cell is already oxidized immediately after preparation. Moreover, we show that even when storing the sample in inert gas such as, e.g., nitrogen the n-Si/SiO_x/PEDOT:PSS interface continues to further oxidize. Thus, without further surface treatment, an unstable Si suboxide will always be present at the hybrid interface.

KEYWORDS: solar cells, hybrid materials, conducting polymers, interface, hard X-ray photoelectron spectroscopy, inorganic/organic, device stability

INTRODUCTION

The rectifying hybrid inorganic–organic interface between the semiconductor silicon and the polymer blend poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is widely investigated for application in solar cells.¹ Numerous approaches aiming toward highly efficient n-Si/PEDOT:PSS solar cells have been presented, including interface engineering by the incorporation of inorganic interlayers,² passivation with organic molecules,³ or nanostructured surfaces.⁴ By using advanced solar cell device

concepts, efficiencies up to 17% have been reached.⁵ The inorganic semiconductor silicon as well as the very conductive polymer PEDOT:PSS are used in many applications, and thus the individual materials have been thoroughly investigated in recent decades.⁶ Although the n-Si/PEDOT:PSS junction has been characterized indirectly by multiple electrical and optical

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device measurements,^{7,8} the structural and chemical details of the interface are still unresolved.

While n-Si/PEDOT:PSS solar cells are commonly fabricated on H-passivated silicon substrates,^{7–11} numerous groups have intentionally grown a native oxide on the silicon surface prior to solution processing the PEDOT:PSS on top.^{12–16} These studies have shown that n-Si/PEDOT:PSS solar cells produced with and without the intentionally introduced interfacial oxide perform well. Detrimental effects on device performance are only observed when the oxide layer is too thick and inhibits charge carrier transport.^{12,13} In general, the polymer is cast and post-treated under ambient conditions. To our best knowledge, there is no study found in the literature that reports how this might affect the interface.

In terms of the long-term photovoltaic device performance of hybrid n-Si/PEDOT:PSS solar cells, the dominant degradation mechanism in air is the degradation of the polymer itself. The polymer exhibits a reduced conductivity, most likely due to the uptake of water,¹⁷ greatly affecting the solar cell performance. Even with encapsulation of the polymer layer¹⁸ or of the complete n-Si/PEDOT:PSS solar cell,¹⁴ this process can so far be only slowed down. Because this strong degradation of the polymer dominates and possibly overshadows other effects, it is unclear whether the buried n-Si/PEDOT:PSS interface is stable or might change with storage time, which would represent another inherent source of degradation.

Although chemically stripping off the PEDOT:PSS layer after complete preparation has been used to probe the underlying silicon surface,¹⁹ a direct study of the buried n-Si/PEDOT:PSS interface after preparation and with storage time was yet to be reported.

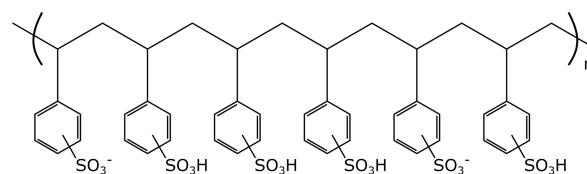
An additional post-treatment of the PEDOT:PSS films by immersion of the whole sample in polar solvents after preparation has recently been suggested in the literature to increase the specific conductivity of the polymer films.^{20–22} It has been observed that such a post-treatment also reduces the thickness of the films by up to 50%.^{20,21} These studies were performed on the PEDOT:PSS material, leaving open how such a post-treatment might affect the performance of n-Si/PEDOT:PSS solar cells.

In this work, we produce PEDOT:PSS layers that are sufficiently thin to allow for nondestructive probing of the buried hybrid n-Si/PEDOT:PSS interface by synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES), while making sure that the electronic properties required for efficient hybrid solar cells are maintained. We take a detailed look at the effect of solvent post-treatment on the morphology and chemical composition of the PEDOT:PSS layers. With this post-treatment, we are able to probe the buried inorganic–organic hybrid interface on freshly prepared n-Si/PEDOT:PSS sample as well as test its stability when stored under inert conditions.

EXPERIMENTAL SECTION

Sample Preparation and Device Measurements. All samples were prepared on n-type silicon (100) wafers with a resistivity of 1–5 Ω cm, cut into smaller samples (1.5 \times 1.5 cm² for solar cell fabrication; 0.7 \times 0.7 cm² for HAXPES measurements) and cleaned by ultrasonication in acetone and isopropyl alcohol. The native oxide on the silicon surface was removed by hydrofluoric acid (5% HF for 30 s), followed by a subsequent dip in deionized (DI) water. PEDOT:PSS (PH1000, Heraeus Clevios, chemical formula displayed in Figure 1) was filtered with a polyvinylidene fluoride membrane (0.45 μ m porosity) to remove agglomerations. To increase the conductivity of

poly(styrenesulfonate)



poly(3,4-ethylenedioxythiophene)

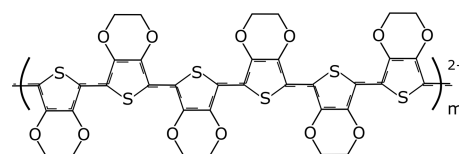


Figure 1. Chemical formula of the PEDOT:PSS solution (Clevios PH 1000)³⁰

the final film, 5 vol % dimethyl sulfoxide (DMSO) was added to the PEDOT:PSS solution. Since PEDOT:PSS is dispersed in water, it was necessary to add a wetting agent (0.1 vol % FS31, Capstone) to ensure a proper layer/interface formation on hydrophobic H-passivated silicon. PEDOT:PSS was spin coated at 4000 rpm for devices and at 10000 rpm for HAXPES samples for 20 s and subsequently annealed at 130 $^{\circ}$ C for 15 min in ambient air. To define an active area for the hybrid junction in solar cells and to reduce edge effects, an area of 1.17 cm² was masked and the surrounding polymer was etched away by a strong oxygen plasma. For complete photovoltaic devices, an In/Ga eutectic was scratched into the silicon as a back-contact and a gold grid (finger width, 80 μ m) was evaporated by an electron beam through a shadow mask on the polymer as a front contact. As a post-treatment to obtain thinner PEDOT:PSS layers, the samples were additionally immersed for 15 min in a DMSO bath following the standard annealing step. After removal from the bath, the excess DMSO was blown off with a nitrogen gun and the samples were dried a second time for 15 min on a hot plate under ambient conditions at 120 $^{\circ}$ C.

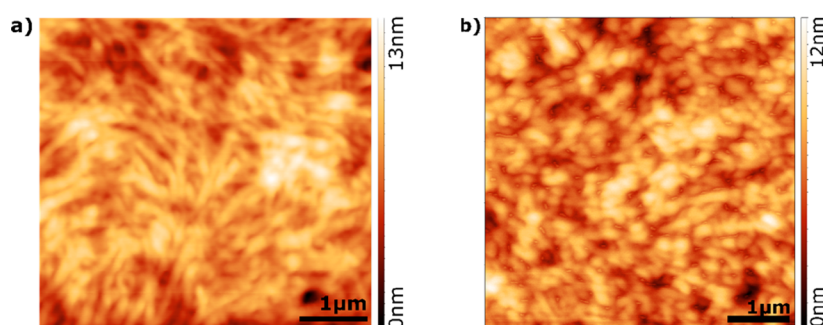
The average thickness of the polymer layer on different sized silicon substrates was determined by a stylus profiler (Veeco Dektak 150, Bruker). The thickness profile, the roughness, and the morphology of the polymer layers were recorded by a Bruker AFM in nontapping mode on an area of 5 \times 5 μ m² in the center of the smaller silicon substrates. The sheet resistance of the polymer layers was determined by the van der Pauw method with a Hall measurement system (HMS5000, Ecopia). Electrical device characterization was carried out with a Keithley SCS 4200 semiconductor characterization system. Current density–voltage (J – V) characteristics were measured in the dark and under illumination. To characterize the photovoltaic response of the devices, samples were irradiated through the transparent PEDOT:PSS layer with an AM1.5 reference spectrum (Oriel Sol3A Class AAA Solar Simulators, Newport) by using a shadow mask for the active area. The external quantum efficiency (EQE) was measured using light from a 300 W xenon source coupled through a CS260 monochromator (Newport) and a calibrated silicon reference cell.

HAXPES Measurements. The measurements were conducted at the HIKE end-station²³ installed at the KMC-1 bending magnet beamline²⁴ that is located at the storage ring BESSY II (Helmholtz-Zentrum Berlin). To prevent any possible beam-induced sample degradation, the measurements have deliberately been performed using BESSY II's low- α multibunch hybrid mode A with an initial ring current of 15 mA (compared to 300 mA that are reached during top-up operation). All measurements were performed with an excitation energy of 3 keV. A VG Scienta R4000 electron analyzer was used to record HAXPES spectra. The binding energy (E_{bind}) was calibrated with a gold reference (setting Au 4f_{7/2} = 84.0 eV). WinSpec 2.09 (University of Namur, Belgium) was used for data analysis, subtracting

Table 1. Thicknesses of PEDOT:PSS Layers from Standard Processing and with DMSO Post-treatment, Measured by a Stylus Profiler Averaging over the Whole Sample (solar cell: $1.5 \times 1.5 \text{ cm}^2$, 4000 rpm; HAXPES: $(0.7 \times 0.7 \text{ cm}^2$, 10 000 rpm)^a

sample	solar cell		HAXPES					
	profiler thickness (nm)	profiler thickness (nm)	sheet resist. (Ω/sq)	specific conduct. (S/cm)	AFM av (nm)	AFM max (nm)	AFM min (nm)	AFM rms (nm)
standard	62(2)	36(2)	170	470(30)	42(2)	48	34	1.7
post-treated	34(1)	21(1)	200	950(20)	25(2)	31	18	1.6

^aFor the HAXPES samples, the sheet resistance, as measured by the van der Pauw method, the conductivity, and statistics of AFM measurements at the center of the substrates (see Figure 2) are also presented.

**Figure 2.** AFM images of PEDOT:PSS films (a) before and (b) after the additional DMSO post-treatment. The images show an area of $5 \times 5 \mu\text{m}^2$.

linear backgrounds, and fitting the core level peaks with Shirley backgrounds and symmetric as well as asymmetric Gaussian/Lorentzian line shapes. A fresh and a natively oxidized (2 weeks in ambient conditions) bare HF-dipped silicon wafer were measured for comparison.

RESULTS AND DISCUSSION

The standard solution-processed fabrication of efficient hybrid n-Si/PEDOT:PSS solar cells is spin coating PEDOT:PSS solution mixed with DMSO at a moderate spin speed (e.g., between 2000 and 4000 rpm). This leads to a polymer film thickness of 50–150 nm,^{8,25} depending mainly on the spin speed but also slightly on the substrate size used. We made solar cells on HF-dipped silicon with a size of $1.5 \times 1.5 \text{ cm}^2$ by spin coating the PEDOT:PSS (PH1000, chemical formula depicted in Figure 1) mixed with 5% DMSO at 4000 rpm. This yields an average thickness of around 62(2) nm. By increasing the spin speed to 10000 rpm and decreasing the sample size to $0.7 \times 0.7 \text{ cm}^2$ (i.e., the sample size for HAXPES measurements discussed below), the average thickness could be decreased to around 36(2) nm. The sheet resistivity of these polymer films, measured in a van der Pauw setup on the smaller substrates, is $170 \Omega/\text{sq}$, with a corresponding specific conductivity of around 470(30) S/cm, as expected for the solution PH 1000 mixed with 5% DMSO.^{6,20,22} The results are summarized in Table 1.

We post-treat our PEDOT:PSS layers on silicon by immersing them for 15 min in DMSO. After this post-treatment the polymer layers exhibit a reduced average thickness of 34(2) nm for the moderate spin speed and $1.5 \times 1.5 \text{ cm}^2$ substrates, while for the high spin speed $0.7 \times 0.7 \text{ cm}^2$ samples they are 21(1) nm thin. The sheet resistance of the latter films only slightly increases to $200 \Omega/\text{sq}$ upon the post-treatment. Since the thickness is almost decreased by half, the corresponding specific conductivity doubles to 950(20) S/cm. The same effect has also been observed previously for immersion in ethylene glycol.²¹ This leads to the assumption that, by immersion in a suitable solvent, mainly material from

the polymer film that does not actively take part in the conduction mechanism is removed.

The surface topology of the polymer films was recorded on a $5 \times 5 \mu\text{m}^2$ spot in the middle of the sample by AFM in nontapping mode, displayed in Figure 2. Additionally, the thickness of the polymer layer is measured by partially scratching off the polymer from the substrate and averaging the step height over a larger AFM scan. Table 1 shows that the middle of the sample is slightly thicker compared to the average thickness of the whole sample, as measured by a stylus profiler. Figure 2 shows that the surface of the polymer films is quite rough, with a mean roughness of 1.6–1.7 nm, which is in good agreement with values from literature.^{6,20–22} Note that the minimal values in film thickness are well below the average. The DMSO post-treated sample even exhibits small plateaus at the minimum regions in the AFM image in Figure 2b, which are most likely artifacts due to the inability of the AFM tip to penetrate the troughs further. The true mean roughness is therefore slightly larger, and some areas in the polymer layer are thinner than the minimum value shown in Table 1. After the DMSO post-treatment the PEDOT:PSS layer exhibits a fine grain-like structure. In literature it is suggested that PEDOT:PSS consists of $\sim 20 \text{ nm}$ large conductive PEDOT:PSS grains surrounded by excess PSS,^{6,9,26–28} depending very much on the particular PEDOT:PSS solution used. This leads to the assumption that the structure in Figure 2a is mainly excess material that is removed by the DMSO post-treatment, uncovering the grain-like structure of PEDOT:PSS in Figure 2b, an interpretation that has also been supported for a similar post-treatment.²⁹

The change in chemical composition of PEDOT:PSS related to the DMSO post-treatment was observed using HAXPES. Within our experiments, no degradation of the samples due to X-ray radiation was observed (see Supporting Information section S1). The 3 keV excitation energy allows one to probe the S 1s core level in addition to the S 2p core level accessible also by standard laboratory-based X-ray photoelectron spectroscopy (XPS) experiments. The fact that the S 1s line shows

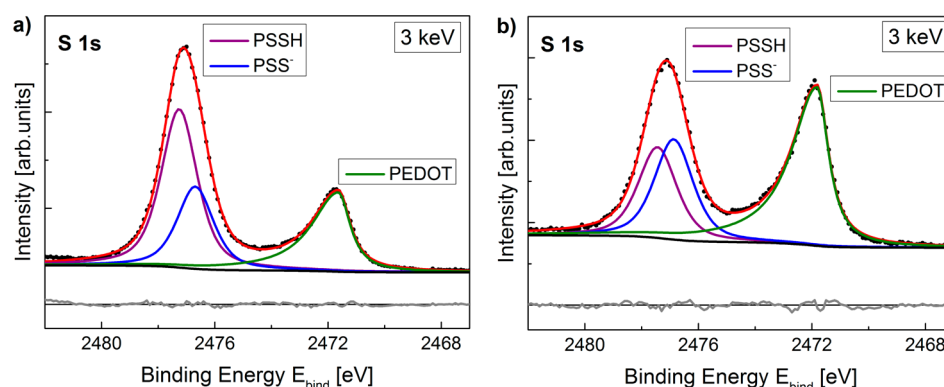


Figure 3. S 1s core level spectra of PEDOT:PSS (a) before and (b) after the additional DMSO immersion treatment. Fitting of the spectra is based on Greczynski et al.²⁸ The residual plot of the fit sum (red) is shown in gray.

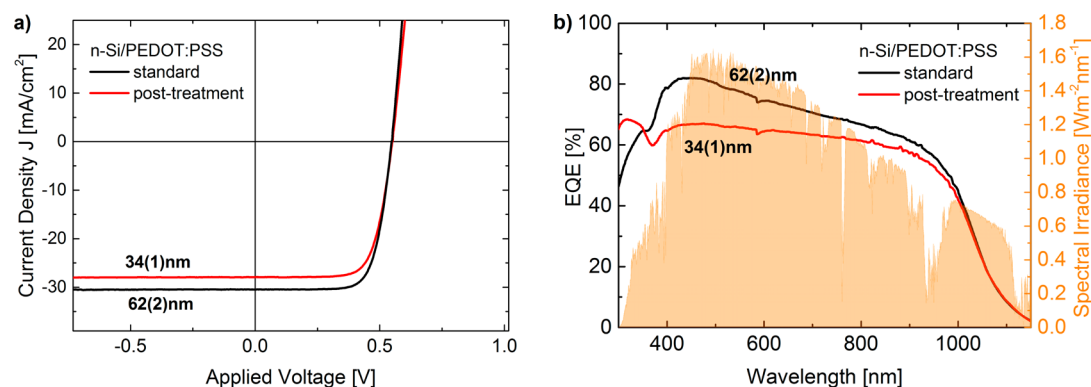


Figure 4. (a) Illuminated J – V characteristics and (b) EQE spectra of hybrid n-Si/PEDOT:PSS solar cells with and without the additional DMSO post-treatment. The AM 1.5G solar spectrum is shown for comparison. The values at the curves represent the average polymer layer thicknesses in the solar cell.

no spin–orbit splitting slightly simplifies the data analysis. The S 1s core level spectra of PEDOT:PSS with and without the DMSO post-treatment are shown in Figure 3. The chemical structure in Figure 1 exhibits three different chemical states of sulfur, related to the thiophene ring in PEDOT as well as to sulfonic acid groups in the neutral PSSH and the charged PSS[−]. The analysis of the S 1s core level spectra in Figure 3 is analogous to the work of Greczynski et al. for the S 2p core level spectra of PEDOT:PSS²⁸ (also compare the S 2p spectra in Supporting Information section S2). The signals from the strongly positive sulfur atoms related to PSS are at higher E_{bind} than the one related to PEDOT. Furthermore, the ionic PSS[−] is at slightly lower E_{bind} than the neutral PSSH. The signal from PEDOT has an asymmetric shape due to a tail at the higher binding energy side resulting from the delocalized positive charge on the polymer chain.²⁸ The peaks are fitted with the ionic PSS[−] component shifted by 5.06 eV to higher binding energies with respect to the PEDOT peak and the neutral PSSH component by 5.63 eV. Both PEDOT:PSS samples (i.e., before and after the DMSO post-treatment) exhibit distinct signals from PEDOT and PSS. The intensity ratio of PEDOT-to-PSS derived from the S 1s spectrum of the standard prepared polymer film is 1:2.5, in very good agreement with the given ratio of 1:2.5 in the used PEDOT:PSS solution (Clevious, PH 1000).³⁰ This is unexpected as most of the signal for the high binding energy core level S 1s originates from the surface, even when using an excitation energy of 3 keV. Films cast from the pristine solution are reported to have a morphology consisting of PEDOT:PSS grains surrounded by a PSS-enriched

shell,^{27,28} and consequently a significantly higher PSS contribution in the surface-sensitive photoemission data is expected. In the present case, however, the used PH 1000 solution is mixed with 5% DMSO, which has been shown to increase the PEDOT-to-PSS ratio,^{9,31} leading to the here measured value of 1:2.5. The S 1s spectrum of the PEDOT:PSS layer post-treated with DMSO, shown in Figure 3b, clearly displays a strongly increased PEDOT-to-PSS signal ratio of 1:1.1. It has also been demonstrated by other groups that an immersion in polar solvents or acids reduces the PSS content drastically.^{21,29,31,32}

The presented result suggests that the DMSO post-treatment removes most or all PSS shell material in the PEDOT:PSS film, leading to a thickness reduction by approximately 40%. The sheet resistance increases only slightly after the post-treatment, indicating that the excess PSS was not actively taking part in the charge transport through the polymer layer.

Hybrid n-Si/PEDOT:PSS solar cells with and without the DMSO post-treatment were produced as described in the Experimental Section. Figure 4a shows the illuminated J – V curves of the solar cells. All solar cell parameters are collected in Table 2. The solar cell characteristics and the power conversion efficiency (PCE) of the standardly processed hybrid n-Si/PEDOT:PSS solar cell are in good agreement with recently published results,^{8,14,33,34} while small deviations can be ascribed to a different doping density of the silicon substrate, variation in polymer film thickness, and device optimization. The post-treatment barely deteriorates the functionality of the hybrid n-Si/PEDOT:PSS solar cells. The immersion in DMSO has no

Table 2. Solar Cell Parameters of n-Si/PEDOT:PSS Solar Cells from Standard Processing and with Additional DMSO Post-treatment^a

solar cell sample	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)
standard	548	30.5	0.73	12.2
DMSO post-treated	550	28.0	0.72	11.1

^aOpen-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill factor (FF), and the power conversion efficiency (PCE) are extracted from the illuminated J - V curves in Figure 4a.

negative effect on the hybrid interface, apparently from the unchanged open-circuit voltage (V_{OC}). Also the fill factor (FF) is hardly affected, consistent with the finding that the DMSO decreases the layer thickness of the polymer but does not considerably increase the sheet resistance (compare Table 1). Only the short-circuit current (J_{SC}) is reduced by the DMSO treatment from 30.5 to 28.0 mA/cm²,² also accounting for the lower PCE. Figure 4b shows that the external quantum efficiency (EQE) of the hybrid solar cell with the polymer thinned down by the DMSO treatment is reduced over a broad wavelength range in the solar spectrum. This reduction of the EQE and correspondingly lower J_{SC} is due to a less favorable antireflective behavior of the thinner polymer layer, as can be estimated by the principle of quarter-wavelength antireflective coating.³⁵ The reflection of silicon with a 34 nm thick PEDOT:PSS layer is almost as high as for bare silicon, resulting in a reflection of more than 30% of the incoming light as also visible in the EQE. Even though the efficiency is slightly reduced by this effect, the functionality of the hybrid n-Si/PEDOT:PSS solar cell characterized by V_{OC} and FF is not significantly affected by the DMSO treatment.

The PEDOT:PSS layers from standard solution processing are too thick to probe the buried hybrid interface with silicon using HAXPES, but the DMSO post-treatment removes enough material so that a clear signal from the Si 2s core level spectrum is visible (spectra for both systems are shown in the Supporting Information Figure S2a). An unambiguous indicator that the complete Si 2s signal exclusively stems from buried silicon covered by the polymer film is the absence of the Si 1s core level peak (see Supporting Information Figure S2b) for which photoelectrons have a considerably smaller inelastic

mean free path (IMPF) due to the higher binding energy. The Si 1s peak would be visible if the signal derived from silicon patches left uncovered due to scratches or pinholes in the polymer films or alternatively silicon-derived contaminants on the surface. The IMPF in PEDOT:PSS can be approximated with the TPP2M formula,³⁶ using the chemical formula of the polymer and assuming a density of 1 g/cm³.⁶ The calculated IMPF of the Si 2s ($E_{kin} = 2.85$ keV) and Si 1s ($E_{kin} = 1.15$ keV) photoelectrons in the polymer are ~ 6.5 and ~ 3 nm, respectively. Assuming a homogeneous coverage and considering that the Si signal will be exponentially attenuated to $1/e^3$ (i.e., to less than 5%) compared to the signal of the bare Si wafer, if the thickness of the polymer layer exceeds $3 \times$ IMPF, this approximation suggests that the PEDOT:PSS layer is in the order of 10–20 nm. Although the values from the AFM measurements in Table 1 indicate an average thickness of 25 nm in the middle of the DMSO post-treated PEDOT:PSS layer, it can be seen from the AFM scan in Figure 2b that many thinner areas exist. PEDOT:PSS is a soft polymeric material with a grain-like structure, visible in Figure 2b. It has been shown before that for soft organic materials, in particular porous materials, the IMPF is largely increased.²³ This rationalizes why it is possible to probe the interface through the polymer layer.

The Si 2s core level spectra of PEDOT:PSS films on silicon with DMSO post-treatment freshly prepared and after being stored for 2 weeks in a nitrogen glovebox are shown in Figure 5c,d, respectively. For reference, spectra for a bare freshly HF-dipped and a 2 weeks in ambient oxidized silicon substrate are also presented in Figure 5a,b. Because the Si 2s signal intensity from the bare silicon references is significantly higher than from the buried silicon, they show a higher signal-to-noise ratio. As expected, the silicon substrate with an H-passivated surface shows essentially only one peak related to elemental silicon (Si⁰).^{37,38} The 2 weeks in ambient air oxidized silicon wafer shows a distinct shoulder related to silicon oxide on the surface.³⁹ The peak is located at ~ 3.6 eV higher E_{bind} , corresponding well to the reported positions for silicon dioxide (Si⁴⁺)³⁷ that dominates native oxide formation on bare H-terminated silicon surfaces.⁴⁰ SiO_x suboxide ($x < 2$) signals are located between this position and the elemental silicon peak.^{37,39} A corresponding signal is hardly detectable for the

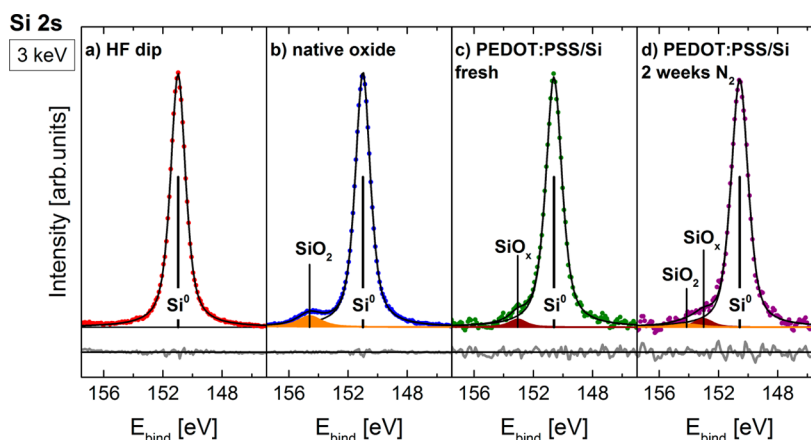


Figure 5. Si 2s spectra of silicon substrates that are (a) freshly HF-dipped and (b) 2 weeks oxidized in ambient, as well as those that are covered with PEDOT:PSS and post-treated with DMSO (c) directly after preparation and (d) after storing 2 weeks in nitrogen. Besides the elemental silicon, silicon dioxide and silicon suboxides (if present) at the surfaces are indicated. The peaks in each spectra are fitted simultaneously, and the backgrounds are subtracted for good comparison.

natively oxidized Si substrate (also compare the Si 1s core level spectra in Supporting Information Figure S3). Close inspection of the Si 2s core level spectra of the freshly prepared n-Si/PEDOT:PSS sample in Figure 5c also reveals a clear shoulder at the high binding energy side of the main Si⁰ feature. A reasonable fit of the spectrum can be achieved assuming two components. Compared to the SiO₂ contribution of the Si 2s peak of the natively oxidized silicon substrate, here the position of the shoulder is less shifted with respect to the elemental silicon peak ($\Delta E \sim 2.4$ eV), pointing to the presence of a suboxide species (i.e., Si²⁺ and/or Si³⁺).^{37,39} This indicates that upon deposition and processing of the PEDOT:PSS on the H-passivated silicon substrate, the latter partially oxidizes. Although to our best knowledge nobody has reported on the chemical structure of a buried n-Si/PEDOT:PSS interface so far, it has been reported that the surface that is exposed by stripping off the polymer with water, acetone, and isopropyl alcohol after processing is oxidized.¹⁹

To give a rough upper estimate of the thickness of the interfacial oxide layer, the intensity ratio of the elemental and suboxide peak of the fresh n-Si/PEDOT:PSS sample is compared with the intensity ratios of Si 2s and Si 1s of the natively oxidized silicon substrate (for details see Supporting Information section S3). This procedure allows us to estimate the interfacial suboxide layer—that is already present at the freshly prepared n-Si/PEDOT:PSS interface—to be approximately 1.5 nm. For comparison, a monolayer of silicon oxide corresponds to about 0.3 nm.⁴⁰ A moist atmosphere can greatly enhance oxide growth on silicon,⁴¹ suggesting that the hygroscopic PEDOT:PSS¹⁷ promotes fast oxidation of the silicon surface. Furthermore, it has been shown that especially in hot DI water the oxidation is a very rapid process.⁴² Since PEDOT:PSS is a colloidal dispersion in water, and the produced samples are heated after solution processing, the remaining water in the films and the preparation conditions (i.e., annealing step) might generate an environment that leads to a very fast oxidation of the silicon surface. Note that from these results the possibility that other PEDOT:PSS-related species might also bind to the silicon at the surface (e.g., Si—O—C or Si—S) cannot be excluded, as the chemical shifts of these potential chemical species would place them in the same binding energy region as the oxide peak.^{43,44} However, compared to the oxide peak, these additional peaks would be of lower intensity as they can at most form a monolayer on the silicon surface. Therefore, we interpret the results as a clear indication of an immediate oxidation of the silicon surface upon n-Si/PEDOT:PSS interface formation.

Figure 5d presents the Si 2s core level spectra of a n-Si/PEDOT:PSS sample that has been stored for 2 weeks in nitrogen after preparation. Although stored under inert conditions, it shows a more pronounced shoulder at the high binding energy side of the main Si⁰ feature than the freshly prepared sample. In this case, the spectrum can only be fitted by assuming an additional contribution to the Si 2s photoemission line that we interpret as being indicative for the presence of silicon dioxide in comparison to the natively oxidized silicon reference. The thickness estimation for the interfacial mixed silicon dioxide and silicon suboxide layer reveals an increase to approximately 1.9 nm (see Supporting Information section S3). This shows that the silicon surface at the buried hybrid interface continues to oxidize even if stored in nitrogen. It has been pointed out that PEDOT:PSS easily takes up water because of the hygroscopic behavior of PSS.^{6,21}

Although a large fraction of PSS was removed by the DMSO post-treatment, it is still very likely that the polymer takes up some water during processing under ambient conditions. As water on the silicon surface steadily leads to further oxidation of the silicon surface with time,⁴⁵ this could explain that even if stored in nitrogen, the silicon surface is not stable and continues to oxidize. This shows that for long-term stable hybrid n-Si/PEDOT:PSS solar cells, in addition to a proper encapsulation of the polymer itself, also a stable interface has to be ensured. Corresponding optimization approaches include the addition of a thin interfacial aluminum oxide layer² or methyl passivation^{3,46} of the silicon surface prior to solution processing. However, detailed studies of these passivated buried interfaces have not been presented yet.

CONCLUSION AND OUTLOOK

By immersion of PEDOT:PSS on silicon in DMSO, a large amount of excess PSS, not actively taking part in the charge transport, is removed from the film leaving conductive PEDOT:PSS grains behind. Hence the thickness of the layer is reduced, while the sheet resistance remains mostly unchanged. We were able to reproduce these morphological changes shown in the literature for a similar post-treatment and, furthermore, prove that the immersion in DMSO has no negative impact on the principle functionality of hybrid n-Si/PEDOT:PSS solar cells. Especially the unchanged open-circuit voltage suggests that the mechanisms at the hybrid interfaces with and without post-treatment are comparable. Thus, the tailored reduction of the PEDOT:PSS layer thickness available by the post-treatment allows the direct study of the chemical structure at the buried n-Si/PEDOT:PSS interface via HAXPES, by matching the polymer layer thickness to the information depth of the emitted core level electrons while maintaining a closed layer.

As the main conclusion, our results prove that hybrid n-Si/PEDOT:PSS solar cells fabricated under ambient conditions, as usually done, will always have a thin interfacial suboxide layer present in the device. Moreover, we also find that this suboxide layer increases in thickness and in degree of oxidation state when storing the device even in an inert atmosphere such as nitrogen. Hence, the thickness of this interfacial oxide layer will not only vary with the preconditioning of the substrate and humidity of the atmosphere during preparation but also with the time until measurement.

Although n-Si/SiO_x/PEDOT:PSS solar cells work initially quite well, the continuous oxide growth will deteriorate the interface with time, eventually leading to a degradation of the initial cell performance. Therefore, we conclude that a stable interface passivation, by, e.g., a defined inorganic tunnel layer or an organic termination through stable covalent bonds of the silicon surface, will be indispensable to guarantee device stability and, thus, further advancement of this intriguing hybrid photovoltaic technology.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b01596.

Stability study of PEDOT:PSS during HAXPES measurements, S 2p/Si 2s and Si 1s core level spectra of PEDOT:PSS on silicon before and after DMSO post-treatment, and approximation of the thickness of the

interfacial oxide including the S 1s core level spectrum of the natively oxidized silicon reference. (PDF)

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Notes

The authors declare no competing financial interest.

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