Supporting Information

Unveiling the Hybrid n-Si/PEDOT:PSS Interface

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S1 Stability of PEDOT:PSS during HAXPES measurements
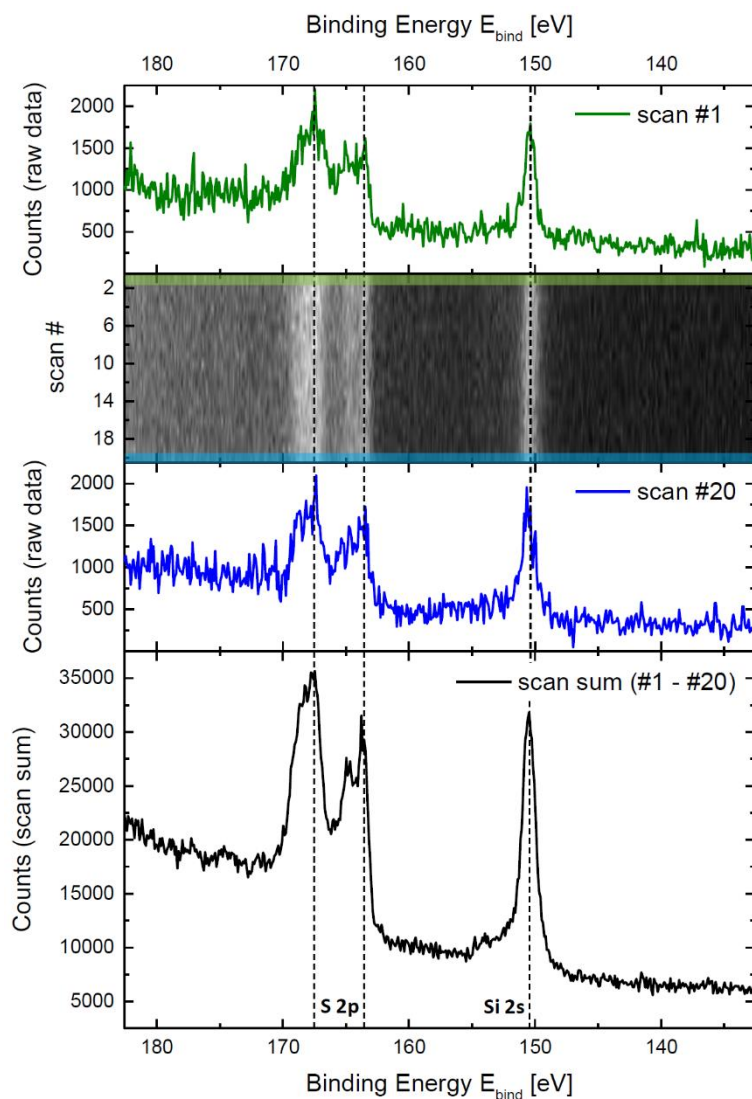
Figure S1. S 2p/Si 2s core level spectra of n-Si/PEDOT:PSS. Comparison of the first (green) and last (blue) single scan and the summed up spectrum (black). The black and white image plot shows all taken single scans in a 3D intensity plot. No significant change of the spectra can be observed over 20 scans.

Figure S1 shows that the core level spectra of S 2p (related to PEDOT:PSS) and Si 2s (related to silicon at the interface) do not change during the HAXPES measurement. Over 20 scans (corresponding to ~1 h of X-ray irradiation) no change in spectral intensity, shape or position of the peaks is observed. Additionally, for samples with thicker PEDOT:PSS films (data not shown) no silicon peak arises upon increasing exposure time and none of the C, S, O core level peaks of the bulk PEDOT:PSS exhibit an energy shift or changes in peak shape or intensity ratio. In addition, inspection of the samples after measurement using an optical microscope showed no visual change in the film surface at the spot of irradiation. In summary, we observe no indications for beam-induced degradation of the samples when exposed to a moderate flux (low intensity mode of storage ring with current of 13.75 mA, bending magnet beamline) of 3 keV photons.

S2 Combined core level spectra of S 2p and Si 2s as well as of Si 1s
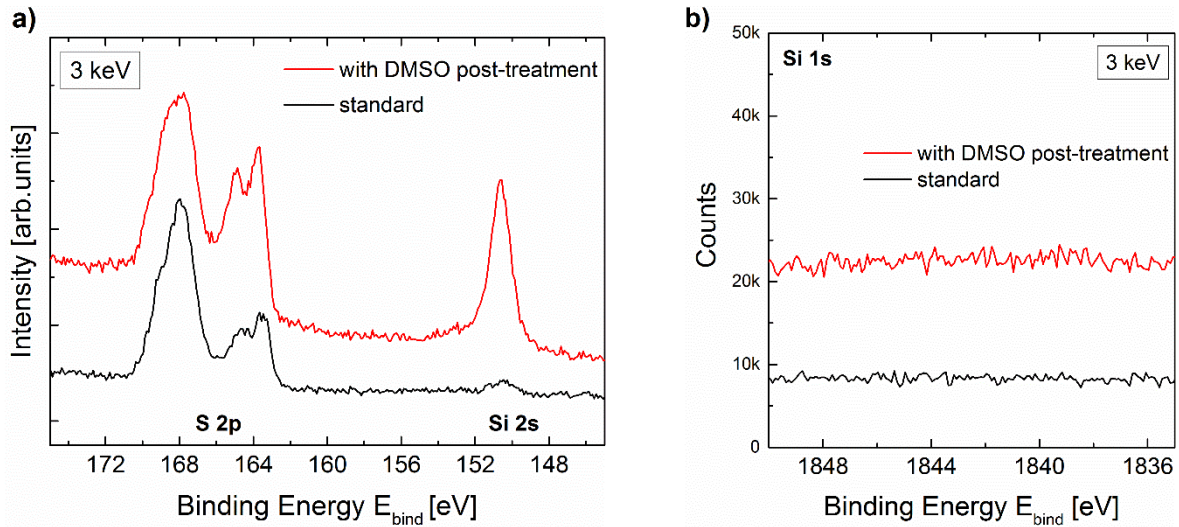
Figure S2. a) S 2p/Si 2s and b) Si 1s core level spectra of PEDOT:PSS before (black) and after the additional DMSO immersion (red).

Figure S2a shows the core level spectra of S 2p and Si 2s. The S 2p peaks at higher binding energies are related to PEDOT and PSS. As for the S 1s core level, the PSS peaks are at higher binding energy than those for PEDOT.[1] In contrast with the S 1s, the S 2p peaks exhibit a spin-orbit splitting of ~1.2 eV. As in the S 1s spectra (see main text), it is clearly visible that after the DMSO treatment the peaks corresponding to PEDOT are enhanced compared to those related to PSS. At approximately 150 eV, the peak related to the Si 2s core level is visible.[2] The thicker, as-cast polymer layer shows only a very weak Si 2s signal, while after the removal of excess PSS by DMSO post-treatment the signal from the silicon substrate is clearly visible. At the same time, no Si 1s signal can be observed (cf. **Figure S2b)** for the n-Si/PEDOT:PSS sample before and after the DMSO post-treatment. Due to the higher binding energy (E_{bind}) and therefore a lower kinetic energy (E_{kin}) photoelectrons related to the Si 1s core level have a considerably smaller IMFP compared to photoelectrons related to the Si 2s core level and thus are much more surface sensitive. The fact that Si 2s peaks can be clearly observed in **Figure S2a** while the Si 1s line is not visible in **Figure S2b** proves that the Si 2s signal exclusively stems from the *buried* n-Si/PEDOT:PSS interface and that uncovered silicon patches due to scratches or pinholes in the polymer films or alternatively silicon-derived contaminants on the surface can be excluded.

S3 Approximation of the thickness of the interfacial oxide

When assuming a simple bilayer of thin, smooth silicon oxide of uniform thickness d on top of a thick ($d_{Si} \gg \lambda$) smooth silicon wafer, the photoemission intensity of a particular core level is given by:[3]

$$I_{SiO_x} \propto \int_0^d e^{-x/\lambda}\, dx \quad \text{and} \quad I_{Si} \propto \int_d^\infty e^{-x/\lambda}\, dx$$

where λ is the inelastic mean free path (IMPF) of the photoelectrons of a given kinetic energy (i.e., of a particular core level). By integration, the ratio of the intensities follows as:

$$R = \frac{I_{SiO}}{I_{Si}} \propto e^{\frac{d}{\lambda}} - 1$$

Using the ratios from the core level spectra of Si 1s and Si 2s of the oxidized silicon reference sample, the thickness can be estimated:

$$\frac{R_1(\text{Si 1s})}{R_2(\text{Si 2s})} = \frac{(e^{\frac{d}{\lambda_1}} - 1)}{(e^{\frac{d}{\lambda_2}} - 1)}$$

From the Si 1s and Si 2s core level spectra we find:
$$R_1(\text{Si 1s}) \approx 0.2$$
$$R_2(\text{Si 2s}) \approx 0.07$$

The IMPF for the corresponding kinetic energies are:[4]
$$\lambda_1(\text{Si 1s} \approx 1.2 \text{ keV}) \approx 24 \text{ Å}$$
$$\lambda_2(\text{Si 2s} \approx 2.8 \text{ keV}) \approx 48 \text{ Å}$$

The approximated thickness of the silicon oxide that natively grows on the initially H-terminated silicon surface that has been left in ambient air for two weeks (cf. **Figure S3**, for the respective Si 1s spectrum) is:

$$d \approx 3 \, nm$$

Keeping in mind that this is only an approximation, the thickness is in good agreement with results for the saturated silicon oxide thickness forming on Si(100) reported in literature [5].

By comparing the ratios of the Si 2s core level of the n-Si/PEDOT:PSS samples with the ratio of the oxidized reference sample, also the interfacial thickness at the hybrid interface can be estimated:

$$\frac{R_1(\text{oxidized Si wafer})}{R_2(\text{nSi/PEDOT:PSS})} = \frac{(e^{\frac{d_1}{\lambda}} - 1)}{(e^{\frac{d_2}{\lambda}} - 1)}$$

Figure S3. S 1s core level spectrum of the natively oxidized silicon substrate surface that has been left in ambient air for two weeks. Besides the elemental silicon, a shoulder to higher binding energies (shifted by ~4.3 eV) corresponding to silicon dioxide [3,6] is visible. The residual plot is shown in gray.

From the Si 2s core level spectrum of the freshly prepared n-Si/PEDOT:PSS we find:
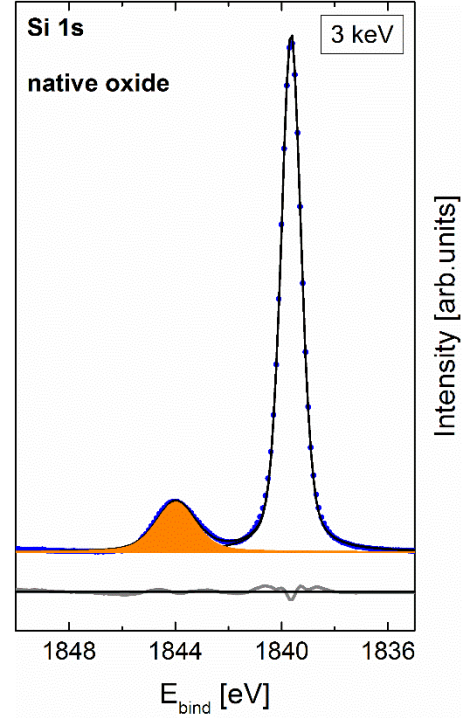$$R(\text{Si 2s}) \approx 0.03$$

This results in a thickness of:
$$d \approx 1.5 \, nm$$

From the Si 2s core level spectrum of the n-Si/PEDOT:PSS stored for two weeks in nitrogen we find:
$$R(\text{Si 2s}) \approx 0.04$$

resulting in a thickness of
$$d \approx 1.9 \, nm$$

References

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