Electronic Supplementary material (ESI) for

Replacement of n-type layers with non-toxic APTES interfacial layers to improve the performance of amorphous Si thin-film solar cells

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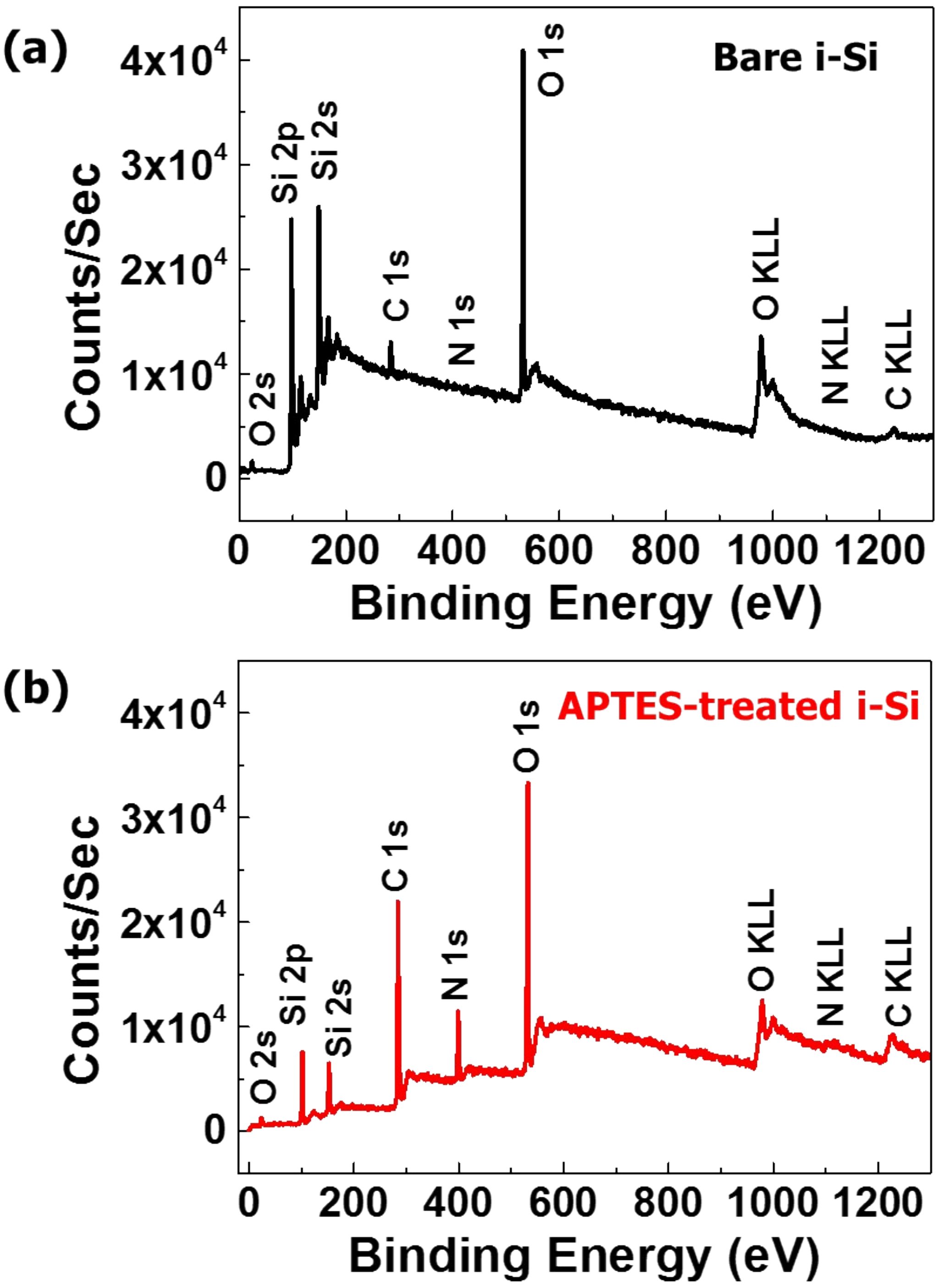
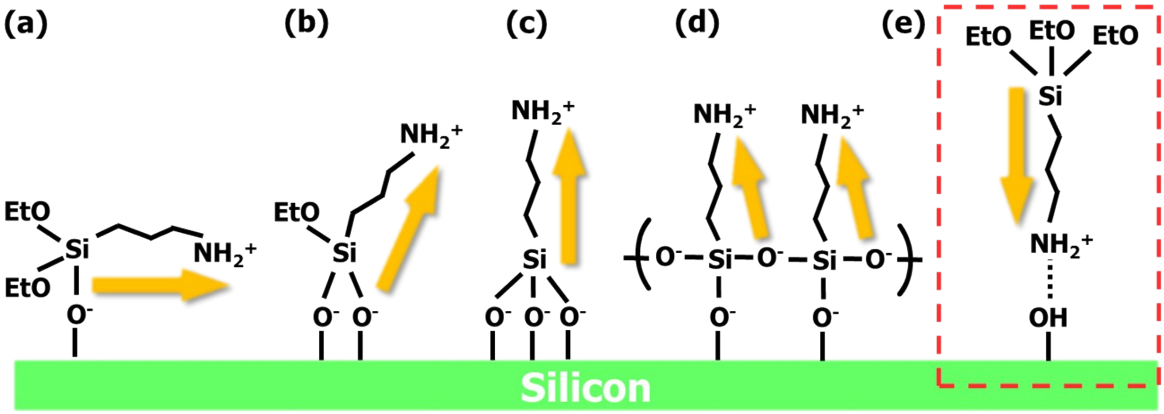
Figure S1. Survey and high-resolution XPS analysis of the (a) bare i-Si and (b) APTES-treated i-Si layers.



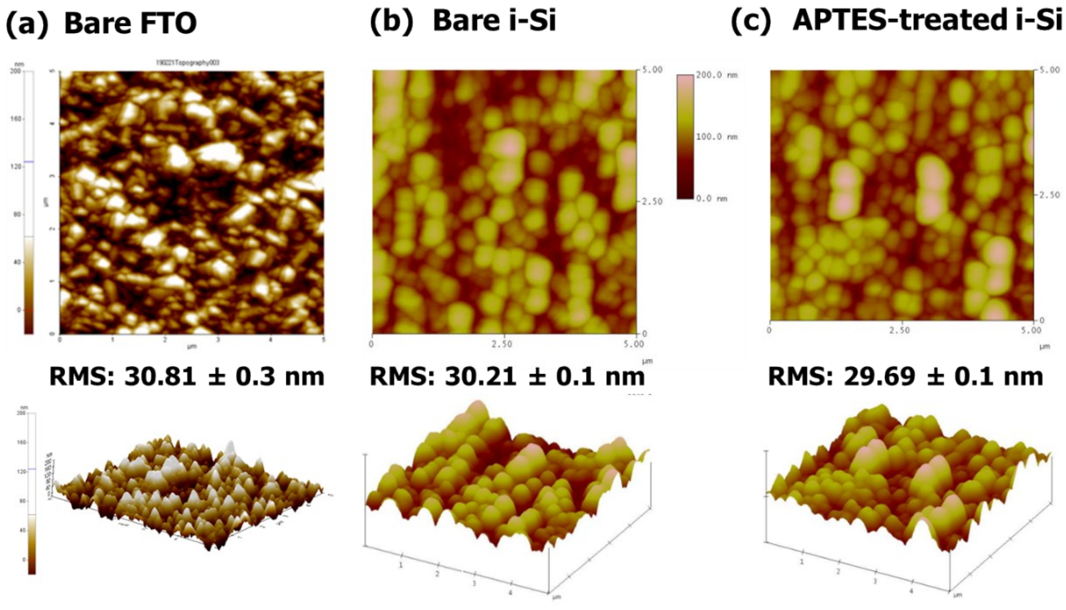
The bare i-Si and APTES-treated i-Si layers showed significantly different Si2p, Si2s, C1s, and N1s profiles. With the addition of APTES, the intensity of the Si peaks decreased, while that of the C1s and N1s peaks increased. The Si peaks (103 and 150 eV) correspond to Si-O bonds, while the N1s peak at 400 eV corresponds to the N from the -NH_2 groups of APTES. No N peak was observed for the i-Si layer. These results indicate that the APTES layer was uniformly deposited. With the addition of APTES, the intensity of the Si peaks decreased (because of its lower Si content than that of i-Si), while that of the C peaks increased (because of its higher C content than that of i-Si).

Figure S2. (a–e) The possible orientation of APTES molecules on the silicon surface.



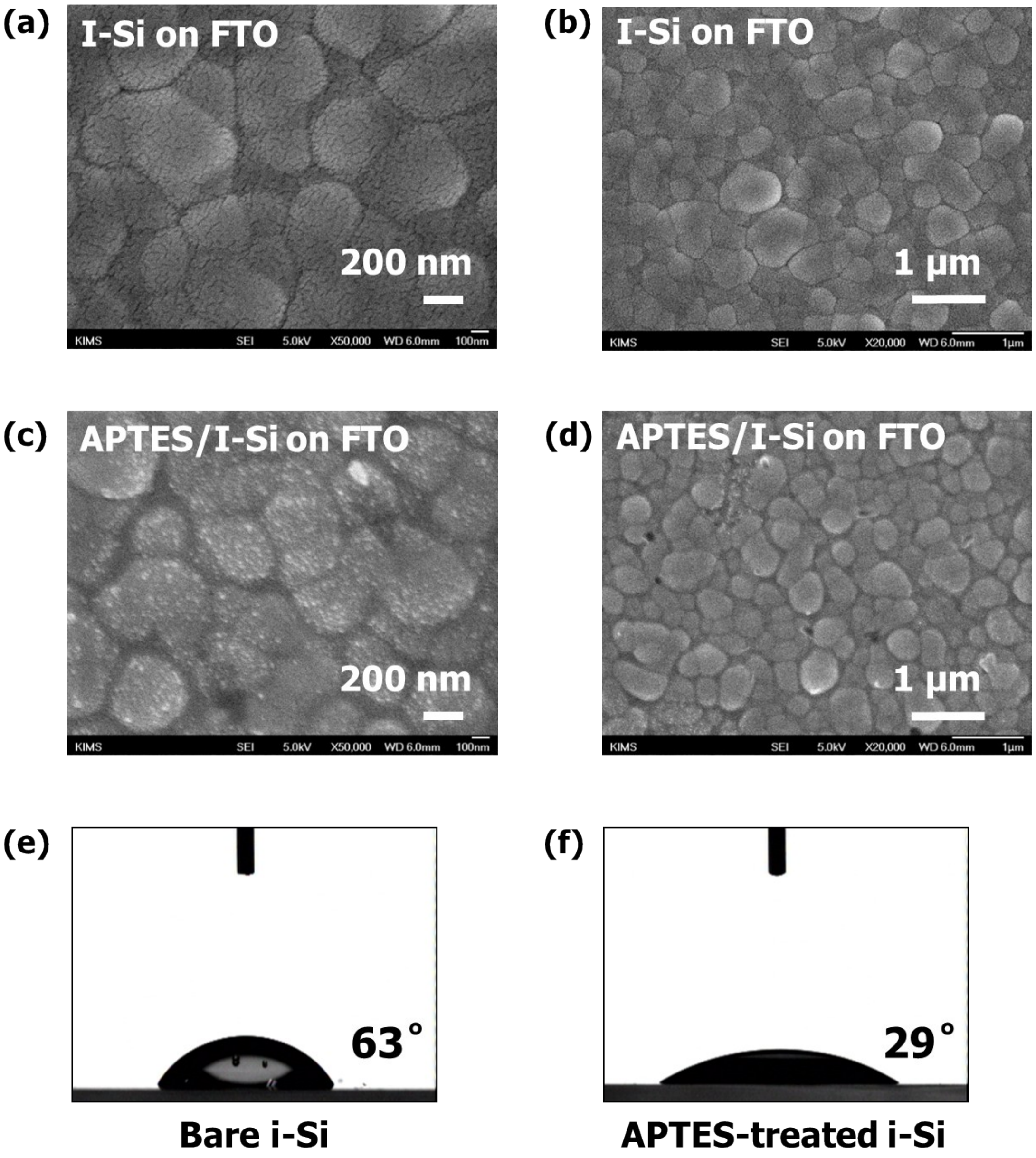
The orientation of APTES molecules on the silicon surface was analyzed by Acres et al.[1] using metastable induced electron spectroscopy (MIES), UPS, and XPS. We have demonstrated the speculated dipole directions for each orientation of the molecules on the surface. The presence of an additional -NH_2 peak (at ~401 eV, Fig. 2) in the N1s XPS profile indicates that an inverse molecular orientation (Fig. S2(e)) was achieved in this study. This additional peak corresponds to the presence of hydrogen-bonded -NH_2 and is similar to the bonding peak reported previously[1]. In addition, we also observed a Si-O peak at ~103 eV, indicating the presence of Si-O bonds at the surface of i-Si. This shows that the dipole orientation was towards the i-Si layer and away from the cathode.

Figure S3. AFM analysis of the (a) bare FTO and (b) bare i-Si and (c) APTES-treated i-Si layers along with their representative root mean square (RMS) values.



We analyzed the surface roughness of bare FTO using AFM and the RMS value was found to be ~30.81±0.3 nm. The bare i-Si layer showed a slightly smoother surface (RMS = ~30.21±0.1 nm) which indicated a uniform deposition of i-Si on FTO and the roughness value observed was owing to the high surface roughness of the underlying FTO substrate. However, the surface roughness for APTES-treated i-Si layer was further decreased RMS = ~29.69±0.1 nm, which presents that there was no significant change in the surface morphology after the deposition of APTES layer in fact a uniform and smoother coating of APTES on i-Si layer was obtained. This surface morphology is beneficial in terms of low optical losses as APTES already lacks the presence of any chromophores that could absorb light (especially >290 nm). So, we speculate that the adverse absorbance/reflectance effect in the device due to the incorporation of this thin layer (~2 nm) could be neglected.[2, 3]

Figure S4. UHR FE-SEM images of (a), (b) i-Si on FTO (c), (d) APTES deposited on i-Si/FTO at magnifications of ×50K and ×20K. CA analysis of a deionized water droplet on the (e) bare i-Si and (f) APTES-treated i-Si layers



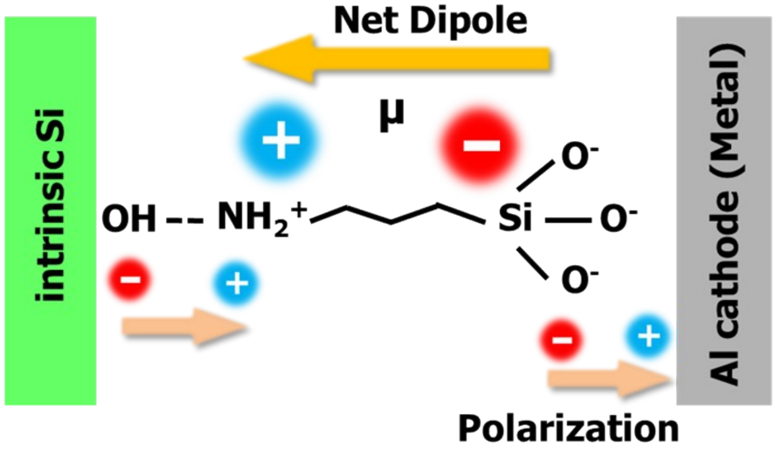
Bare i-Si

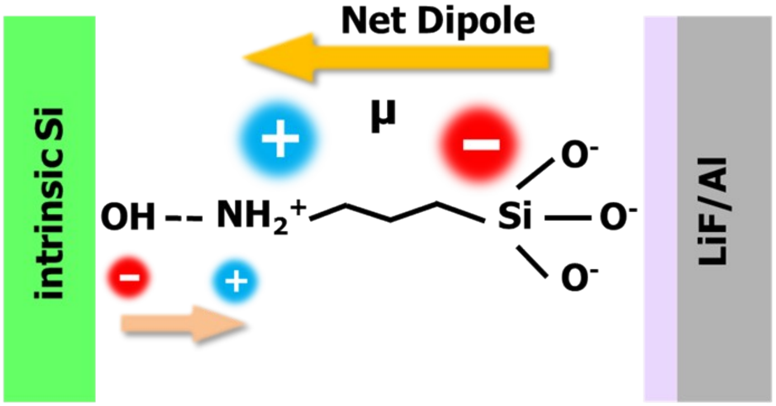
APTES-treated i-Si

The UHR FE-SEM images were in coherence with the observed surface roughness (RMS = 30.21 nm) for the i-Si layer owing to the underlying FTO layer's rough morphology (RMS = 30.81 nm), as shown in Fig. S3. Also, the APTES-deposited i-Si layer demonstrated slightly lower surface roughness (RMS 29.69 nm) indicating a uniform deposition of the APTES layer.

The results showed that both the layers were deposited uniformly and the smoother surface of the APTES layer resulted in a better contact between the interfaces for efficient charge extraction. The CA analysis results showed that the bare i-Si layer was hydrophobic (~63°), while the APTES-treated i-Si layer was hydrophilic (~29°). The CA of the surfaces was mainly affected by two factors; their physical morphologies and chemical compositions. The UHR FE-SEM images showed that the surface morphologies of the bare i-Si and APTES-treated i-Si layers were similar. Hence, the decrease in the CA of the i-Si layer with the addition of APTES can be attributed only to the chemical nature of the layer. As mentioned before, APTES is a NH_2-based material, and the arrangement of its functional groups facilitated the generation of an interfacial dipole. The hydrophilic nature of the APTES layer can be attributed to the bipolar nature of APTES by which it attracts bipolar liquids (such as water) and could conclude the presence of interfacial dipole.[4]

Figure S5. Schematic of the dipoles formed when APTES was in (a) contact with the metal surface (b) contact with the LiF/Al surface


(a) APTES in direct contact with metal surface


(b) APTES in contact with LiF surface

The APTES-treated devices showed a high Rs of ~27.60 Ω.cm^2 as compared to the devices without APTES (18.20 Ω.cm^2). This higher Rs (for APTES-based devices) can be explained using the polarization model for SAM layers[5] according to which the direct contact of dipolar molecules with a metal surface induces molecule-metal polarization. When APTES molecules were in direct contact with the Al cathode, the molecular-metal interface induced a dipole opposite to the net dipole of the molecule at the junction. This reduced the overall effect of the net dipole formed by the APTES layer, thus increasing the Rs of the device. When LiF (1.5

nm) was deposited in front of the Al cathode (LiF/Al), the direct contact of APTES molecules with the metal could be avoided. This resulted in a decrease in the Rs of the APTES/LiF/Al device (11.70 $\Omega.cm^2$) and was found coherent with the model [5], where polarization effect was avoided in case of free/organic surface.

Reference

1. R. G. Acres, A. V. Ellis, J. Alvino, C. E. Lenahan, D. A. Khodakov, G. F. Metha and G. G. Andersson, *The Journal of Physical Chemistry C*, 2012, **116**, 6289-6297.
2. *MSDS (Materials Safety Data Sheet) for 3-Aminopropyltriethoxysilane)* *https://pubchem.ncbi.nlm.nih.gov/compound/3-Aminopropyltriethoxysilane#section=Ecological-Information*.
3. S. Mallakpour and F. Zeraatpisheh, *Journal of Experimental Nanoscience*, 2014, **9**, 1035-1050.
4. C. Van Oss, L. Ju, M. Chaudhury and R. Good, *Journal of Colloid and Interface Science*, 1989, **128**, 313-319.
5. H. L. Yip, S. K. Hau, N. S. Baek, H. Ma and A. K. Y. Jen, *Advanced Materials*, 2008, **20**, 2376-2382.