Open-Circuit Photovoltage Exceeding 950 mV with an 840 mV Average at Sb$_2$S$_3$–Thianthrene$^{+/0}$ Junctions Enabled by Thioperylene Anhydride Back Contacts

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ABSTRACT: Covalently attached perylene monolayers serve as back contacts for Sb$_2$S$_3$ photoelectrochemical cells with a thianthrene$^{+/0}$ front, rectifying contact. Covalent attachment of perylenetetracarboxylic dianhydride, PTCDA, to Si(111) utilizes an anhydride-to-imide conversion at surface-attached amines. For Sb$_2$S$_3$ solar absorbers, we hypothesized that a terminal thioperylene anhydride, i.e., S=C–O–C=S, formed from thionation of the terminal perylene anhydride would serve as a soft, electron-selective and hole-blocking back contact. We explored several routes to convert carbonyls to thiocarbonyls on surface-attached perylene anhydrides including Lawesson’s reagent, P$_4$S$_{10}$, and a P$_4$S$_{10}$–pyridine complex. Here, P$_4$S$_{10}$ in toluene yielded the highest conversion as quantified by thioperylene-anhydride-S-to-imide-N ratios in X-ray photoelectron spectroscopy (XPS). Spectra demonstrated minimal residual reagent as determined by the absence of quantifiable phosphorus following sonication and rinsing. Photoelectrochemistry yielded an average $|V_{oc}| = 840 \pm 90$ mV with the highest value of 952 mV under ELH-simulated AM1.5G illumination for chemical-bath-deposited Sb$_2$S$_3$ in the strongly oxidizing thianthrene$^{+/0}$ redox couple when thioperylene-anhydride-tethered surfaces formed the back contact. Sb$_2$S$_3$ absorbers in which perylene anhydride, esters, thionoesters, and thiols form the back contact yielded signiﬁcantly decreased $|V_{oc}|$ magnitudes vs Sb$_2$S$_3$ on perylene-thioanhydride-terminated surfaces. We attribute the large $V_{oc}$ to the combination of favorable sulfur-functionalized surfaces for deposition, charge transfer properties of the perylene layer, and use of the thianthrene$^{+/0}$ redox couple.

1. INTRODUCTION

Stacking multiple solar absorbers with different band gaps in a tandem configuration represents one viable pathway for overcoming the Shockley–Queisser limit on the efficiency of nonconcentrated single-absorber photovoltaics. While III–V tandem-junction solar cells enjoy high efficiency, their large expense drives research into inexpensive alternatives in which silicon forms the bottom, low-band-gap light-absorbing material. Recent pathways to such inexpensive morphologies include perovskite–silicon tandem-junction cells; however, materials beyond perovskites must be considered as well.

Among the ~1.6–1.8 eV band gap materials that would best pair with a bottom silicon absorber, chalcogenide materials demonstrate promise. Various sulfides of tin, lanthanum, cerium, cadmium, copper, and antimony are highly stable, straightforwardly synthesized, and have favorable band gap energies for tandem photovoltaics (PV). Antimony sulfide, Sb$_2$S$_3$, in particular possesses an ideal 1.7 eV band gap to pair with silicon bottom absorbers and has been studied extensively. Despite early results of open-circuit photovoltages of 770 mV from bath-deposited Sb$_2$S$_3$, one-half of a volt remains “missing” from experimental $V_{oc}$ values for Sb$_2$S$_3$, and research must address this shortcoming for this otherwise compelling PV absorber material. Among the challenges for Sb$_2$S$_3$, researchers implicate possible interfacial chemical defects that lead to deleterious recombination centers and a concomitant decrease in performance. Thus, we are motivated to explore soft materials and surfaces that would enable a high-electronic-quality interface between lattice intervening 25 years have seen little improvement. One report of 900 mV derives from a bath-deposited film with preannealed material that is likely the ~2.2 eV band gap amorphous, molecular precursor of Sb$_2$S$_3$, rather than the crystalline inorganic material itself.

As such, approximately one-half of a volt remains “missing” from experimental $V_{oc}$ values for Sb$_2$S$_3$, and research must address this shortcoming for this otherwise compelling PV absorber material. Among the challenges for Sb$_2$S$_3$, researchers implicate possible interfacial chemical defects that lead to deleterious recombination centers and a concomitant decrease in performance. Thus, we are motivated to explore soft materials and surfaces that would enable a high-electronic-quality interface between lattice...
mismatched Si and Sb₂S₃, which may one day be extended to enable tandem-junction PV arrangements.

Ordered, well-defined organic monolayers may provide such a high-quality interface between silicon and a top-absorber material. In establishing “well-defined” organic monolayers, we consider those that are covalently bound to silicon on one end and on the other end terminate in some chemical functionalities that resemble the top-absorber material. We recently demonstrated that ammonium-terminated short alkyl chains can chemically glue perovskites to silicon to yield good photoelectrochemical performance.9,19 While this established the viability of a monolayer of soft, organic back contacts, alkyl chains do not demonstrate electron or hole selectivity that is desirable at semiconductor contacts.20,21 Separately, we demonstrated the covalent attachment of perylenetetracarboxylic dianhydride, PTCDA, to Si(111) that leverages the anhydride-to-imide conversion on a surface-attached aniline molecule.22 As part of a broader class of rylene compounds, perylenes are particularly desirable for their electronic tunability, covalent coupling, redox activity, and their low cost due to their use as industrial pigments.23−30 Therefore, rylene and their derivatives should enable an interconnection layer between inorganic absorbers that is soft, electronically tunable, and chemically matched to each contacting phase.22,33 However, such interconnections have not been demonstrated to metal sulfides such as Sb₂S₃. We hypothesize that sulfur termination on the organic perylene monolayers may yield such an interconnection between silicon and Sb₂S₃. The creation and testing of such connections motivates the present investigation.

Herein, we attached PTCDA to a silicon surface, explored methods to effect sulfurization of the terminal anhydride species, bath-deposited Sb₂S₃ from literature techniques, and investigated the resulting solar-energy-conversion performance. Figure 1 outlines the reaction schemes under study to yield sulfur-terminated surface 4 with a series of thionation reagents that, respectively, yield a thionated anhydride-terminated surface 5 or a di(ethyl thionoester)-terminated surface 6. Thionation reagents included Lawesson’s reagent (LR),35 P₄S₁₀,36 and a P₄S₁₀-pyridine complex4 that each convert C=O to C=S.41−43 X-ray photoelectron spectroscopy (XPS) verified thionation and the presence or absence of reagent contaminants on surfaces. Nonaqueous photoelectrochemistry of Sb₂S₃ deposited on surfaces 1−3, 5−6, and thiol-terminated control surface 7 in thianthrenes/Py correlated the relationship between the chemical structure of the back contact and the subsequent open-circuit photovoltage, V_OC, under illumination. We utilized thianthrenes33−34 for its facile, one-electron transfer at a strongly oxidizing potential to yield a large rectifying barrier height in contact with n-type Sb₂S₃ and for its use in other energy-conversion applications.44 We discuss the results in the context of soft, monolayer interconnections for tandem-junction photovoltaics that combine nontraditional absorbing materials with silicon.

2. RESULTS

2.1. Thionation of Surface-Tethered Perylene Anhydrides. As presented in Figure 1 and described more thoroughly in Section 5 and the Supporting Information section, formation of an amine-terminated surface 2, a perylene-anhydride-terminated surface 3, and a diethyl-ester-terminated surface 4 followed efforts as described previously.22 Treatment of degenerately doped n⁺-Si(111) with 3-amino-propyltrimethoxysilane yields amine-terminated surface 2, from which treatment with PTCDA and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in ethanol and dimesitylformamide (DMF) yielded perylene-anhydride-terminated surface 3. Subsequent reaction of the perylene-anhydride-terminated surface 3 with additional DBU in ethanol and bromoethane yielded the diethyl-ester-terminated surface 4. Validation by XP and transfection IR spectroscopy revealed features that were well aligned with those previously published spectra and will not be presented herein. The present study focuses on the thionation of surface 3 and resulting impact of solar-energy conversion at Sb₂S₃ electrodes with such thionated surfaces serving as back contacts.

Figure 2 presents XP spectra for two representative thioperylene-anhydride-terminated surface 5 samples that were produced by a three-day, room-temperature reaction
Figure 2. XP spectra for representative samples of thiophenyl-p-phenylene-anhydride-terminated surface 5 following (A) a singular rinse and (B) repeated sonication and rinsing. Fits to Si-phonon-ascribed features are in tan, with green features fit sulfur- and phosphorus-ascribed photoelectrons. The presence of oxidized phosphorus for the once-rinsed sample in (A) and the absence of such features for the sonicated sample in (B) indicates that a thorough sonication protocol is necessary to sufficiently remove the byproducts of the thionation procedure that converts surface 3 to surface 5.

with $P_4S_{10}$ in toluene. Each set of scans employs $y$-axis scaling relative to the amplitude of the O 1s feature as denoted. Importantly, frame A presents spectra from a sample that was not aggressively cleaned following the thionation reaction, while frame B presents spectra from a sample that was cleaned with repeated sonication and rinsing steps as detailed in Section 5. The N 1s region for the once-washed sample in frame A includes two features that may include the imide and amine nitrogen at $\sim 401$ eV as well as a feature at $403$ eV that may be due to the interaction of nitrogen atoms with oxidizing species that remain following insufficient rinsing. In contrast to the N 1s region for the once-washed sample that region for the sonicated sample in frame B reveals a singular feature that well resembles N 1s signals observed for imide-containing, surface-tethered perylenes in our previous study. Both regions reveal O 1s and Si 2p structures as previously observed for perylene attachment that utilizes silane linkages to silicon with a thin interfacial chemical oxide layer as well as C 1s features that include desired surface species and adventitious contamination.

Figure 2 clusters the S 2s together with S 2p and the P 2s and P 2p regions for relational comparison. Important to the interpretation of sulfur and phosphorus features, the S 2p and P 2p regions are both complicated by the overlap of phonon-loss features from crystalline silicon. The S 2p region coincides with the first plasmon loss feature from Si 2s at $\sim 169$ eV, while the P 2p region coincides with the second plasmon loss feature from Si 2p at $\sim 134$ eV. Importantly, these plasmon loss features are significantly more broad than typical photoelectron features and may be deconvoluted from photoelectron signals with care. In the present work, such care includes the observation of the respective 2s regions for S and P in addition to their more typical 2p regions to help establish the relative contribution to each photoelectron signal. Figure 2 displays green-shaded fits for S- and P-ascribed photoelectron signal with 2s features utilizing a singular Gaussian feature and 2p features including their respective spin-orbit-split structure with mutually identical full width at half-maximum (fwhm) values. Figure 2 includes tan-shaded fits in the sulfur and phosphorus regions that we ascribe to the broad features of silicon-phonon-loss photoelectrons. For each of the P 2p regions shown, two features best fit the silicon-phonon-ascribed features that we constrained by mutually identical fwhm values within a region. While the P 2p region for the once-rinsed sample in Figure 2A contains numerous features, analysis of the sonicated surface in Figure 2B informs the fitting methodology. The absence of P 2s features for the well-sonicated sample in frame B indicates that there should be no phosphorus contributions to the respective P 2p region, and that the broad spectral features at $\sim 133$ and $\sim 138$ eV are due to silicon-phonon-loss photoelectrons. The phonon structure determined for the P 2p region in frame B instructs the relative assignments of phonon structure for the P 2p region in frame A, and we ascribe the remainder of the photoelectron signal to contribution from phosphorus itself. The overall similarity of the shape, size, and location of the silicon-phonon-ascribed features between the spectra in frames A and frame B gives confidence in sulfur or phosphorus feature contributions versus silicon phonons to the overall photoelectron structure. For the XP spectra analyzed for each thionation reagent as with the representative spectra in Figure 2, the green fitted features ascribed to S 2p occur at $\sim 164$ eV with S 2s features at $\sim 228$ eV that reasonably correspond to nonoxidized, organic sulfur. Nonoxidized organic sulfur features for thiols, sulfides, and thiones typically appear between 163.5 and 164 eV and are well differentiated from increasingly oxidized organic sulfur groups including sulfinyl, sulfone, and sulfonate species that appear between 165.5 and 168 eV. Importantly, the energetic separation between nonoxidized and oxidized sulfur features is greater than the 1.18 eV spin-orbit splitting between the $J = 3/2$ and 1/2 peaks for S 2p photoelectrons, which appears as a resolvable shoulder in our instrument as shown for the S 2p region in Figure 2A. Thus, we interpret the sulfur features to indicate the successful conversion of the C=O groups of surface 3 to the C=S species on surface 5. The green fits to P 2p$_{1/2}$-ascribed photoelectrons are centered at $\sim 134$ eV and the P 2s-ascribed photoelectron features at $\sim 192$ eV, which indicate highly oxidized phosphorus. Importantly, the presence of oxidized phosphorus for the once-rinsed sample in frame A and the absence of such features for the sonicated sample in
frame B indicates that a thorough sonication protocol is necessary to sufficiently remove the byproducts of the thionation procedure that converts surface 3 to surface 5.

As a thionation control, we reacted the aminopropyl-terminated surface 2 with P₄S₁₀ under similar reaction conditions as converted surface 3 to surface 5 above with multiple thorough sonication and rinsing steps prior to photoelectron analyses. XP spectra demonstrated no features ascribable to sulfur and only those of the silicon-phonon-loss feature that resembled the broad, tan-fitted curve in the S 2p region as in Figure 2. Across the three samples studied, XP spectra of the P 2s and P 2p regions demonstrate trace- to no-fittable feature that may be ascribable to phosphorus. One sample demonstrated trace features ascribable to oxidized phosphorus with a P 2p₃/2 peak centered at ~134 eV. We interpret these results to indicate that P₄S₁₀ does not thionate surface 2.

Beyond P₄S₁₀ reactions as presented in Figure 2, initial thionation reactions utilized LR in refluxing solvent and in line with previous reports.38–40 Instead of S 2s and S 2p features corresponding to newly formed C==S bonds on the surfaces, XP spectra demonstrated both oxidized sulfur and phosphorus species with no-fittable features ascribable to nonoxidized organic sulfur. Other reports of LR mention its instability toward decomposition or polymerization at temperatures above 110 °C.38,48 Thus, the refluxing LR may be favoring other pathways over the successful conversion of surface 3 to surface 5. Instead, we focused on longer, ambient-temperature thionation experiments.

In observing sulfur attributable to C==O-to-C==S conversions and in establishing a procedure to clean thionated surfaces 5, Figure 3 presents representative XP spectra of the S 2s region for the thionation protocols that utilized a three-day, ambient-temperature reaction. Figure 3 normalizes the amplitudes and magnifies each S 2s spectrum by 5X vs the amplitude of each respective Si 2p spectrum, as in Figure 2. Reactions were attempted on at least three samples to develop statistics and obviate possible negative results. As revealed by the trace-fittable feature in frame A and the absence of fittable features in frame B, both LR in toluene and the P₄S₁₀-pyridine complex yielded very low quantities of sulfur that we could attribute to C==S production. In contrast to the sulfur-donating organic complexes that demonstrate only trace reactivity, P₄S₁₀ in either toluene or dichloromethane (DCM) demonstrates significant S 2s features ascribable to C==S production.

An analysis of S 2s to N 1s peak areas more rigorously quantifies the coverage of sulfur ascribed to organic C==S bonds and guide ongoing thionation procedures. Accounting for relative sensitivity factors as described in the Supporting Information, S/N ratios of surface 5 samples produced by P₄S₁₀ in either toluene or DCM as in Figure 3C or D were 2.1 ± 0.4. Sensitivity-factor-corrected S/N ratios for surface 5 samples produced by LR in toluene as in Figure 3A were 0.4 ± 0.1 and produced via the P₄S₁₀-pyridine complex as in Figure 3B ratios were 0.1 ± 0.1. This analysis of area ratios does not rigorously employ overlayer models that account for the attenuation of N 1s photoelectron signals that have to travel through the perylene overlayer.23,49,50 As such, we interpret the sulfur-to-nitrogen area ratio to imply a qualitatively high conversion of C==O to C==S groups as affected by the reaction with P₄S₁₀ in toluene or DCM. Considering the high thionation conversion afforded by the 3-day, ambient-temperature reaction of P₄S₁₀, all subsequently presented surface 5 and surface 6 samples with Sb₂S₃ deposition utilized the P₄S₁₀-in-toluene thionation procedure.

2.2. Deposition and Surface Etching of Sb₂S₃. Figure 4 presents representative XP spectra of the combined Sb 3d and O 1s region for Sb₂S₃ that highlight the effect of an HCl(aq) etch. Figure 4 includes spectra from (A) a nascent sample of Sb₂S₃ and (B) a 10-s HCl(aq) etch. As revealed by the relative decrease in the contribution of the blue fitted area for (B) an etched sample spectrum, the HCl(aq) etch greatly attenuates the oxygen-to-sulfur ratio relative to the contribution on a nascent Sb₂S₃ sample, (A).
directly following, and (B) a sample following in HCl(aq) etch consisting of 10 s in 1.2 M HCl(aq) followed by a water rinse and drying in argon. With Sb 3d \textsubscript{5/2} peak centers at ~529.5 eV, we ascribe fitted doublets in green to photoelectrons from antimony in Sb\textsubscript{2}S\textsubscript{3}. Similarly, oxidized antimony features are well fit by blue doublets with Sb 3d \textsubscript{5/2} at ~531.0 eV. A broad, red-shaded feature centered at ~532 eV represents O 1s features that likely originate both from adventitious sources and from metal oxides that are not straightforwardly deconvolved from photoelectrons emanating from Sb 3d \textsubscript{5/2}. The y-axis scaling in Figure 4 accommodates equal total fitted areas between the two frames, which highlights the relative contribution of the blue oxidized antimony features to the green antimony-in-Sb\textsubscript{2}S\textsubscript{3} features in each spectrum. A comparison of the nascent sample spectrum in frame A to the etched sample in frame B reveals that the large relative contribution of interfacial oxidized antimony is significantly attenuated by the HCl(aq) etch. Considering the efficient removal of oxidized antimony species, Sb\textsubscript{2}S\textsubscript{3} electrode preparation included a 10 s submersion in 1.2 M HCl(aq) followed by a water rinse and drying in argon that directly preceded transfer to the recirculating glove box for photoelectrochemistry.  

2.3. Photoelectrochemistry in a Thianthrene\textsuperscript{+0} Redox Couple. We deposited Sb\textsubscript{2}S\textsubscript{3} on surfaces 1–3 and on surfaces 5–7 via previously published bath-deposition protocols for photoelectrochemical quantification. Figure 5A presents photoelectrochemical current-density–potential, J–E, scans for a Sb\textsubscript{2}S\textsubscript{3} electrode on the thioperylene-anhydride-terminated surface 5 with a particularly high open-circuit photocurrent under ELH-simulated 100 mW cm\textsuperscript{-2} AM1.5 G “1 Sun” illumination (solid trace) and in the absence of illumination (dashed trace). For the photoelectrochemical scan in Figure 3, the open-circuit photovoltage, \( V_{oc} \), is ~952 mV as revealed by the 100\times inset but suffers from very low short-circuit current density, \( J_{sc} \), and fill factor, ff, values. For the illuminated electrode in Figure 3, \( J_{sc} \) = 2.25 mA cm\textsuperscript{-2} and ff = 0.07. The difference between the solid trace for an electrode under illumination and the dashed trace for the same electrode in the absence of illumination demonstrates good photocurrent response. 

From the well-established behavior of n-Si in nonaqueous photoelectrochemistry,\textsuperscript{51–53} scans of lightly doped, 1.3–2.5 Ω cm n-Si(111) established the performance of a thianthrene\textsuperscript{+0} photoelectrochemical cell with 1 M LiClO\textsubscript{4} in acetonitrile. Figure 5B presents a characteristic scan for a lightly doped n-Si electrode in which \( V_{oc} \) = −560 mV, \( J_{sc} \) = 0.99 mA cm\textsuperscript{-2}, and ff = 0.26. For five lightly doped n-Si electrodes in the nonaqueous thianthrene\textsuperscript{+0} cell, \( V_{oc} \) values ranged between ~500 and ~650 mV, which agrees well with previous photoelectrochemical results for n-Si at highly rectifying liquid contacts (i.e. acetylferrrocene\textsuperscript{+0}).\textsuperscript{54} However, present current density and fill factor values remain well below ~25 mA cm\textsuperscript{-2} for highly polished and AM1.5G light-limited n-Si.\textsuperscript{51} As mentioned in the Supporting Information, only a small, ~10–15 mV, quantity of the added thianthrene dissolved into the acetonitrile with visibly nondissolved solid at the liquid surface. We interpret the poor current density and fill factor values observed for both silicon and Sb\textsubscript{2}S\textsubscript{3} electrodes to the low solubility of neutral thianthrene in the electrochemical cell. The low solubility of thianthrene bears similarity to the low solubility both of neutral decamethylferrocene and of methyl viologen dichloride in acetonitrile that limits interpretation of \( J_{sc} \) and ff values, while \( V_{oc} \) interpretations remain valid.\textsuperscript{55} Given the present cell limitations, we do not ascribe rigorous meaning to redox-concentration-limited \( J_{sc} \) and ff values, but rather utilize \( V_{oc} \) behavior to understand Sb\textsubscript{2}S\textsubscript{3} electrodes as a function of Sb\textsubscript{2}S\textsubscript{3} back-contact surface chemistry. Separately from photoelectrochemistry of lightly doped n-Si(111), the dashed trace in Figure 5B presents a scan under illumination for a degenerately doped n-Si(111) electrode that demonstrates \( |V_{oc}| < 10 \) mV. Importantly, the dashed trace for n-Si in Figure 5B represents the effective performance of surface 1 by itself with no Sb\textsubscript{2}S\textsubscript{3} deposited on top of it. The minimal \( V_{oc} \) at n-Si(111) electrodes demonstrates that n-Si(111) substrates contribute negligibly to the overall \( V_{oc} \) values acquired for Sb\textsubscript{2}S\textsubscript{3} electrodes when surfaces 1–3 and 5–7 serve as the back contacts. 

Table 1 presents absolute value \( V_{oc} \) average and standard deviation values for Sb\textsubscript{2}S\textsubscript{3} electrodes in thianthrene\textsuperscript{+0} as a function of their back-contact surfaces 1–4 and 5–7. Sample sizes of at least four serve each electrode type. As revealed by Table 1, the changes in interfacial chemistry at back contacts yield a profound impact to the resulting \( V_{oc} \) of Sb\textsubscript{2}S\textsubscript{3} photoelectrodes. For instance, \( V_{oc} \) values are nearly zero for Sb\textsubscript{2}S\textsubscript{3} photoelectrodes with amine-terminated back-contact surfaces. From 2, \( V_{oc} \) magnitudes increase for electrodes with propane-thiol-terminated back-contact surfaces, with di(ethyl thionoester)-terminated back-contact surfaces 6, and with both nonfunctionalized n-Si 1 and perylene-anhydride-terminated
Table 1. With Surfaces 1–3 and 5–7 Serving as Back Contacts, Open-Circuit Photovoltage Magnitudes, $|V_{oc}|$, Quantify the Performance of Sb$_2$S$_3$ Photoelectrodes ELH-Simulated AM1.5G “1 sun” Illumination

| Sb$_2$S$_3$ back-contact surface | $|V_{oc}|$ (mV) |
|----------------------------------|-------------|
| 1, n’-Si                         | 380 ± 160   |
| 2, aminopropyl                   | 8 ± 6       |
| 3, perylene anhydride            | 380 ± 140   |
| 5, thioperylene anhydride        | 840 ± 90    |
| 6, di(ethyl thionoester)         | 300 ± 200   |
| 7, propanethiol                  | 220 ± 110   |

“The $|V_{oc}|$ values were the highest for electrodes of Sb$_2$S$_3$ that was deposited on thioperylene-anhydride-terminated surface 5. Each value represents a minimum sample size of four electrodes.

Back-contact surfaces 3. Sb$_2$S$_3$ photoelectrodes with the thioperylene-anhydride-terminated back-contact surfaces 5 demonstrated the highest magnitude $|V_{oc}| = 840 ± 90$ mV based on four electrodes with $V_{oc}$ values of $-741, -827, -844,$ and $-952$ mV, as shown in Figure 5A. Thus, thioperylene-anhydride-terminated surfaces yield back contacts to Sb$_2$S$_3$ that enable very large $V_{oc}$ magnitudes relative to other back-contact surface terminations.

Lastly, scans established potentials for the thianthrene$^{+/0}$ cell with 1 M LiClO$_4$ in acetonitrile vs standard potentials. The open-circuit voltage scans acquired the potential of a Pt wire in a solution of thianthrene$^{+/0}$, with 1 M LiClO$_4$, di(ethyl thionoester) 300 ± 140 mV, thioperylene anhydride 840 ± 90 mV and, n +-Si 380 ± 140 mV, as shown in Figure 5A. Thus, thioperylene-anhydride-terminated surfaces yield back contacts to Sb$_2$S$_3$ that enable very large $V_{oc}$ magnitudes relative to other back-contact surface terminations.

3. DISCUSSION

The present study sequentially investigated methods for producing a soft, organic-monolayer-based surface for Sb$_2$S$_3$ back contacts and quantifying the energy conversion behavior at a highly rectifying liquid-junction front contact to Sb$_2$S$_3$ photoelectrodes. We initially hypothesized that back contacts comprised of sulfur-terminated perylene-based monolayers would yield high open-circuit photovoltages at bath-deposited Sb$_2$S$_3$ photoelectrodes. The perylene itself should enable electron conduction and hole blocking at the back contact. Researchers report half-wave oxidation and reduction potentials at $+1.56$ V and $-0.55$ V vs SCE for perylene di(phenyl)imides with no bay-position derivatization. If $-qE_{SCE} = -4.69$ eV vs $E_{ac}$ based on conversions above, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of molecular perylene diimide species would be at approximately $-4.1$ and $-6.25$ eV vs $E_{ac}$. Thus, the perylene LUMO should be well aligned to enable photo-generated electron conduction from the Sb$_2$S$_3$ conduction band to the back electrode potentialstat contact, while the HOMO should effectively block hole conduction from the Sb$_2$S$_3$ valence band.

In concert with our previously reported attachment of perylenes to silicon surfaces, photoelectron spectra reveal successful thionation and cleaning procedures. Spectroscopic determinations of the conversion of O=C−O−C=O perylene anhydrides to S=C−O−C=S thioperylene anhydrides presents challenges. Previous perylene surface attachment utilized infrared-active carbonyl stretching modes that are unique among anhydride, imide, and ester moieties. Further, the C=O vibration is particularly strong in infrared spectra due to the large dipole change during the carbon–oxygen vibration that enables submonolayer detection of carbonyl-containing surface adsorbates. In contrast to C=O, there is a significantly smaller electronegativity difference between carbon and sulfur, and the resulting C=S oscillation presents observational challenges at monolayer-level surface coverages via traditional IR techniques. Thus, observation of X-ray photoelectrons that are ascribable to nonoxidized, organic

Figure 6. CV at a Pt wire in a solution of thianthrene$^{+/0}$, Th$^{+/0}$, with 1 M LiClO$_4$ in acetonitrile. Spiking the solution with ferrocene$^{+/0}$, Fc$^{+/0}$, and acetylferricene$^{+/0}$, AcFc$^{+/0}$, establishes a Nernstian formal potential for thianthrene$^{+/0} = 820$ mV vs $E^0(Fc^{+/0})$ in this supporting electrolyte and solvent combination.
sulfur is a viable—albeit indirect—method for revealing thionation, particularly when thionated surfaces demonstrate an absence of byproduct contaminants. Among thionating agents, Lawesson’s reagent, LR, demonstrates high success in converting molecular C==O species to C==S groups.\(^{35}\) However, in our hands, LR did not thionate the carbonyls of the perylene anhydrides in surface 3 as well as thionation via P_{S_{10}} in dry, nonpolar solvents. Similarly to LR, the P_{S_{10}}−pyridine complex demonstrated very low thionation yields as compared to noncomplexed P_{S_{10}}. The limited flexibility in the surface-tethered perylene anhydrides, steric crowding from adjacent perylene anhydrides, and the overall size of both the LR complex and the P_{S_{10}}−pyridine complex may cumulatively limit available orientations between those reagents and the anhydride to realize successful thionation. In contrast to both LR and the P_{S_{10}}−perylenecomplex, the smaller P_{S_{10}} molecule additionally has a higher degree of symmetry that may enable more favorable orientations in the limited space available for converting surface 3 to surface 5.

Exploration of the \(V_{oc}\) values in Table 1 supports the hypothesis of sulfur-terminated perylene-based monolayers yielding large \(V_{oc}\) magnitudes at Sb_{2}S_{3} photoelectrodes with important subtleties. For instance, the presence of sulfur in the interfacial region of the organic molecule does not necessarily yield high \(V_{oc}\) values. The high magnitude of the \(V_{oc}\) values for Sb_{2}S_{3} on the thioperylene-anhydride-terminated surface 5 directly supports the hypothesis, but values show the comparatively smaller magnitudes for Sb_{2}S_{3} on the di(ethyl thionoester)-terminated surface 6. Further, propanethiol-terminated surface 7 as a back contact yielded Sb_{2}S_{3} electrodes with even poorer \(V_{oc}\) values as compared to Sb_{2}S_{3} on surface 6. Such divergent \(V_{oc}\) magnitudes between the sulfur-containing surfaces may be due to different interfacial carrier transfer efficiencies, different templating of the Sb_{2}S_{3} films on the surfaces, or other reasons that merit future study. The possibility of templated growth is particularly intriguing as researchers implicate high performance when film growth aligns with the Sb_{2}S_{3} ribbon propagation vector,\(^{13}\) which is the [010] vector in recent reports\(^{38}\) and the [001] vector in older studies.\(^{34}\) Separate, the contrasting \(V_{oc}\) magnitudes for Sb_{2}S_{3} with perylene-anhydride-terminated surface 3 vs perylene-thioanhydride-terminated surface 5 indicate that sulfoxidation of these otherwise identical back-contact surfaces is critically important for large \(V_{oc}\) values at Sb_{2}S_{3} photoelectrodes.

The 840 ± 90 mV average and the 952 mV maximum-observed \(|V_{oc}|\) magnitude represents a significant gain, but further improvements remain for realizing high-efficiency Sb_{2}S_{3} photoelectrodes. Based on the n-Sb_{2}S_{3} band edge positions and its highly oxidizing formal potential, thianthrene\(^{3/0}\) forms highly rectifying contacts that are necessary for large \(V_{oc}\) magnitudes. However, experimental current density values in the present study were poor as photogenerated holes had an insufficiently low interfacial concentration of thianthrene to oxidize, due to its poor solubility in acetonitrile. Unfortunately, neutral thianthrene and thianthrene tetrafluoroborate salts necessary for a stable redox contact demonstrate nearly orthogonal solubility by, respectively, best dissolving in nonpolar and polar-aprotic solvents. Solid-state or more concentrated liquid-junction contacts with work functions exceeding 5.5 eV should yield light-limited photocurrents and significantly improved fill factors. Further, the purple color of the solution indicates strong absorption of longer wavelengths in the visible spectrum that are already overrepresented by the tungsten−halogen ELH bulb as employed vs the solar spectrum.\(^{65}\) Taken together, the present results demonstrate significant gains toward finding the missing \(V_{oc}\) of Sb_{2}S_{3} photoelectrodes and imply that changes in illumination and the front, rectifying contact may yield further gains. Ongoing studies must address the precise carrier dynamics and possible templating phenomena that yield high \(V_{oc}\) magnitudes for Sb_{2}S_{3} electrodes with a thioperylene-anhydride-based back contact. Carrier dynamics studies should include quantifying the effect of thionation on the HOMO and LUMO energies via electrochemistry and optimizing those energy levels through bay-position derivatization on the aromatic chain.\(^{23,62}\) Such insight should yield further optimization to that interface with concomitant improvements to solar-energy-conversion efficiencies and pathways to inexpensive Si−Sb_{2}S_{3} tandem-junction photovoltaics.

4. CONCLUSIONS AND FUTURE WORK

We prepared perylene-based surfaces on degenerately doped, optically “dead” n^{−}Si and explored methods to convert terminal perylene anhydride groups into thioperylene anhydrides. In our hands, P_{S_{10}} in either dry toluene or in dry DCM demonstrated good conversion of terminal C==O groups to C==S, while Lawesson’s reagent, LR, demonstrated minimal reactivity as revealed by X-ray photoelectron spectroscopy (XPS). Spectra further demonstrated that rigorous sonication and rinsing procedures were necessary to fully remove reagents and byproducts of the thionation reaction from the surfaces. We deposited Sb_{2}S_{3} via two cycles of chemical bath deposition on each prepared surface that became the back contacts to the resulting Sb_{2}S_{3} photoelectrodes. Sb_{2}S_{3} photoelectrochemistry in a highly rectifying thianthrene\(^{3/0}\) redox couple demonstrated a strong dependence on the chemical structure of the back contact. Scans demonstrated large open-circuit photovoltage, \(V_{oc}\), magnitudes at Sb_{2}S_{3} photoelectrodes when thioperylene-anhydride-terminated surface 5 formed the back contact and significantly smaller \(V_{oc}\) magnitudes for other back contact surface chemistries that both did and did not contain sulfur termination. Results indicate that back-contact surface chemistry advantageously affects the resulting solar-energy-conversion performance of bath-deposited Sb_{2}S_{3} that partially miss the finding \(V_{oc}\) and provide avenues for ongoing improvements.

5. EXPERIMENTAL SECTION

The Supporting Information section details in full the experimental methods that we briefly summarize here. Silicon substrates for surface science were S25 ± 15 μm thick, \(\leq 0.006 \text{ cm}\) resistivity, and degenerately arsenic-doped n^{−}−Si(111), while control samples for thianthrene\(^{3/0}\)−photoelectrochemistry testing were doped n^{−}−Si(111), 1.3−2.5 Ω cm resistivity, 500 ± 25 μm thick, and double-sided polished wafers. Wafers were thoroughly cleaned before use in a procedure that ended with the formation of a thin chemical oxide layer to yield surface 1 for the formation of silane-based monolayers. Reaction with (3-aminopropyl)triethoxysilane yielded surface 6 and the missing \(V_{oc}\) of Sb_{2}S_{3} (DBU) in ethanol and dimethylformamide (DMF) activated perylenetetracarboxylic dihydride (PTCDA) to convert surface 2 into a perylene-anhydride-terminated surface.
3, and DBU in ethanol and bromoethane yielded diethyl-ester-terminated surface 4 from surface 3.22

Optimal thionation protocols were established by quantifying sulfur coverage in the conversion of surface 3 to thioperylene-anhydride-terminated surface 5. Thionation reagents alternatively utilized Lawesson’s reagent (LR), P4S10, or a P4S10−pyridine complex with 3-day reactions at ambient temperature. Upon determining the optimal reagent conditions, only P4S10 in dry, nonpolar solvent was utilized to convert surface 4 to a di(ethyl thionoester)-terminated surface 6.

Sb2S3 was deposited in two successive cycles of chemical bath deposition with antimony potassium tartrate hydrate, triethanolamineaq solution, thioacetamideaq, and silicotungstic acidaq followed by annealing in argon.11 Sb2S3 bath-deposited surfaces were etched in 1.2 M HCl(aq) to remove interfacial oxides.

X-ray photoelectron spectroscopy, XPS, quantified the surfaces under study as previously described19,22 For thionation quantification for the conversion of surface 3 to surface 5, XPS established the conversion of C=O to C=S and remaining byproducts with observation of sulfur, phosphorous, carbon, oxygen, nitrogen, and silicon features. S 2s and P 2s region scans complemented the respective 2p regions and were particularly important for deconvoluting sulfur and phosphorus photoelectron contributions from those arising from silicon phonon modes. Before-and-after XP spectra of the S 2p as well as the combined O 1s + Sb 3d region quantified the impact of the 1.2 M HCl(aq) etch to remove interfacial oxides from Sb2S3 bath-deposited surfaces.

Photoelectrochemistry experiments utilized the thianthrene+0/− redox couple with 1 M LiClO4 in dry acetonitrile. Experiments with n-Si electrodes established the expected behavior and validated the utilization of thianthrene+0/−. Photoelectrochemistry of Sb2S3 working electrodes in which surfaces 1−3, and 5−7 individually served as back-contact substrates established a relationship between the back-contact surface chemistry and the resulting open-circuit photovoltage under 300 W ELH-simulated AM1.5 G illumination. Cyclic voltammetry at a platinum wire established the thianthrene+0/− cell potential and Nernstian formal potential vs ferrocene+0/− and acetylferrrocene+0/− nonaqueous standards.43

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02077.

Materials and chemicals; chemically oxidized Si(111) substrate surface 1; silanization of surface 1 to yield surfaces 2 and 7; preparation of perylene-anhydride-terminated surface 3; conversion of surface 3 to di(ethylester)-terminated surface 4; thionation of 3 to yield thioperylene-anhydride-terminated surface 5; thionation of 4 to yield di(ethyl thionoester)-terminated surface 6; chemical bath deposition of Sb2S3; XPS; photoelectrochemistry (PDF)

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Notes
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