Atomic Layer Deposition of the Quaternary Chalcogenide Cu₂ZnSnS₄

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ABSTRACT: Atomic layer deposition (ALD) is a layer-by-layer synthesis method capable of depositing conformal thin films with thickness and compositional control on subnanometer length scales. While many materials have been synthesized by ALD, the technologically important metal sulfides are underexplored, and homogeneous quaternary metal sulfides are absent from the literature. We report an ALD process to synthesize Cu₂ZnSnS₄ (CZTS), a potentially low cost semiconductor being explored for photovoltaic applications. Two strategies are reported: one in which a trilayer stack of binary metal sulfides (i.e., Cu₂S, SnS₂, and ZnS) is deposited and mixed by thermal annealing, as well as a supercycle strategy that is similar to the conventional ALD procedure for forming nanolaminates. Both routes rely on the facile solid state diffusion of chalcogenides for mixing. For this ALD route to the CZTS system, the challenges are nucleation, ion-exchange between the film and the volatile chemical precursors, and phase-stability of binary SnS₂. The thin films were made with no sulfurization step. The X-ray diffraction and Raman spectra were consistent with the formation of CZTS. X-ray fluorescence measurements revealed that the films contained the expected amount of sulfur based on the target oxidation states. Photoelectrochemical measurements under simulated AM1.5 illumination using Eu³⁺ as an electron acceptor demonstrated that the films were photoactive and had an average internal quantum efficiency (IQE) of 12%.

KEYWORDS: chemical vapor deposition, metal sulfide, kesterite, photoelectrochemical, photocathode, photovoltaic, solar cell, solar energy conversion, nanostructure, mesoscopic

Atomic layer deposition (ALD) is emerging as the premier thin film deposition method to synthesize conformal layers with control over composition and thickness at the angstrom to nanometer length scale. ALD syntheses operate by alternating exposures to complementary chemical precursor vapors. In the ALD window, each of these precursors reacts with the surface sequentially in a self-limiting fashion to deposit one monolayer or less. Binary compounds, such as metal sulfides (e.g., ZnS), can be deposited by alternating exposures of the substrate to a metal cation precursor (e.g., diethyl zinc) and a chalcogen anion precursor (e.g., H₂S) with purge steps between. Due to the self-limiting nature of the complementary surface reactions, conformal pinhole-free films can be deposited on nanostructured surfaces with very high aspect ratios (>1000).¹ ²

For photovoltaic solar energy conversion, the unique capabilities of ALD could enable next-generation high efficiency nanostructured devices. One example is plasmon enhancement, which can increase the open-circuit photopotential,³ by for example, concentrating photoexcited charge carriers.⁴ Absorption enhancements based on the localized surface plasmon resonance (LSPR) are highly localized to within approximately 10 nm of the metal nanoparticle surface,⁵–⁷ and so conformal absorber layers must be synthesized on the rough substrate at this length scale—a challenging task ideally suited for ALD.

Another example where ALD can contribute to improved photovoltaic performance is through minority carrier collection. For semiconductors, in general, the minority carrier collection distance is often incommensurate with the light absorption depth, limiting conversion efficiencies in planar configurations—especially at wavelengths near the band gap for materials with short-lived, low-mobility photoexcited charge carriers. ALD allows one, in principle, to decouple light absorption from photoexcited charge carrier collection using interpenetrating device geometries. This concept of decoupling light absorption from photoexcited charge carrier (excitons or minority carriers) collection has been proposed in various forms over the years; some classic examples are the dye-sensitized solar cell (DSC),⁶ bulk-heterojunction (BHJ)⁷ solar cell, and extremely thin absorber (ETA) solar cells.⁸ The scalable fabrication of a thin absorber layer that exhibits high internal quantum efficiency from earth-abundant, low cost components remains a central challenge to fully realizing the nanostructured device designs. Beyond the nanostructured device designs, ALD could also have an impact for absorber
layer fabrication by filling pinholes that may result from conventional deposition processes.

Compared to metal oxides, metal sulfides have received relatively little attention from the ALD community. Self-limiting chemistry often proceeds readily using H2S as the sulfur source. Beyond binary and ternary metal-sulfides, to the best of our knowledge, there are no examples in the published literature for the synthesis of quaternary sulfides by ALD.

Cu2ZnSnS4 (CZTS) is an absorber layer that has attracted attention recently for solar energy conversion because of its band gap (Eg ≈ 1.4 eV), the relative abundance and low cost of its constituent elements, and its demonstrated solar-to-electricity power conversion efficiencies over 8%.11 In CZTS the oxidation states are Cu(+I), Zn(+II), Sn(+IV) and S(−II). Control over composition in this system is important. CZTS compositions in the best devices are Cu-poor and Zn-rich. For example, the 8.4% efficient CZTS device reported by Shin et al. had a Cu/Sn ratio from 1.7 to 1.8, and a Zn/Sn ratio from 1.2 to 1.3.12 It has been proposed that this empirical observation could be a result of the domain acceptor defect, which is expected to change with composition.12,13 In stoichiometric CZTS, the lowest energy acceptor defect has been reported to be the Cu2−Sn antisite (i.e., Cu+ sitting on a Zn site), which has a relatively high acceptor level of 0.12 eV above the valence band maximum.12,13 The higher energy Cu vacancy defect is more attractive because of its shallower level, only 0.02 eV above the valence band maximum.12,13 The hypothesis is that the Cu-poor, Zn-rich CZTS favors the formation of the Cu vacancy defect and suppresses the Cu2−Sn antisite, thereby improving performance.12,13 While the hypothesis regarding the role of the dominant acceptor defect in performance remains experimentally untested, the empirical observation of the composition correlation stands. It is clear that a given synthesis process for CZTS must demonstrate control over composition. We note that even while CZTS devices have exhibited very promising performance, the best devices still have low open-circuit voltages compared to the band gap (Voc ≈ 0.66 V; Eg ≈ 1.4 eV). They also have relatively low quantum efficiencies at wavelengths near the band gap transition (900 nm), as well as below 500 nm where parasitic absorption by the window layers becomes important. The published short circuit photocurrent densities in the highest efficiency CZTS photovoltaic solar cells are approximately 20 mA cm−2,11 well below the theoretical maximum of 33 mA cm−2 under AM1.5 illumination, leaving room for improvement.

Many synthesis routes to CZTS have been explored. The most common ways to fabricate devices of reasonable efficiency are physical vapor deposition of metal or binary sulfide stacks followed by sulfurization;11,14–16 or solution-phase nanoparticle synthesis17,18 followed by deposition onto a substrate and annealing.19,20 For physical vapor deposition, a common route is to thermally evaporate metal films (e.g., Cu, Zn and Sn) onto a substrate, and then anneal the metal film stack in a sulfur atmosphere at T > 500 °C to generate CZTS. One can also do the same procedure using binary metal sulfide film stacks (e.g., CuS, SnS and ZnS). For nanoparticles, they must be deposited on the substrate by for example, spreading20 or dip-coating.19 Like the metal film stacks, nanoparticle deposition is typically followed by annealing in some type of chalcogen-containing atmosphere to obtain efficient solar cells.

In this work, we explored the synthesis of CZTS by atomic layer deposition. Two different strategies were employed. The “trilayer” strategy involved depositing a stack of three binary metal sulfides (i.e., Cu2S, ZnS, and SnS) and then mixing by a postdeposition heat treatment in argon. For the trilayer strategy, we use the notation: substrate/xCu2S/ySnS2/zZnS to describe a trilayer stack consisting of x cycles of Cu2S deposited on the substrate, followed by y cycles of SnS2 and z cycles of ZnS. The “supercycle” strategy is the conventional ALD procedure for forming nanolaminates, in which a sequence of cycles for the binary metal sulfides is repeated many times to form the film. For the supercycle strategy, the notation: substrate/n(xCu2S/ySnS2/zZnS) means that a sequence of x cycles of Cu2S followed by y cycles of SnS2 and z cycles of ZnS was repeated n times to form the film. The cycle ratios can be tuned to control composition. Photoelectrochemical (PEC) characterization of the films revealed that they were photoactive, although we did not attempt to optimize performance or fabricate complete all-solid-state device stacks in this work.

### EXPERIMENTAL SECTION

Atomic layer deposition was performed in a Savannah S200 (Cambridge Nanotech, Cambridge, MA) customized for compatibility with H2S.22 The reactor was integrated with a glovebox, although we do not believe this to be important for the results presented herein. For all depositions, the hot-wall chamber temperature was 135 °C. The high-purity nitrogen flow rate was 10 scm, and deposition was carried out in pulse mode (continuous flow). Under nitrogen flow with no precursor pulsing, the chamber pressure was approximately 0.5 Torr. For all materials, the sulfide source was 1% H2S balance N2 (safety note: H2S is poisonous at 1% but not flammable). The H2S was delivered to the precursor manifold through a 0.3 mm orifice (Lennox Laser) that was placed just upstream of the pneumatic ALD valve. The delivery pressure from the corrosive gas regulator was 18 in. of mercury gauge pressure.

The substrates used were either fused silica (quartz), fluorine-doped SnO2-coated glass (TEC 15, Pilkington Glass), or polished silicon. The SnO2-coated glass is abbreviated as FTO.

Cu2S was deposited using our previously published procedure adapted for use on the Savannah S200.22 The precursor for Cu+ was bis(N,N′-disec-butylacetamidinato)dicopper(I) (Strem Chemicals), which is abbreviated as Cu2DBA. The Cu2DBA precursor reservoir was kept at 160 °C. The vapor was fed into the chamber using a nitrogen-assisted vapor delivery system. The procedure to dose the Cu2DBA precursor reservoir was to repeat the following steps five times: pressurize the Cu2DBA cylinder for 0.015 s using nitrogen at 25 psia, wait 1.0 s for the nitrogen to equilibrate and the precursor to mix, pulse the nitrogen/Cu2DBA mixture into the chamber. One cycle of Cu2S was completed by first dosing Cu2DBA, followed by a 10 s purge, 1.0 s H2S dose, finishing with a 10 s purge. While two groups have reported on the ALD synthesis of SnS using Sn(II) precursors,23,24 a process for SnS has not been reported. We therefore developed a new process. One cycle of SnS2 means a 1.0 s pulse of tetrakis(dimethylamido)Sn(IV) (SnTDMa, Sigma-Aldrich), followed by a 20.0 s nitrogen purge, followed by a 1.0 s H2S dose, finishing with a 20.0 s nitrogen purge. The temperature of the SnTDMa reservoir was maintained at 55 °C. The vapor pressure of the SnTDMa at this temperature was sufficient to feed the chemical from the chamber to the nozzle with no assistance from pressurized nitrogen.

For ZnS, we used the well-known process employing diethyl zinc (DEZ, Sigma-Aldrich) and H2S. The diethyl zinc was kept at room temperature. One cycle of ZnS consisted of a 0.015 s pulse of DEZ, followed by a 20.0 s purge, followed by a 1.0 s H2S pulse, finishing with a 20.0 s purge. Safety note: DEZ is a pyrophoric, volatile liquid and must be handled with caution.

Select films were annealed under argon in a quartz tube furnace of 1 in. internal diameter. The flow rate of argon was 0.33 L/min. The temperature was ramped up to the set point over a period of 50 min, allowed to soak for the specified time, and then cooled at the natural...
rate of the system back to below 150 °C before sample removal. The cooling step took approximately 30 min.

X-ray fluorescence (XRF, ED2000, Oxford Instruments) was used to quantify composition. Calculations were performed using the Berkeley Lab X-ray Interactions with Matter tool\(^{25,26}\) to verify that XRF measurements were performed in the thin film limit using a fixed angle of 45° in the energy range from 2 to 10 keV. All samples had a thickness <10% of the attenuation length and an X-ray transmission >90% in the energy range of interest. Samples for XRF were deposited on fused silica (quartz) to minimize interference from substrate impurities. The XRF standards were a 40.7 nm Cu metal film for [Cu], 40.7 nm Sn metal film for [Sn], and 22 nm ZnS film for [Zn] and [S]. Raman spectroscopy was performed using an Renishaw Ramascope spectrometer with a 633 nm laser. The spot was approximately 1 μm in diameter. Several locations were measured that all gave similar spectra. The laser power was 13 mW. The power incident on the sample was not measured, but it was estimated that the combined transmission of the spectrometer and microscope optics was from 10 to 50%. Visual inspection showed no evidence of the sample overheating and sequential measurements on the same location showed identical spectra, which is an indication that sample heating did not affect the acquired spectra. Raman spectroscopy was performed on samples deposited on both quartz and FTO. The substrate did not have an apparent effect on the Raman scattering spectra. X-ray diffraction (XRD, Rigaku minilx) was carried out in θ-2θ mode on samples deposited on quartz. Cross-sectional scanning electron microscope (SEM) images were taken in a Hitachi S4700-II. The substrate was quartz and the samples were coated with a thin layer of Au to prevent charging.

The electrolyte was 0.1 M Eu(III)(NO₃)₃ in a supporting electrolyte of 1 M KCl. The active area on the photoelectrode was 1.7 cm². The PEC measurements were carried out in a three-electrode configuration using an Ag/AgCl in saturated KCl reference electrode. The electrolyte was 0.1 M Eu(III)(NO₃)₃ in a supporting electrolyte of 1 M KCl. The active area on the photoelectrode was 1.7 cm². The sample was illuminated using a 300 W arc lamp equipped with an AM1.5 and ultraviolet (UV) filter. The output from the lamp was calibrated using a silicon photodiode by the procedure outlined in ref 28 to simulate the AM1.5 condition (100 mW cm⁻²).

### RESULTS AND DISCUSSION

**Trilayer Strategy.** There are six possible deposition orders that the binary sulﬁdes can be deposited by the trilayer strategy:

(a) substrate/SnS₂/Cu₂S/ZnS
(b) substrate/SnS₂/ZnS/Cu₂S
(c) substrate/ZnS/SnS₂/Cu₂S
(d) substrate/ZnS/Cu₂S/SnS₂
(e) substrate/Cu₂S/ZnS/SnS₂
(f) substrate/Cu₂S/SnS₂/ZnS

It will be shown that only one of these ALD reaction sequences works for the binary processes under study. Three failure modes were identified. The first is nucleation failure, which means a given binary metal sulﬁde does not grow to an appreciable extent on the layer deposited before it. The second failure mode is facile ion exchange between the ﬁlm and the gas-phase precursor. For ion-exchange, one of the volatile chemical precursors reacts with the ﬁlm already on the substrate to cause a bulk transformation in the preexisting thin ﬁlm. We have previously published two such ion exchange reactions relevant to the CZTS system, which were demonstrated by isolating the interaction between the organo-metallic precursor vapor and thin ﬁlm:

\[
\text{Cu}_2\text{S}(s) + \text{Zn}(\text{C}_2\text{H}_3)_2(g) \rightarrow \text{ZnS}(s) + 2\text{Cu}(s) + \text{C}_6\text{H}_{10}(g) \quad (1)
\]

\[
\text{ZnS}(s) + \text{Cu}_2\text{DBA}(g) \rightarrow \text{Cu}_2\text{S}(s) + \text{ZnDBA}(g) \quad (2)
\]

For reaction 1, the DEZ reacts with the Cu₂S to form ZnS, and the Cu⁺ is reduced to Cu metal. In reaction 2, the ZnS reacts with the Cu₂DBA, resulting in conversion to Cu₂S and, astonishingly, a complete removal of Zn⁺ from the film with no change in sulfur areal density. The gas-phase products for these ion exchange reactions have not yet been identiﬁed, but the products listed in Eqns. 1 and 2 are the most likely candidates. The third and final mode is stability failure, that is, a given compound is unstable on a particular surface.

Nucleation failure occurred for the deposition of Cu₂S on substrates that had a preexisting SnS₂ ﬁlm on them, where SnS₂ forms a ﬁlm by the SnTDMA/H₂S process, not necessarily the stoichiometry. This will be illustrated qualitatively by analyzing the XRF spectra presented in Figure 1. The S kz peak was present but has been omitted for clarity.

Peaks at the energy of the Cu kz and Cu kβ lines were observed for 167 cycles of Cu₂S on a quartz substrate, as expected (Figure 1). For the sequence quartz/800SnS₂/167Cu₂S, Sn and Zn were observed in the XRF spectra, but there was a conspicuous absence of Cu. Thus, it can be said that the Cu₂S did not nucleate on the quartz/SnS₂ surface under these conditions. Therefore, sequence c can be eliminated, since the film contained no Cu⁺ so CZTS formation was impossible. Sequence c fails by similar reasoning given the XRF spectra for quartz/230ZnS/800SnS₂/167Cu₂S (Figure 1). It was expected that sequence b would fail by the ion exchange reaction 2, but in fact, no copper was observed in the film!
Therefore, given the absence of Cu in the XRF spectra for quartz/800SnS2/230ZnS/167Cu2S in Figure 1, sequence b resulted in nucleation failure on the quartz/SnS2/ZnS surface. A more detailed analysis of this phenomenon is ongoing in our laboratory. In total, half of the possible sequences (a–c) have been eliminated.

Sequences d, quartz/ZnS/Cu2S/SnS2, and e, quartz/Cu2S/ZnS/SnS2, both failed by ion exchange via reactions 2 and 1, respectively. For sequence d, the Zn2+ was completely removed from the film after depositing the Cu2S. This can be seen qualitatively in the XRF spectra of Figure 2. After deposition of 167 cycles of Cu2S on the quartz/230ZnS surface, no Zn was observed by XRF in the sample. Furthermore, the area of the Cu Kα XRF peak in the quartz/230ZnS/167Cu2S sample was significantly larger than in the case of quartz/167Cu2S, indicating more Cu2+ was added to the film than would be expected if only a Cu2S film were deposited. Thus, given the present results and previous work,22 it is clear that sequence d fails by reaction 2. Sequence e failed by the ion exchange reaction 1. This can be seen by examining the areal densities for Cu and Zn presented in Table 1. For a sample of sequence e, quartz/Cu2S/230ZnS/800SnS2, both failed by ion exchange via reactions 2 and 1, respectively. For sequence d, the Zn2+ was completely removed from the film after depositing the Cu2S. This can be seen qualitatively in the XRF spectra of Figure 2. After deposition of the Zn areal density was more than two times larger than what would be expected based on the cycle numbers and ALD growth rate (Table 1), consistent with reaction 1. The Zn areal density for sequence e was higher than what would be expected based on the cycle numbers and ALD growth rate (Table 1), consistent with reaction 1. The Zn areal density was more than two times larger than what would be expected based on the cycle numbers and ALD growth rate (Table 1), consistent with reaction 1.

The only remaining sequence is f, and it will be shown that it works to obtain a composition controllable through the cycle ratios. Before discussing sequence f, we first discuss the synthesis of SnS2. As was mentioned in the Experimental Section, an ALD process for SnS2 has not been reported. The SnTDMA/H2S process is viable, and presented herein are some first observations of the dependence of the [S]/[Sn] ratio on the chemical composition of the substrate.

Using the SnTDMA/H2S process, stoichiometric, crystalline SnS2 could be deposited on quartz/Cu2S; however, films deposited on quartz or quartz/ZnS were sulfur deficient. Plotted in Figure 3 is the ratio of sulfur associated with Sn calculated by eq 3 to Sn, for SnS2 deposition on different surfaces.

\[
\frac{[\text{S}]_{\text{Sn}}}{[\text{Sn}]} = \frac{[\text{S}]_{\text{tot}} - r[\text{M}]}{[\text{Sn}]} 
\]

where [S]_{tot} is the total measured areal density of sulfur, [M] is the areal density of the other metal (either Cu or Zn), and r is the stoichiometric ratio of sulfur to metal in the other metal sulfide (r = 0.5 for Cu2S; r = 1 for ZnS). It can be seen from Figure 3 that only the SnS2 deposited on Cu2S had an [S]_{Sn}/[Sn] ratio of 2, while both of the others were sulfur deficient.

XRD patterns are presented in Figure 4. The quartz/230Cu2S sample exhibited peaks for the (002) and (004) reflections of hexagonal chalcocite, as expected for this ALD process. The quartz/800SnS2 exhibited virtually no features in 3191

![Figure 2](image)

**Figure 2.** XRF spectra showing ion exchange via reaction 2 would occur for sequence d. The quartz/Cu2S and quartz/ZnS controls are included for reference. The plots have been offset for clarity.

**Table 1.** Cu and Zn Areal Atomic Densities Showing the Ion Exchange Reaction 1 occurred for Sequence e

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Cu], nmol cm⁻²</th>
<th>[Zn], nmol cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz/167Cu2S</td>
<td>167</td>
<td>0.0</td>
</tr>
<tr>
<td>quartz/230ZnS</td>
<td>0.0</td>
<td>93</td>
</tr>
<tr>
<td>quartz/167Cu2S/230ZnS/800SnS2</td>
<td>161</td>
<td>211</td>
</tr>
</tbody>
</table>

"The error is ±6.5% of the value.

![Figure 3](image)

**Figure 3.** Areal atomic density ratio of sulfur associated with Sn calculated by eq 3 to Sn, for SnS2 deposition on different surfaces.

![Figure 4](image)

**Figure 4.** XRD patterns for SnS2 deposited on quartz alone and on a Cu2S layer on quartz. Also shown for clarity is an XRD pattern of the quartz/Cu2S film without SnS2. The Cu2S and SnS2 were indexed to PDF cards 26-1116 and 1-1010, respectively. The plots have been offset for clarity.
the XRD pattern, indicating that it contained a large amorphous fraction, likely caused by the sulfur deficiency illustrated in Figure 3. The quartz/167Cu2S/800SnS2 exhibited a strong XRD peak for the (100) reflection of SnS2. Interestingly, the peaks observed for Cu2S were absent from the quartz/167Cu2S/800SnS2 sample, which could be a result of extensive mixing between the phases.

XPS measurements revealed significant copper content on the surface of the film for the case of as-deposited silicon/190Cu2S/800SnS2. The survey spectrum used for quantification is presented in Figure 5. The measurement probed only the near surface region, 1 to 3 nm away from the vacuum—film interface. The thickness of the SnS2 layer based on the areal atomic density determined by XRF measurements was 46 nm. Cu+ diffused up through the SnS2 layer to the surface of the film. Such facile Cu+ diffusion in SnS2 has been observed before and is consistent with the disappearance of the CuS peaks in the XRD spectrum for the 167Cu2S/800SnS2 bilayer (Figure 4). For the surface of the film, the Cu atomic concentration based on Sn was estimated to be 10% by the standard CasaXPS procedure using core level Cu 2p and Sn 3d lines.

While XRD demonstrates crystallinity, many of the binary and ternary metal sulfides in the Cu–Zn–Sn–S system have reflections at nominally the same angles (such as 2θ ≈ 28.5°), often rendering XRD results ambiguous. Raman scattering is a more conclusive characterization technique for the CZTS system, despite the drawback of no centralized, vetted database for peak assignments. The Raman scattering spectra of quartz/230Cu2S, quartz/800SnS2, quartz/230ZnS/800SnS2, and quartz/167Cu2S/800SnS2 are plotted in Figure 6. The quartz/230Cu2S sample was featureless in the spectral range of interest. The quartz/800SnS2 exhibited a broad peak centered at approximately 173 cm−1 and two sharper peaks at 189 cm−1 and 221 cm−1. These peaks, as well as the small peak at 288 cm−1, can be reasonably assigned to SnS. The Raman scattering spectra of the quartz/230ZnS/800SnS2 sample was similar to the SnS2 on quartz. Considering that [Sn]/[S] >> 1 (Figure 3) for these samples, the SnS2 deposited on quartz and quartz/ZnS was likely a mixture of SnS and amorphous SnS2. The quartz/167Cu2S/800SnS2 sample exhibited a sharp peak at 313 cm−1, consistent with SnS2. The shoulders to either side of the SnS2 peak could be assigned to Cu2SnS3, although the one on the low wavenumber side had a low intensity. The conclusion is that the CuS is needed to stabilize the SnS2, and therefore, this layer is described as copper-stabilized tin disulfide. This is fortuitous, considering sequence f is the only remaining route to forming the trilayer. Sequence f was successful in depositing each of the metal sulfides with the target stoichiometry, and the metal ratios were controlled by the cycle ratios for each process. Plotted in Figure 7 is an XRF spectrum for a quartz/190Cu2S/800SnS2/290ZnS trilayer. All four elements were clearly present. The areal densities for various films are presented in Table 2. The error associated with each value was a result of the background subtraction prior to peak integration. All of the samples exhibited [Metal]/[S] ratios expected for the oxidation states:

![Figure 5. XPS survey spectra used for quantification of the Cu atomic percentage (i.e., [Cu]/([Cu] + [Sn])) at the surface of a silicon/190Cu2S/800SnS2 sample.](image)

![Figure 6. Raman scattering spectra for SnS2 deposited on quartz, quartz/ZnS, and quartz/Cu2S. The peak at 288 cm−1 in the black and blue curves can also be assigned to SnS. The quartz/Cu2S control is included for reference. The plots have been offset for clarity.](image)

![Figure 7. XRF spectrum for a trilayer deposited on quartz using sequence f.](image)

<table>
<thead>
<tr>
<th>sample</th>
<th>areal densities, nmol cm−2 (error is ±6.5% of value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>167Cu2S</td>
<td>167</td>
</tr>
<tr>
<td>167Cu2S/800SnS2</td>
<td>159</td>
</tr>
<tr>
<td>230ZnS</td>
<td>93</td>
</tr>
<tr>
<td>167Cu2S/800SnS2/230ZnS</td>
<td>152</td>
</tr>
<tr>
<td>190Cu2S/800SnS2/290ZnS</td>
<td>190</td>
</tr>
</tbody>
</table>

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Cu(1+), Zn(2+), Sn(4+), and S(−2). Samples were deposited with different cycle numbers and different cycle ratios, but the growth per cycle for each of the binary components was unaffected, meaning the cycle number for each component was much larger than the nucleation delay. If a large decrease in the cycle number were made such that it was no longer much greater than the nucleation delay, a significantly smaller average growth per cycle would be expected. For the samples containing copper, the CuS growth per cycle was the same within the experimental error of XRF and the average was equal to 0.44 nmol cm⁻² cycle⁻¹. Similarly, all of the samples containing Zn exhibited the same growth per cycle of 0.40 nmol cm⁻² cycle⁻¹, demonstrating that ZnS growth on Cu₂S/SnS₂ was virtually identical to that on quartz. The SnS₂ showed an average growth per cycle of 0.14 nmol cm⁻² cycle⁻¹ under these conditions. Since the oxidation states were the target ones for CZTS, and the growth per cycle of the binary components was constant, the cycle numbers could be tuned to adjust the metal ratios. This can be seen first by examining the last two samples in Table 2. For the cycle ratios Cu₂S/SnS₂ = 0.209 and ZnS/SnS₂ = 0.288, [Cu]/[Sn] = 1.45 and [Zn]/[Sn] = 0.87. To get closer to the metal ratios often used for CZTS absorbers in photovoltaic thin film solar cells, using Cu₂S/SnS₂ = 0.238 and ZnS/SnS₂ = 0.363 results in [Cu]/[Sn] = 1.88 and [Zn]/[Sn] = 1.16. Plotted in Figure 8 is the measured [Cu]/[Sn] areal atomic density ratio for different Cu₂S/SnS₂ cycle ratios at constant ZnS/SnS₂ = 0.363 and constant 800 SnS₂ cycles. As expected, the areal atomic density ratio [Zn]/[Sn] remained constant, and [Cu]/[Sn] increased with increasing Cu₂S/SnS₂ cycle ratio. Therefore, it has been demonstrated that the trilayer strategy using sequence f was effective for placing the metal and sulfur atoms on the substrate in the correct oxidation state, and the metal ratios could be controlled using the ratios of the number of cycles for each binary process.

The trilayer strategy is effective for placing the metal and sulfur atoms on the substrate, but as deposited, the elements are not mixed or crystallized. Crystallization of the CZTS can be accomplished by a thermal treatment of the as-deposited Cu₂S/SnS₂/ZnS trilayer. Plotted in Figure 9 are the Raman spectra of a 190Cu₂S/800SnS₂/290ZnS trilayer before and after annealing for 2 h at 450 °C in argon. As deposited, the trilayer exhibited a prominent peak at 313 cm⁻¹ that was assigned to SnS₂, and a well-defined shoulder at 349 cm⁻¹ consistent with Cu₂SnS₃. After annealing in Ar at 450 °C for 2 h, the main peak shifted to 336 cm⁻¹ and the shoulder shifted to 373 cm⁻¹, consistent with the formation of CZTS. The Raman spectra in Figure 9 for the annealed sample closely resembles that found for a Cu₂ZnSnS₄ film that achieved a power conversion efficiency of 7.3% for photovoltaic solar cells. The XRD pattern for the same 190Cu₂S/800SnS₂/290ZnS trilayer before and after annealing is plotted in Figure 10. As deposited, the XRD pattern was consistent with the (100) reflection at 28.3° of SnS₂ observed for quartz/Cu₂S/SnS₂ (Figure 4). After annealing, the peaks become sharper, and in addition to the prominent peak for the (112) reflection of CZTS at 28.5°, small peaks for the (200) and (220) reflections of this phase also become visible. A cross-sectional SEM image of an as-deposited 190Cu₂S/800SnS₂/290ZnS trilayer sample on a silicon trench wafer is shown in Figure 11. The film was compact, conformal, and continuous. The absorption coefficient for an annealed trilayer film, calculated using the equation α = −ln(T/(1 − R))/d, where T is the transmittance, R is the reflectance, and d is the film thickness, is plotted in Figure 12. The absorption onset was approximately 895 nm, consistent with Eg = 1.4 eV. The XRF spectra showed a slight decrease in [S] after annealing for 3 h at 450 °C in Ar, but the 1 standard deviation confidence intervals before and after annealing overlapped, so the difference was insignificant. After annealing, the CZTS was photoactive. While a full study of the behavior of this material is beyond the scope of this synthesis paper, we present a photoelectrochemical verification.

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**Figure 8.** Areal atomic density ratio as a function of Cu₂S cycle number for a constant 800 SnS₂ cycles and constant 290 ZnS cycles.

**Figure 9.** Raman scattering spectra for a 190Cu₂S/800SnS₂/290ZnS trilayer on FTO before and after annealing at 450 °C in Ar for 2 h. The plots have been offset for clarity.

**Figure 10.** XRD patterns for a quartz/190Cu₂S/800SnS₂/290ZnS trilayer before and after annealing at 450 °C in Ar for 2 h. The SnS₂ and CZTS were indexed to PDF cards 1-1010 and 26-0575, respectively. The plots have been offset for clarity.
that the CZTS film produced photocurrent with a reasonable internal quantum efficiency. Plotted in Figure 13 is the photocurrent density of a CZTS film annealed in argon at 450 °C for 1 h. The electrolyte contained 0.1 M Eu³⁺ as an electron acceptor and 1 M KCl supporting electrolyte. The area exposed to the electrolyte was 1.7 cm². Figure 13 was measured at an applied potential of −0.6 V vs Ag/AgCl. Before illumination, very little dark current was measured (J_{dark} = −0.06 mA cm⁻²). After opening the shutter to illuminate the film through the semiconductor–electrolyte interface, a large decrease in current to −1.4 mA cm⁻² was observed, consistent with the expected behavior of a p-type photocathode. The photocurrent magnitude decreased slightly with time under illumination. For subsequent light pulses, the initial photocurrent was higher in magnitude than the last photocurrent measurement of the previous pulse (data not shown here), indicating that the 20% decrease in photocurrent in Figure 13 could have been due to consumption of the Eu³⁺ in the near surface region under illumination. In the dark, the Eu³⁺ concentration in the near surface region increased as it was replenished. Over longer time scales, the photocurrent magnitude at the end of subsequent pulses decreased slightly with time. Plotted in Figure S1 (Supporting Information) is the normalized photocurrent at the end of a 6 s light pulse minus the dark current immediately after. The time between light pulses was approximately 10 s. It can be seen from Figure S1 (Supporting Information) that, over the course of the 100 s experiment, the photocurrent magnitude decreased by approximately 6%, indicating that the CZTS film was slightly unstable under these reducing conditions in the aqueous electrolyte. While the aqueous electrolyte is sufficient to demonstrate photoactivity, clearly an operating device would require an all-solid-state configuration.

The theoretical maximum AM1.5 photocurrent from a semiconductor with a 1.4 eV band gap is 33 mA cm⁻². The absorption depth from the annealed trilayer in Figure 12 at 850 nm was 1.69 μm, much greater than the film thickness of 0.09 μm. When the absorption efficiency spectrum (i.e., \( a = 1 - T - R \)) for the film of Figure 13 was integrated over the AM1.5 spectrum, the maximum theoretical photocurrent was −12.1 mA cm⁻². Since the initial photocurrent was approximately −1.4 mA cm⁻², the average internal quantum efficiency was approximately 12%. The external quantum efficiency spectrum (i.e., incident photon to current efficiency, or IPCE) was not measured because of the photocurrent instability illustrated in Figure 13. Wavelengths measured at later times would be biased toward smaller values compared to the wavelengths measured first, therefore distorting the spectra.

We note that the photoactivity of CZTS is strongly dependent on the annealing conditions and photoelectrochemistry depends on the surface. For instance, it has been reported that Cu₂ZnSnS₄ decomposes via a first order reaction into Cu₂S.

Figure 11. Cross sectional SEM images of a 190Cu₂S/800SnS₂/290ZnS trilayer deposited on a silicon trench wafer: (a) low magnification of the coated trench, (b) high magnification of the upper right portion of the trench, and (c) high magnification of the lower right portion of the trench.

Figure 12. Absorption coefficient measured from a 90 nm 190Cu₂S/800SnS₂/290ZnS CZTS film after annealing in Ar.

Figure 13. Photocurrent measured in a 0.1 M Eu³⁺ with 1 M KCl electrolyte at an applied potential of −0.6 V vs Ag/AgCl. The film was a trilayer of 190Cu₂S/800SnS₂/290ZnS on FTO annealed for 1 h in Ar at 450 °C.
+ ZnS + SnS + S, where the SnS and S are both potentially volatile depending on the temperature. Even though the metal and sulfur ratios may be correct for the present films, annealing in Ar might have partially decomposed the material thereby inhibiting activity. Optimizing the annealing temperature and including SnS or S in the furnace has been shown on other samples to increase the performance. Studies toward these ends are underway in our laboratory.

Supercycle Strategy. In contrast to the trilayer strategy, the supercycle strategy bears more resemblance to the conventional procedure to synthesize nanolaminates and nanoalloys by atomic layer deposition. In the supercycle strategy, instead of depositing 3 thick binary layers and then mixing them, many trilayers are deposited in sequence, and therefore, the film should start off better mixed and require less annealing to form the CZTS. If we consider the trilayer process based on sequence f, 190Cu2S/800SnS2/290ZnS, an analogous supercycle process would be 10(19Cu2S/80SnS2/29ZnS); that is, repeating the process 19Cu2S/80SnS2/23ZnS 10 times in sequence.

Raman spectra for an as-deposited supercycle film of the process 10(19Cu2S/80SnS2/29ZnS), as well as 190Cu2S/800SnS2/290ZnS before and after annealing, are presented in Figure 14. Interestingly, the as-deposited supercycle film exhibited a Raman scattering spectrum that resembled the annealed CZTS, except that the peaks were much lower in intensity and broader, as one would expect for a material with very small nanometer sized grains. The film thickness, however, was substantially reduced. This can be seen in Table 3, where the areal densities of each atom were reduced by a factor of ∼4 in the supercycle film compared to the trilayer film, despite the same total number of cycles of each binary process. This indicates that each layer had a nucleation delay, and so the average growth per cycle from the trilayer films cannot necessarily be used to predict the growth per cycle of the supercycle film. The measured sulfur areal density of 182 ± 12 nmol cm−2 for the 10(19Cu2S/80SnS2/29ZnS) supercycle film is not statistically significantly less than the expected amount if all of the metals were in their target oxidation states, which would be 213 ± 24 nmol cm−2, given the uncertainty in the areal density of each metal. The metal ratios, however, are different from the trilayer film. For the 190Cu2S/800SnS2/290ZnS trilayer film, [Cu]/[Sn] = 1.88 and [Zn]/[Sn] = 1.16, while for the 10(19Cu2S/80SnS2/29ZnS) film, [Cu]/[Sn] = 0.96 and [Zn]/[Sn] = 0.52. It is interesting that in both cases the [Cu]/[Zn] ratios are similar, 1.62 ± 0.15 in the trilayer case and 1.84 ± 0.15 in the supercycle case. When a supercycle film was deposited using the process 10(19Cu2S/40SnS2/31ZnS), the measured [S] = 56 ± 0.15 nmol cm−2 was much less than the expected sulfur concentration of 119 ± 13 nmol cm−2 if all of the metals were in their target oxidation states. The films also became delaminated in some places. Thus, 40 cycles of SnS2 seems insufficient to prevent ion exchange and reduction of the film, most likely caused by DEZ.

The Raman scattering spectrum for the as-deposited supercycle film presented in Figure 14 is encouraging. It suggests that a low temperature route for CZTS crystalline synthesis may be possible, with an adjusted pulse sequence to produce the correct composition if the nucleation behavior for each binary process was mapped out in detail, since the rule of mixtures clearly does not apply to this system.

**CONCLUSION**

The synthesis of Cu2ZnSnS4 by atomic layer deposition has been demonstrated. Two different strategies were presented. The trilayer strategy works by depositing thick (order 10 nm) layers of binary sulfides and then mixing them by thermal annealing. Only one trilayer sequence was found to be viable: substrate/Cu2S/SnS2/ZnS. Using this sequence, the metals were deposited in their target oxidation states and their ratios could be controlled through the cycle ratios. After annealing, the films exhibit Raman scattering spectra, XRD spectra, and an absorption coefficient consistent with CZTS. The CZTS was photoactive by PEC measurements, and exhibited an internal quantum efficiency of approximately 12% at −0.6 V vs Ag/AgCl under simulated AM1.5 illumination for photoreduction of Eu(III). The supercycle strategy is promising for synthesizing crystalline CZTS as deposited, but the rule of mixtures does not apply, and so, the nucleation behavior must first be mapped out in detail to arrive at the correct composition.

**ASSOCIATED CONTENT**

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

![Figure 14](image.png)

**Figure 14.** Raman spectra of a 190Cu2S/800SnS2/290ZnS trilayer film deposited on quartz before and after annealing in Ar and a supercycle film of 10(19Cu2S/80SnS2/29ZnS) as deposited. The plots have been offset for clarity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Cu]</th>
<th>[Zn]</th>
<th>[Sn]</th>
<th>[S]</th>
</tr>
</thead>
<tbody>
<tr>
<td>190Cu2S/800SnS2/290ZnS (trilayer)</td>
<td>190</td>
<td>117</td>
<td>101</td>
<td>400</td>
</tr>
<tr>
<td>10(19Cu2S/80SnS2/29ZnS) (supercycle)</td>
<td>68</td>
<td>37</td>
<td>71</td>
<td>182</td>
</tr>
<tr>
<td>10(19Cu2S/40SnS2/31ZnS) (supercycle)</td>
<td>49</td>
<td>24</td>
<td>35</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 3. Composition as Measured by XRF for Different Supercycle Films Compared to a Trilayer Film
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