Interfaces and Composition Profiles in Metal–Sulfide Nanolayers Synthesized by Atomic Layer Deposition

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INTRODUCTION

Atomic layer deposition (ALD) is emerging as the premier synthesis method for depositing ultrathin pinhole-free films with control over composition and thickness at the Angstrom to nanometer dimensional scale. ALD processes operate by exposing a substrate to sequential doses of complementary gaseous chemical precursors. Binary materials such as ZnS or ZnO are grown by alternating exposures to a cation precursor (e.g., ZnEt₂) and an anion precursor (e.g., H₂SO₄ or H₂O) in the ALD window. The ALD window is a set of key process parameters such as exposure times, purge times, and deposition temperatures for which the surface reactions are self-limiting. The ALD window is different for multilayers, the energy landscape and diffusion kinetics of the system at the deposition temperature determine the evolution of the composition distribution after the atoms are deposited.

Historically, the ALD community has focused intently on metal–oxides, with much less attention paid to metal–sulfides. It is known that multicomponent metal–oxide films synthesized by ALD often have nanolaminate morphology with the different materials spatially localized in discrete layers separated by sharp boundaries within the designated deposition region. Two examples of ALD nanolaminates are the MgO/ZnO and Al₂O₃/ZnO systems. ¹ ² ³ ⁴ ⁶ Solid-state diffusion at the deposition temperature is negligible for these materials as evidenced by the sharp interfaces.

Much less is known about ultrathin metal–sulfide multilayers synthesized by ALD. There has been a recent study on the ZnS/CdS system, ² but no high-resolution composition versus depth measurements have been made. This paper asks a general question: How sharp are the interfaces between ultrathin metal–sulfide layers synthesized by ALD? A distinctive characteristic of ALD is low growth rates compared to methods such as metal–organic chemical vapor deposition (MOCVD), physical vapor deposition (PVD), or chemical bath deposition (CBD). A low growth rate enables precise control over film
Chemistry of Materials

thickness but also allows more time for solid-state diffusion on the substrate to occur during deposition at elevated temperature.

ALD films can be prepared with a predesigned compositional sequence, which means atoms can be added to the surface in a prescribed order, but measurement of actual elemental profiles with a resolution less than the ultrathin constituent layer thicknesses is not trivial. Electron microscopy is exceptional at providing local information, but to improve statistics and obtain information on device-relevant areas on the order of nm, one must move past it. X-ray photoelectron spectroscopy and Auger electron spectroscopy both have escape depths from 1 to 5 nm, resulting in a depth resolution on the order of the predesigned layer thicknesses. Secondary-ion mass spectrometry (SIMS) is an alternative technique that is in a class of its own. In many SIMS instruments ion beam mixing can also limit depth resolution to a few nanometers, but in principle, SIMS can have a depth resolution characterized by the inherent escape depth of 1 atomic layers if ion beam mixing can be suppressed. In our SIMS setup, using a technique called gentle dual-beam (gentleDB) time-of-flight (TOF) SIMS, we are able to reach the fundamental limit of depth resolution.8 Ion beam mixing is reduced down to the scale of the escape depth by decreasing the milling ion beam energy. Ion milling is accompanied by a pulsed analysis ion beam to measure the intensities of elemental secondary ions generated as a function of sample depth by TOF SIMS.6 Milling ions are extracted from the ion source at a nominal energy of 5 keV and delivered into the target region, where the target potential decelerates them. This permits direct adjustment of the sputtering beam energy (down to the sputtering threshold) without losses of the ion beam current and degradation of the beam spot quality.9

Here we extend our work on the ALD synthesis of SnS/CuS layers described in earlier publications in this journal.10,11 Our interest in this multinary system stems from an alloy of these binary materials, Cu2ZnSnS4 (CZTS), which is an attractive absorber layer being explored for use in next-generation, high-efficiency photovoltaics.12,13 The study of interfaces and composition profiles in SnS/CuS multilayers is therefore of practical interest in terms of forming a homogeneous functional alloy as well as fundamental interest for assessing the sharpness of interfaces between ALD metal–sulfide layers.

### EXPERIMENTAL SECTION

**Atomic Layer Deposition.** ALD procedures below were adapted from those previously reported.10 ALD was performed in a Savannah S200 (Cambridge Nanotech, Cambridge MA) customized for compatibility with H2S.14 For all deposition, the hot-wall chamber temperature was 135 °C. The high-purity nitrogen flow rate was 10 standard cubic centimeters per minute 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). H2S was delivered to the elemental SnS2 deposited on Cu2S at these conditions is polycrystalline and oriented with the close-packed planes parallel to the substrate orientation.

**Secondary-ion mass spectrometry (SIMS).** Secondary-ion mass spectrometry (SIMS) studies were performed in a Savannah TOF SIMS,8 employing diethylzinc (DEZ, Sigma-Aldrich) and H2S.319.10,11 Diethylzinc was used. Diethylzinc was kept at room temperature. One cycle of DEZ consisted of pulsing 0.01 s DEZ dose, followed by a 1.0 s Ar+ pulse, finishing with a 1.0 s Ar+ pulse.

For ZnS, the known process11,14–16 employing diethylzinc (DEZ, Sigma-Aldrich) and H2S was used. Diethylzinc was used at room temperature. One cycle of DEZ consisted of pulsing 0.01 s DEZ dose, finishing with a 1.0 s Ar+ pulse. The ZnS produced by this process is expected to be polycrystalline and oriented with the close-packed planes parallel to the substrate.14 Measurements of SnS on silicon substrates revealed the films were crystalline, but interpretation was obscured when Cu2S was deposited on SnS because of interference from the Cu2S reflection. Safety note: DEZ is a pyrophoric, volatile liquid and must be handled with caution.

For the experiments where Cu2S was deposited on SnS and ZnS capping layers were deposited on annealed CZTS, the following pulse sequences were used at a chamber temperature of 175 °C. Conditions were used where the growth rate on silicon substrates was linear and well behaved. One cycle of ZnO consisted of pulsing DEZ for 0.015 s, purging with N2 for 10 s, pulsing H2O for 0.015 s, and purging with N2 for 10 s. For ZnO, 117 cycles were repeated to form the thin film limit where matrix effects are negligible. Samples for XRF were deposited on fused silica (quartz) to minimize interference from substrate impurities. 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].

**Depth Profile Measurement by gentleDB TOF SIMS.** Secondary-ion mass spectrometry (SIMS) studies were performed in a custom-designed SARISA (Surface Analysis by Resonance Ionization of Sputtered Atoms) instrument in the Materials Science Division at Argonne National Laboratory.19 For sputter depth profiling measurements, SARISA combines two independently optimized Ar+ ion beams: one of low energy (a few hundred electronvolts) at normal incidence for gentle ion milling enabling high depth resolution and another with 5–10 keV energy, obliquely incident (60°) and pulsed, for elemental time-of-flight (TOF) SIMS and/or laser postionization secondary neutral mass spectrometry (LPI SNMS) analysis with high lateral resolution. Elemental depth profiles, intensity versus depth, of samples were obtained by a sequence of alternating cycles. Ion milling by a raster scanned primary direct current (dc) Ar+ ion beam at 250 eV and normal incidence was followed by TOF SIMS analysis of the revealed subsurface (at various depths) by a raster scanned pulse (200 ms long) Ar+ ion beam at 5 keV energy, as shown schematically in Figure S1, Supporting Information. This pair of cycles was repeated multiple times until the Si substrate was reached, which was monitored.
by the Si$^+$ peak intensity in the mass spectrum. In the depth profile, the Si substrate grew in as a spike attributed to the enhanced secondary-ion yield due to oxidized Si substrate surface. The Si$^+$ peak intensity then stabilized at a lower constant level, as shown in Figure S2 (see Supporting Information). Depth resolution is controlled ultimately by the ion-milling beam characteristics. This condition is fulfilled if the effective erosion efficiency, $E \approx \gamma/\epsilon$, for the milling beam is much higher than that of the analysis beam or $\alpha = E_{\text{analytical}}/E_{\text{milling}} \ll 1$. Here, $Y$ is a sputtering yield, which depends on a beam energy $\epsilon$, the primary projectile species, and the incident angle, $j$ is the current density, and $t$ is the total sputtering time during which the ion beam is on. In the presented experimental setup, $\alpha$ was $\sim 10^{-3}$. The milling beam was digitally raster scanned over a square region with an area of $\sim 1 \text{mm}^2$ (blue square in Figure S1, Supporting Information), while the analytical beam was raster scanned over a square of $\sim 300 \times 300 \mu m^2$ (green square in Figure S1, Supporting Information). Both raster areas were precisely overlapped using an in situ Schwarzschild microscope and ex situ using white light interferometry-based optical profilometry.9

Ion beam currents were measured in situ by a custom graphite Faraday cup (FC) consisting of an internal pin (inlet holes of 250 $\mu m$ diameter) and the external surface. This design provides coarse control over the ion beam focusing conditions by measuring “internal” and “external” (mostly attributed to “wings”) components of the delivered current. Position of the FC precisely simulates a sample surface positioning with respect to focusing and directing ion optics of our mass spectrometer.9 The ion beam profiles were found to have a symmetric Gaussian-like distribution by burning dents in an Si fragment and then profiling them by ex situ optical profilometry.9 The well-defined beam profile allows one to precisely calculate the ion beam current density using the dc current value measured on the FC. The milling beam parameters at 250 eV were $\sim 1.5 \mu A$ dc and a full width at half-maximum (fwhm) of $\sim 150 \mu m$. The analytical beam characteristics at 5 keV were 300 nA dc and a fwhm of $\sim 40 \mu m$ and then reduced by choosing an appropriate aperture.

Measurement of energy spread $\Delta \epsilon$ of the low-energy system can be accomplished using the same FC. In this case, FC can be externally biased by a voltage of 0–5 kV, and the total current versus suppression voltage is measured. In such manner, inherent $\Delta \epsilon$ was estimated as 23 eV. Thus, the milling beam can be considered as monoenergetic to 23 eV/250 eV $\approx 1/10$ extent. In addition, we preselect pure Ar$^+$ ions component out of total current constituents by Wien filtering directly at the outlet of the ion source.

## RESULTS AND DISCUSSION

### Mixing Number

A dimensionless mixing number ($Mx$) is proposed to differentiate between ALD in three regimes of interfacial sharpness relative to the layer thickness. This number is a process parameter and can be used to describe mixing due to solid-state diffusion during film growth. In ALD, the thickness of a layer for a given growth rate and deposition time is

$$L_{\text{layer}} = \frac{\text{GPC}}{t_{\text{cycle}}} t \quad (1)$$

where GPC is the growth per cycle, $t_{\text{cycle}}$ is the cycle time (i.e., sum of exposure and purge times for both half reactions), and $t$ is the total elapsed time during growth of the layer ($t = n t_{\text{cycle}}$ where $n$ is the number of cycles). Consider that layer 2 is deposited on a pre-existing layer 1 (Figure 1) and a species in layer 1 (e.g., Cu$^+$) is allowed to diffuse, potentially resulting in a diffuse interface between layer 1 and layer 2. The diffusion distance is

$$L_D = \sqrt{D_t} \quad (2)$$

where $D$ is the diffusion coefficient of the mobile species (e.g., from layer 1) in the matrix (e.g., layer 2) and $t$ is the same as in eq 1, the elapsed time during growth of layer 2. If it is assumed that layer 1 is a constant source and layer 2 is a semi-infinite film, $L_D$ is the distance into layer 2 where the concentration of the diffusing species (e.g., Cu$^+$) is approximately 50% of the concentration in layer 1.

The mixing number, $Mx$, which describes the dispersion of the interface due to diffusion relative to the layer thickness, can be calculated by

$$Mx = \frac{L_D}{L_{\text{layer}}} \quad (3)$$

There are two different cases that must be considered for determining a value for $L_{\text{layer}}$. In the first case, diffusion from the preexisting layer (layer 1) into the layer being deposited (layer 2) is considered and $L_{\text{layer}}$ is calculated using eq 1. In the second case, diffusion from the layer that is being deposited (layer 2) down into the preexisting layer (layer 1) is considered and $L_{\text{layer}}$ is equal to the preexisting layer (layer 1) thickness. Three different regimes of $Mx$ are illustrated in Figure 1. If $Mx \ll 1$, then extensive mixing is expected resulting in a homogeneous multicomponent nanolayer. It should be noted that in the case of large $Mx$, assumption of a species diffusing from a constant source into a semi-infinite film is no longer valid and the boundary conditions must be adjusted if one wishes to accurately describe the mixing transient. Only a simple criterion is sought here, so the full mixing model is set aside for a later time. If $Mx \approx 1$, then well-defined nanolayers are expected with sharp interfaces. ALD research to date has predominantly been conducted in the $Mx \ll 1$ regime due to the very low diffusion coefficients characteristic of common metal oxides such as Al$_2$O$_3$, ZnO, TiO$_2$, and MgO. There is an intermediate regime for $Mx \approx 1$ where the layers exist as

![Figure 1. Schematic illustration of multicomponent thin film profiles resulting from different mixing during deposition for a given prescribed composition profile (i.e., layer order). Interfacial composition dispersion much smaller than the layer thickness ($Mx \ll 1$), interfacial composition dispersion on the order of the layer thickness ($Mx \approx 1$), and homogeneous composition from a diffusion length much longer than the layer thickness ($Mx \gg 1$).](image-url)
regions enriched in a particular species and some mixing occurs resulting in a graded profile and diffuse interfaces.

For an example calculation, consider the case of Cu⁺ diffusion into a 20 nm CdS layer (layer 2) that is deposited on top of a Cu₂S layer (layer 1) at a temperature of 135 °C. The case of Cu⁺ diffusion in CdS has been extensively studied. Using the data published by Sullivan, which represents a lower bound for $D$, at 135 °C the diffusion coefficient of Cu⁺ in CdS is 0.29 nm² s⁻¹. Using this value for $D$, a cycle time for the CdS process of 21 s, the measured GPC = 1.3 Å cycle⁻¹ and $n = 153$ by eq 3 $M_x = 1.5 \approx 1$, and therefore, a diffuse interface is expected separating layers of the intended Cu₂S and CdS.

Thin film metal–sulfide multilayers were deposited on silicon substrates at 135 °C, and depth profiles were measured by gentleDB TOF SIMS. The estimated resolution of the SIMS measurement under the conditions used for this work was 0.5 nm. Thin films with the structure 290cycle ZnS/800cycle SnS₂/Si substrate were deposited by ALD according to the procedures outlined in the Experimental Section. The total areal density of all atoms of interest (Cu, Zn, Sn, and S) was measured by X-ray fluorescence (XRF) on witness silica substrates, and it was found that the metal to sulfur ratios were consistent with the oxidation states Cu(+)I, Zn(++)II, Sn(++)IV, and S(--)II. If it is assumed that every binary compound was homogeneous with the bulk density in the position in which it was deposited (i.e., no mixing), then the multilayer structure would be 31 nm ZnS/37 nm SnS₂/24 nm Cu₂S/Si. The sum of these ideal layer thicknesses, 92 nm, is in excellent agreement with the overall thickness measured by cross-sectional SEM, 90 nm, for the same cycle numbers and deposition conditions.

Samples were annealed at 275, 350, and 425 °C for 60 min in Ar to study the effect of temperature on mixing. The as-deposited (AD) and annealed samples were pinhole free, as evidenced by no measurable silicon signal during SIMS measurement until the sputtering crater reached the substrate.

**Depth Profiles.** The depth profiles for the ZnS/SnS₂/Cu₂S/silicon multilayer are presented in Figure 2. Profiles are presented for an AD sample as well as samples deposited at the same conditions that were postannealed under argon at different temperatures. Profiles correspond to the integrated peak area of $m/z = +63$ for Cu, $m/z = +120$ for Sn, $m/z = +64$ for Zn, and $m/z = +32$ for S, which are unique for these elements. The theoretical laminate morphology is represented in Figure 2 as gray boxes that correspond to the ideal ZnS, SnS₂, and Cu₂S layers.

In the AD sample, Cu clearly diffused up through the SnS₂ and ZnS layers, resulting in a diffuse interface (Figure 2). The copper profile revealed that the SnS₂/Cu₂S interface diffused 16 nm into the SnS₂ layer from where it was expected based on the theoretical nanolaminate morphology. The movement of interfaces in this manner has been observed before for multilayers undergoing cation diffusion. Enrichment of Cu was observed at the ZnS/SnS₂ interface, with the concentration dropping through the ZnS layer toward the vacuum/ZnS interface (depth = 0). Enrichment of Cu at the ZnS/SnS₂ interface is consistent with defect-mediated transport through the SnS₂ and subsequent accumulation at the interface. SnS₂ is polycrystalline. X-ray diffraction patterns for SnS₂ synthesized at the same conditions as those used herein can be found in ref 10. A likely explanation is transport through grain boundaries, but at the moment we can only speculate about which defect is responsible. The intensity of the Cu signal at the vacuum/ZnS interface was very low, similar to the intensity deep into the Si substrate. X-ray photoelectron spectroscopy (results not shown here) detected only a trace signal for Cu at the surface of an AD

Figure 2. Composition profiles for Cu, Zn, Sn, and S measured by SIMS from 31 nm ZnS/37 nm SnS₂/24 nm Cu₂S/Si samples as deposited (AD) and annealed in Ar for 60 min at different temperatures. Theoretical nanolaminate morphology is shown as gray boxes.
sample prior to SIMS measurement. After annealing at 275 °C for 60 min in Ar, the Cu signal throughout the thin film homogenized, indicating that the structure was reasonably well mixed in terms of Cu concentration. Higher temperature annealing at 350 and 425 °C further flattened the Cu profile.

Examination of the Zn profile revealed that the ZnS/SnS2 interface occurred at the expected depth in the AD sample, according to the theoretical nanolaminate morphology and XRF measurement. However, in the AD sample Zn was detected throughout the structure until the Cu2S/Si interface, after which it dropped to the detection threshold of this species. Within the metal–sulfide multilayer, the concentration drop of Zn occurred across the SnS2 layer in the AD sample, with the Zn intensity in the Cu2S layer being approximately constant and equal to 4% of the value in the ZnS layer. This indicates that the diffusion coefficient of Zn in the SnS2 layer is lower than in Cu2S for these nanomaterials at the deposition temperature (135 °C). Upon annealing at 275 °C, the Zn concentration in the Cu2S layer increased by approximately a factor of 2 but the ZnS surface layer remained significantly enriched in Zn relative to the rest of the film. This is in contrast to the Cu, which had a relatively constant intensity throughout the depth after annealing at 275 °C. At 350 °C the Zn concentration near the vacuum/ZnS interface remained enriched relative to the rest of the film by approximately a factor of 2. Upon a further increase in temperature, at 425 °C the Zn concentration was relatively homogeneous, with only a slight decrease in the direction from the vacuum to the substrate interface.

Sn appeared only to mix with the Cu2S layer as deposited. The intensity of Sn in the ZnS layer for the AD sample was at the detection threshold of the measurement and similar to the intensity deep into the silicon substrate. Extensive diffusion of Sn into the Cu2S layer beneath it occurred, as expected given the movement of the SnS2/Cu2S interface observed in the Cu profile. The intensity of Sn in the Cu2S layer was more than 10% of the highest value at the ZnS/SnS2 interface. Annealing at 275 °C resulted in a relatively homogeneous Sn distribution. More mixing occurred at the higher temperatures of 350 and 425 °C, resulting in flatter composition profiles.

We next calculate the $Mx$ values for the as-deposited case. Since $Mx$ is defined as the ratio of the diffusion length to the thickness of the matrix in which the mobile species is diffusing, estimates of these parameters must be made. Only diffusion in the adjacent layer is considered here. There are then 4 calculations: Cu+ in SnS2, Sn4+ in Cu2S, Zn2+ in SnS2, and Sn4+ in ZnS. $L_{\text{diff}}$ is taken as the ideal layer thickness for each compound (i.e., the gray boxes in Figure 2). $L_{\text{D}}$ for Cu+ in SnS2 and Sn4+ in Cu2S are both estimated to be the distance that the SnS2/Cu2S interface moved, which is 16 nm (Figure S3, Supporting Information). For Zn2+ in SnS2, the case, the Zn signal in the SnS2 layer was fit using an exponential decay and the inverse of the argument was taken as $L_{\text{D}}$ (Figure S3, Supporting Information). The same procedure was used for Sn4+ in ZnS. The parameters used to calculate the $Mx$ values and results are summarized in Table 1.

For Cu+ in SnS2, Sn4+ in Cu2S, and Zn2+ in SnS2, the mixing numbers were similar to 1. Since the composition profiles are consistent with mixing for these species, the result confirms that using the $Mx$ process parameter is a reasonable way to form a first-order hypothesis on the sharpness of interfaces that will result from a given process. The $Mx$ value for Sn4+ in ZnS is much smaller than 1 because of the small $L_{\text{D}}$ value, which is

**Table 1. Summary of Relevant Mixing Parameters for the AD Case of 290ZnS/800SnS2/190Cu2S/Si**

<table>
<thead>
<tr>
<th>Mobile species</th>
<th>Matrix</th>
<th>$L_{\text{diff}}$ (nm)</th>
<th>$L_{\text{D}}$ (nm)</th>
<th>$Mx$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu+ SnS2</td>
<td>37</td>
<td>16</td>
<td>48.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Sn4+ Cu2S</td>
<td>24</td>
<td>16</td>
<td>48.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Zn2+ SnS2</td>
<td>37</td>
<td>4</td>
<td>11.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Sn4+ ZnS</td>
<td>31</td>
<td>1</td>
<td>11.9 &lt;8.4 × 10−3</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$Mx$ is the mixing number given in Table 1 is the upper limit. All of the other coefficients are in the range from $10^{-3}$ to $10^{-2}$ nm2 s−1. Compare this to the lower estimate of $10^{-1}$ nm2 s−1 for Cu+ in CdS at 135 °C described above. Despite these small diffusion coefficients, the consequence of the deposited layers being ultrathin and the deposition times being long is that diffuse interfaces are formed with mixing between the phases. This is beneficial for forming ultrathin homogeneous multicomponent films.

The behavior of ZnS/SnS2/Cu2S multilayers is of practical importance in forming Cu2ZnSnS4 nanolayers for use in photovoltaics. We have previously shown that when these multilayers were annealed at elevated temperatures in excess of 400 °C they formed Cu2ZnSnS4 as evidenced by Raman spectroscopy and X-ray diffraction.10 The present observation of homogenization at 425 °C is consistent with these earlier indirect measurements of the composition distribution. Considering that the Cu and Sn concentrations in the film homogenize at a much lower temperature than Zn, the present results are consistent with the predicted24 solid-state reaction mechanism

\[ \text{Cu}_{2}S + \text{SnS}_{2} + \text{ZnS} \rightarrow \text{Cu}_{2}\text{SnS}_{3} + \text{ZnS} \]  

\[ \text{Cu}_{2}\text{SnS}_{3} + \text{ZnS} \rightarrow \text{Cu}_{2}\text{ZnSnS}_{4} \]

where the second step described by eq 5 limits the overall rate of solid-state reaction.

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**Table 2. Summary of the ALD Process Times for Each Layer**

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_{\text{cycle}}$ (103 s)</th>
<th>$n$</th>
<th>$t$ (103 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2S</td>
<td>0.0311</td>
<td>190</td>
<td>5.90</td>
</tr>
<tr>
<td>SnS2</td>
<td>0.0455</td>
<td>800</td>
<td>36.4</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.0410</td>
<td>290</td>
<td>11.9</td>
</tr>
</tbody>
</table>

$D_{\text{eff}}$ is the apparent diffusion coefficient with the constraint $D_{\text{eff}} < D_{\text{D}}$.
ZnO and ZnS Capping Layers on CZTS. Since the mixing behavior of metal–sulfide and metal–oxides is so different, a natural curiosity arises about the behavior of an oxide/sulfide heterojunction. The Zn(O,S)/CZTS heterojunction is of interest for next-generation CZTS solar cells because it would allow for the toxic CdS buffer layer to be removed from the device stack and so the diffusion barrier properties of ALD ZnO and ZnS on the fully mixed CZTS (annealed at 425 °C) were examined. This CZTS annealed at 425 °C is crystallized in the Cu2ZnSnS4 structure. The depth profile for a 20 nm ZnO film deposited on a CZTS surface was compared to 22 nm ZnS, all other parameters associated with the CZTS being the same.

Two 31 nm ZnS/37 nm SnS2/24 nm Cu2S/Si samples with the same composition as those shown in Figure 2 were annealed at 425 °C for 60 min in Ar to mix them. Following annealing of the quaternary sulfide, 20 nm of ZnO was deposited on one sample by the ZnEt2/H2O process and 22 nm of ZnS was deposited on the other sample by the ZnEt2/H2S process, both depositions at the same temperature of 175 °C. The composition profiles are presented in Figure 3.

![Figure 3. Composition profiles for 20 nm ZnO (top) and 22 nm ZnS (bottom) capping layers deposited at 175 °C by ALD on the surface of a CZTS film. CZTS means a 31 nm ZnS/37 nm SnS2/24 nm Cu2S/Si sample that was annealed at 425 °C in Ar for 60 min prior to deposition of ZnO or ZnS. Blue (top) and gray (bottom) boxes indicate the ideal nanolaminate morphology.](image)

The 20 nm ZnO layer on the surface suppresses the transport of Sn and Cu relative to the 22 nm ZnS layer, but there was still significant Cu and Sn measured in the oxide. The intensity of the Cu signal at the vacuum/ZnO interface (I_Cu = 9) was similar to the intensity in the CZTS bulk but lower than the value at the vacuum/ZnS interface (I_Cu = 30). The observation that the Cu intensity reached a minimum in the ZnO layer (also within the ZnS layer) and then increased at the vacuum/ZnO interface indicates surface segregation of Cu and transport via defects in the polycrystalline ZnO layer. At this point we can only speculate about which defects are responsible. Grain boundaries are a likely candidate to cause such Cu behavior. The intensity of Sn in the ZnO (I_Sn = 0.1) was lower than in the ZnS (I_Sn = 0.3), again indicating that the oxide suppressed cation transport to some extent but did not completely prevent it. These results contrast with previous results on Cu2O/20 nm ZnO layers, where no Cu+ transmission through the ZnO was detected. It is also interesting to note that Figure 3 indicates significant mixing of the S and O anions at the ZnO/CZTS interface. While further work is clearly necessary to fully characterize the oxide/sulfide heterojunction, these first results on the ALD ZnO/CZTS heterojunction indicate that the mobility of cations in the substrate or underlying layer, onto which the ALD layer is being deposited, plays a critical role in determining the elemental composition of the ALD layer itself. This is reasonable because the cations must be mobile in the substrate for it to act as a source of impurities in the thin film.

CONCLUSION

The depth profiles of metal–sulfide multilayers synthesized by atomic layer deposition have been measured using high depth resolution gentleDB TOF SIMS. Depth profiles of ZnS/SnS2/Cu2S/Si multilayers revealed that even at the low deposition temperature of 135 °C extensive mixing takes place between the layers resulting in a graded composition profile. This result means that the deposition of metal–sulfide multilayers by ALD is in an entirely different regime than metal–oxides. For metal–sulfide deposition at typical ALD conditions, the diffusion length of cations can be expected to be on the order of the layer thickness and so diffuse interfaces will form. This is different from ALD of metal–oxides, for which sharp interfaces are often reported and the diffusion length is much shorter than the layer thickness. The 31 nm ZnS/37 nm SnS2/24 nm Cu2S/Si multilayer can be mixed by annealing at 425 °C for 60 min in Ar, and so this is the starting point for device performance-driven process optimization at these thicknesses. ZnO was found to be more effective than ZnS as a diffusion barrier for Cu and Sn when used as a capping layer on CZTS, but significant transmission of both species occurred. The concave up composition profile for copper in the ZnO capping layer indicates segregation via defects to the interface at depth = 0. Further process optimization to increase growth rate or eliminate the defects responsible could suppress cation transmission through the oxide.

ASSOCIATED CONTENT

Supporting Information

Experimental details and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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