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Ion Exchange in Ultrathin Films of Cu_2S and ZnS under Atomic Layer Deposition Conditions

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Supporting Information

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Chalcocite, Cu_2S, is a p-type semiconductor that is an attractive absorber for solar energy conversion because of its band gap (E_g = 1.2 eV), its nontoxicity and the abundance of its constituent elements. The n-CdS/p-Cu_2S heterojunction was extensively studied for its use in photovoltaic (PV) cells throughout the 1970s and 1980s,[1−3] with power conversion efficiencies approaching 10%.[4] However, concerns about the junction stability[5] and the toxicity of cadmium led to abandonment of this system for large-scale power production. The limited performance was attributed in part to a short minority carrier (electron) diffusion length in the Cu_2S, which has been reported to be from 100 to 700 nm in high quality devices.[1] The minority carrier diffusion length is incommensurate with the absorption depth near the band gap (α^{-1} (975 nm) = 1.3 μm), necessitating a folded PV geometry with aspect ratios from 2 to 13 to absorb over 90% of the photons in AM1.5 sunlight with energies greater than E_g. Even higher aspect ratios could, in principle, allow for lower quality Cu_2S to be used.

Atomic layer deposition (ALD) is an attractive layer-by-layer synthesis process for Cu_2S-based photovoltaics because it can be used to coat high-aspect-ratio substrates with conformal layered structures that can have a precisely prescribed compositional profile, which would be necessary to form a p/n heterojunction to make a photovoltaic operate. One could imagine synthesizing a p-Cu_2S/n-ZnO heterojunction, which has theoretical energetic advantages compared to the n-CdS/p-Cu_2S heterojunction,[6] and is hypothetically more stable due to anion asymmetry at the interface and slower cation diffusion in the oxide. The design alleviates the toxicity and stability concerns associated with CdS and has the added potential benefit of higher power conversion efficiency.

ALD processes operate by alternating doses of different volatile reactants (e.g., cation and anion precursors) with purge steps in between.[7] For true ALD, the process must operate within the ALD window,[8] which is a set of temperatures, partial pressures, and timings where the half reactions on the surface are self-limiting. Our studies on the synthesis of layered ZnO and Cu_2S by ALD revealed an unexpected phenomenon that occurred between the ALD precursors and ultrathin films during the synthesis process. In this letter, we discuss this phenomenon, which has important consequences for the synthesis of layered sulfide structures by ALD.

In this report, we demonstrate that diethyl zinc (DEZ), the standard metalorganic Zn^{2+} precursor used to synthesize ZnO by ALD,[9] can be used to convert an ultrathin Cu_2S film into ZnS and copper metal at low temperatures on a time scale of minutes. Furthermore, exposure of ZnS to bis(N,N′-disec-butylacetamidinato)dicopper(I) {[Cu(^{s}Bu-amd)]$_2$, Cu_2DBA}, a Cu(I) ALD precursor[10−12] for Cu_2S,[13] at low temperature results in the conversion of ZnS into Cu_2S and further results in the removal of Zn from the film. Ion exchange has been studied in solvated ionic systems[14−16] and at solid−solid interfaces,[16,17] but only preliminary reports have been made (for the CdS/ZnS ALD system) of ion exchange at gas−solid interfaces.[18] Moreover, such a dramatic exchange resulting in conversion of an entire film, to our knowledge, has not been reported in the ALD literature.

Cu_2S and ZnS films were synthesized by atomic layer deposition using standard A-B cycles at temperatures ranging from 135 to 150 °C as described in the experimental details section of the Supporting Information. The films were deposited onto quartz substrates for ex situ characterization and quartz crystal microbalance (QCM) sensors for in situ studies of the mass evolution. The Cu_2S and ZnS films were then exposed to controlled pulses of DEZ and Cu_2DBA respectively (A cycle only) under standard growth conditions. Cu_2S+DEZ denotes Cu_2S exposed to DEZ and ZnS+Cu_2DBA denotes ZnS exposed to Cu_2DBA. The Cu_2S and ZnS films were not exposed to air between deposition and exposure to the respective precursor, although it was found that the native oxide formed on ZnS through air exposure did not significantly affect the ion exchange. The Cu_2S and ZnS films were characterized before and after exposure to DEZ and Cu_2DBA respectively, by ultraviolet−visible−near-infrared (UV−vis−NIR) absorbance spectroscopy, X-ray diffraction (XRD) for crystalline phase analysis, X-ray energy dispersion spectroscopy (EDS) for elemental analysis, and X-ray fluorescence (XRF) for compositional quantification.

We postulate that the following reactions take place between the bulk of the sulfide thin films and the opposing metalorganic precursor:

$$Cu_2S(s) + Zn(C_2H_5)_2(g) \rightarrow ZnS(s) + 2Cu(s) + C_4H_{10}(g) \quad (1)$$

$$ZnS(s) + Cu_2DBA(g) \rightarrow Cu_2S(s) + Zn(DBA)(g) \quad (2)$$

Where (g) and (s) indicate whether the species is a gas or solid, respectively. In reaction 1, Zn^{2+} is exchanged for $2Cu^+$ in the sulfide sublattice and copper is reduced from Cu_2S to Cu metal. For

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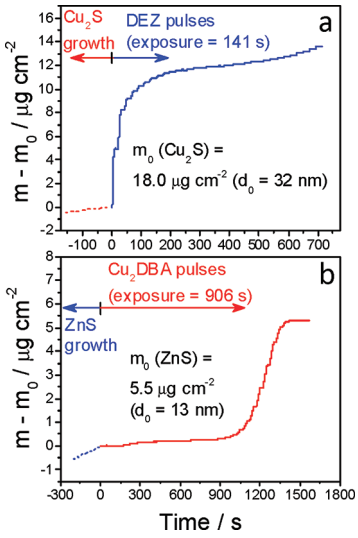

Figure 1. Summary of QCM measurements. The mass on the QCM is referenced to the initial mass of the Cu_2S (a) or ZnS (b) film before exposure to DEZ (a) or Cu_2DBA (b). The dashed curve is the mass before exposure, and the solid curve is the mass during exposure to repeated precursor pulses. The time is referenced to the end of film deposition, and the beginning of DEZ (a) or Cu_2DBA exposure (b). The mass equivalent thickness of each film is given as d_0. The expected mass changes if the surface reactions were self-limiting are more than 2 orders of magnitude smaller (0.072 and 0.057 $\mu g\ cm^{-2}\ cycle^{-1}$ for Cu_2DBA and DEZ, respectively) than what was observed.

2, there is no redox reaction and the cation in the sulfide sublattice (Zn^{2+}) simply exchanges with the two Cu^+ in the metal organic precursor, which is then pumped away resulting in a loss of Zn from the film but an overall mass gain due to the uptake of 2 Cu and loss of 1 Zn. We note that eqs 1 and 2 were postulated based on solid-state characterization, and no direct measurements have been made at present of the gas-phase products, but work is ongoing.

The QCM measurements revealed large mass increases upon exposure of Cu_2S to DEZ and ZnS to Cu_2DBA (Figure 1). In both cases, the mass gains were more than 2 orders of magnitude larger than what would be expected for self-limiting surface reactions typically observed for ALD. In the Cu_2S+DEZ case, the final mass after 141 s of DEZ exposure was 14 $\mu g\ cm^{-2}$ higher than the initial Cu_2S mass of 18 $\mu g\ cm^{-2}$ (18.0 $\mu g\ cm^{-2}$ = Cu_2S mass equivalent thickness of 32 nm). In the ZnS+Cu_2DBA case, the final mass after 906 s of Cu_2DBA exposure was 5.0 $\mu g\ cm^{-2}$ higher than the initial mass of ZnS 5.5 $\mu g\ cm^{-2}$ (5.5 $\mu g\ cm^{-2}$ = ZnS mass equivalent thickness of 13 nm), and did not increase upon further Cu_2DBA exposure. We observed a significant delay for the mass increase in the ZnS+Cu_2DBA case which we attribute to the complete consumption of the Cu_2DBA on surfaces upstream of the QCM. The very large mass increase in both cases upon precursor exposure is consistent with eqs 1 and 2, and in particular indicates that Cu is not volatilized in the Cu_2S+DEZ case.

The UV−vis−NIR absorbance spectra (Figure 2) support eqs 1 and 2. The natural absorption coefficient was determined by measuring the transmission spectra and correcting for measured normal incidence reflection. After exposure to DEZ, the Cu_2S (E_g = 1.2 eV) absorbance spectrum lost the band-edge absorption at 1000 nm as well as the strong transition at approximately 600 nm. The spectrum also gained a broadband vertical offset characteristic of a metal and a sharp feature at approximately 350 nm. These results are consistent with the

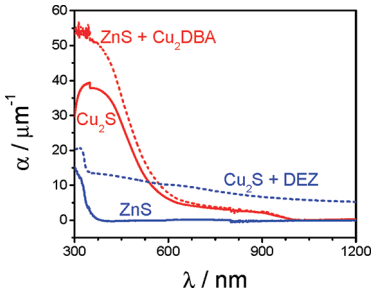

Figure 2. Natural extinction coefficient of Cu_2S and ZnS before and after exposure to DEZ and Cu_2DBA respectively. The Cu_2S, ZnS, and ZnS +Cu_2DBA film thicknesses were measured by ellipsometry to be 59, 54, and 68 nm respectively. The thickness of the Cu_2S+DEZ film was calculated assuming complete conversion of Cu_2S to ZnS + Cu^0 and S^{2-} conservation.

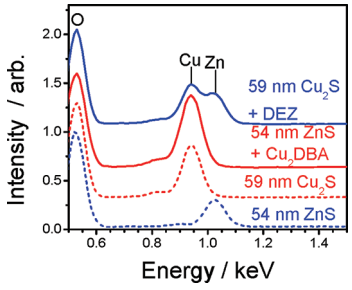

Figure 3. EDS spectra of the Cu_2S and ZnS films before and after exposure to DEZ and Cu_2DBA respectively. The $O_{k\alpha}$ (substrate) $Cu_{L\alpha}$ and $Zn_{L\alpha}$ peaks are labeled. The plotted energy range was chosen to resolve the $Cu_{L\alpha}$ and $Zn_{L\alpha}$ which are very close in energy.

formation of ZnS and Cu metal per eq 1. After Cu_2DBA exposure, the spectrum of the original ZnS film (E_g = 3.6 eV) lost the sharp absorption at 350 nm, and gained an absorption onset at 1000 nm with approximately the same absorption coefficient as the as-deposited Cu_2S, and a stronger transition with an onset of approximately 600 nm. These results are consistent with eqs 1 and 2. Further supporting eq 2 is ellipsometry data for the ZnS+Cu_2DBA case, which yielded a ZnS film thickness of 54 nm before exposure to Cu_2DBA, and a Cu_2S film thickness of 68 nm after exposure. The later value is very close to the predicted Cu_2S thickness of 64 nm for complete conversion of a 54 nm ZnS film, based on the stoichiometry and density ratios, assuming a compact morphology and conservation of S^{2-}. Such agreement for ellipsometry was not observed in the Cu_2S +DEZ case because of delamination that occurred during DEZ exposure (see SEM, Figure S1 in the Supporting Information).

The EDS results for Cu and Zn in the different films provide further support for the proposed reactions (Figure 3). As expected, no Zn was observed in the as-deposited Cu_2S and no Cu was observed in the as-deposited ZnS. After exposure of Cu_2S to DEZ, both Cu and Zn were observed. After exposure of ZnS to Cu_2DBA, only Cu was observed. In each case, sulfur was also observed at 2.307 keV but has been omitted for clarity. XRF measurements of the sulfer, copper and zinc in the ZnS+Cu_2D-BA case as a function of the number of Cu_2DBA doses are plotted in Figures S4 and S5 in the Supporting Information. Again, the results are in excellent agreement with the proposed reactions. It is also noteworthy that copper is present in ZnS at an atomic concentration of 3% based on Zn after only eight 1.0 s Cu_2DBA pulses. Although the reaction takes several minutes to complete, there

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Table 1. Summary of XRD Measurements

	peak presence			
sample	ZnS (111_{ZB}), (002_{WZ})	β-Cu_2S (002), (004)	α-Cu_2S (−216)	Cu^0 (111)
ZnS	yes			
Cu_2S		yes		
ZnS + Cu_2DBA		yes[a]	yes	
Cu_2S + DEZ	yes			yes

[a] Only (004) visible.

is already significant incorporation after only a few seconds. The sulfur content remains constant, as expected for cation exchange.

XRD results further support the proposed reactions (Table 1 and Figure S2 in the Supporting Information). A full analysis of the results is presented in the Supporting Information, with only the conclusions summarized here for brevity. The as-deposited ZnS and Cu_2S exhibited peaks in the expected locations for these materials. After exposure of the Cu_2S to DEZ, the film showed a peak for ZnS and Cu metal with no Cu_2S peaks. After exposure of ZnS to Cu_2DBA, the film exhibited weak peaks at the expected locations for Cu_2S, and no peaks for ZnS.

Combined, the experimental evidence overwhelmingly supports hypothesis (1): Cu_2S+DEZ results in the formation of ZnS + Cu^0 and hypothesis (2): ZnS+Cu_2DBA results in the formation of Cu_2S. However, the precise stoichiometry of the phases is not available at present, and therefore the chemical formulas given above may be considered as approximate. Determination of the precise composition requires a detailed elemental analysis and may benefit from elucidation of the full reaction mechanism via examination of gas-phase products; studies are underway in our laboratory.

The effect of barrier layers on the ZnS+Cu_2DBA ion exchange process was briefly investigated by depositing 10 nm of Al_2O_3, TiO_2, or ZnO on the ZnS by pulsing trimethyl aluminum and water, titanium tetra-isopropoxide and water or diethyl zinc and water, respectively, at 150 °C in the ALD windows outlined in the literature.[9,19] In each case, after application of the oxide barrier layer, no evidence for ion exchange was observed in the UV−vis−NIR spectra. The spectra for 54 nm ZnS/10 nm Al_2O_3 + Cu_2DBA and 54 nm ZnS/10 nm TiO_2 + Cu_2DBA are presented in Figure S3 in the Supporting Information. These results are encouraging within the context of applications, including the improvement of Cu_2S-based photovoltaic stability through the use of an oxide n-type layer.

Given the generality of metal sulfide ion exchange in solution, it is likely that the phenomena identified in this study may apply broadly to the vapor synthesis of metal sulfide multilayer films to differing degrees. If so, this effect could hamper efforts to synthesize well-defined multilayers by ALD. However, when applied with foresight, the gas-phase ion exchange may also provide alternative, facile routes to metal sulfide films. For example, the conversion of ZnS to Cu_2S via Cu_2DBA exposure demonstrated herein produces films with less islanding (see SEM, Figure S1 in the Supporting Information) and requires less time than the traditional ALD route to Cu_2S.

In conclusion, we observed that the exposure of Cu_2S to DEZ at 135 °C with a DEZ partial pressure of approximately 0.5 Torr results in conversion to ZnS and Cu metal. Furthermore, exposure of ZnS to Cu_2DBA at 150 °C, even at low partial pressures (<0.1 Torr), results in conversion to Cu_2S accompanied by volatilization of Zn^{2+} (presumably with ligands attached). Both processes proceed to completion in a matter of minutes under the conditions tested in this study. Multilayer synthesis by ALD requires self-limiting processes for each component that can be executed at a common growth temperature. Typically, this requirement is sufficient to ensure success, but in the case of metal sulfide multilayers, ion exchange phenomena should also be considered.

■ ASSOCIATED CONTENT

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

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