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Electronic structure study of the CdS buffer layer in CIGS solar cells by X-ray absorption spectroscopy: Experiment and theory



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ABSTRACT

A systematic investigation of the electronic structure of the CdS buffer layer of CIGS solar cells has been undertaken using S *K*-edge X-ray absorption spectroscopy (XAS), both experimentally and theoretically. We found from XAS that growing CdS films by chemical bath deposition (CBD) exhibits more long-range disorder when compared to single crystal CdS, CdS grown by atomic layer deposition (ALD) and theory. We investigated the significance of a variety of point defects and potential atomic substitutions in firstprinciples estimates of the differential S *K*-edge XAS sensitivity. We find that substituting some sulfur atoms with e.g. oxygen or selenium does not introduce significant changes to the partial S(3*p*) density of states of the conduction band in CdS and we infer that the electronic structure modifications of these defects are spatially localized and do not hybridize strongly with bands with significant sulfur *p* character. Moreover, by comparison with experimental XAS should be sensitive to CdSO₄; however this is not in the CdS layers of CIGS devices studied here. We also find that the CBD of CdS on FTO-glass and separately on CIGS does not produce any significant changes in the local atomic structure of CdS indicating no CIGS-influenced growth.

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1. Introduction

Cadmium sulfide is commonly used as an interfacial layer in thin film photovoltaic (PV) technologies. [1] A typical solar cell architecture uses CdS as a 'buffer' or 'emitter' layer in contact with an absorber, such as those based on copper indium gallium diselenide (CIGS) or copper-zinc-tin-selenide (CZTS). The CdS layer (for a review see Ref. [1]) has a band gap of 2.4 eV that leads to losses in the blue region of the solar spectrum, which could be potentially recovered by a more transparent layer. The use of a heavy metal (Cd) further motivates the search for an alternative material. [2] For several years there has been interest to identify a replacement for CdS that would not require substantial processing and device architecture changes. [3] This has not been straightforward and many materials have been considered, with Zn(O,S) demonstrating highest efficiency to date for CIGS at 19.7% [4–7], which despite the higher transmission cannot match the recent 20.8% record for CIGS that employed a CdS layer. [4,8]

Chemical Bath Deposition (CBD) of CdS is a common method to deposit the material as the interfacial layer in CIGS and CZTS. CBD CdS has been a component of most solar cell efficiency records in CIGS [6]. The chemical bath processing itself has also been associated with alteration of the CIGS interface that produces favorable device performance. Because of the high overall efficiency, CBD has become the standard method for depositing CdS on CIGS devices. The purpose of this work is to obtain new information on the physical and electronic structure of the CBD CdS to better understand structure-property relationships that would be needed for replacement of CBD CdS. To compare and contrast CBD CdS, single crystal and growth of CdS by atomic layer deposition (ALD), which offers a controlled way to synthesize complex films, by coadsorbing gases which react at surfaces to form well-ordered films by layered growth. [9] ALD enables controlled incorporation of substitutional atoms such as oxygen as discussed below. [10].

The performance of CBD deposited CdS on CIGS devices merits more detailed investigation into the (electronic) structureproperty relationships of CdS and the interface with the absorber. CdS layers have previously been investigated by other techniques including XPS, X-ray emission spectrosocpy, optical

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absorption and reflectance techniques. [11–15] Here we use X-ray absorption spectroscopy (XAS); XAS is an element-specific probe of the (partial) unoccupied electronic structure of a material, explored via core-level transitions, governed by the dipole selection rule, from which the atomic structure or chemistry can be inferred. [16] XAS has previously been applied to a wide range of sulfur materials. [17–19] S 1s XAS is a relatively bulk sensitive method (probing depth on the order of a few microns when measured in the standard fluorescence mode) which can be used to study crystals, liquids, thin films and amorphous materials. Previous studies have studied CdS at both the S *L*-edge [20–23] and S *K*-edge [22,24], with many of the soft X-ray studies focusing on surface coverage and the less surface sensitive *K*-edge spectra largely focusing on mixing CdS with other materials.

In this paper, we investigate the sensitivity of the unoccupied electronic structure of CdS to various preparation methods (experimentally) and with respect to structure, finite temperature induced dynamics and defects (theoretically) as observable in S 1s XAS. We are primarily concerned with the CdS buffer layer itself, and the changes in the conduction band as a function of layer processing that can be observed in the S 1s XAS. This work provides the first direct comparison of the XAS of a variety CdS samples, including single crystals and thin-films grown by CBD and ALD methods. We will address the CBD processing and its effects on the CIGS surface and interface in future work, where we will explore CIGS structures containing various defects associated with the CdS-CIGS interface, often related to sulfur and cadmium migration into the CIGS, in addition to other CIGS-related compounds. [14,15,25–28]

2. Methods

2.1. Samples

The CBD CdS, was deposited on fluorine doped tin oxide glass, using a bath of ammonium hydroxide solution with cadmium sulfate and thiourea stirred at 65 °C. A detailed description of the CBD process has been previously reported. [29] XRD confirmed a cubic structure for CBD CdS. The ALD CdS was grown at 140 °C using alternating pulses of dimethyl cadmium and 15% hydrogen sulfide/85% N2 in a Beneq TFS 200 ALD system. The films were grown on Pyrex glass and consisted of 500 complete ALD cycles yielding a thickness of 60 nm as measured by ellipsometry. XRD confirmed a mixed hexagonal and cubic CdS structure as expected from the literature. [30] The cadmium oxy-sulfide (CdOS) was grown by introducing one pulse of dimethylcadmium and water every fifth ALD cycle yielding a 4:1 H₂S to H₂O ratio. The CdOS films were deposited on Pyrex glass and consisted of 500 ALD cycles with a thickness of \sim 50 nm. CdSO₄ hydrate and CdSO₄ (purchased from Sigma-Aldrich) were placed on low sulfur tape.

CIGS thin films were prepared on molybdenum-coated sodalime glass. The CIGS absorber layer was deposited via NREL's three-stage process with a modification of the second stage. [31,32] Instead of starting stage 2 immediately after the first stage, there was a 3.5 min delay before beginning the Cu deposition. This allowed the substrate temperature to reach 600 °C before the Cu flux was above 3 Å/s. The final flux of Cu in the second stage was 6.8 Å/s, which is higher than that used in our standard three-stage process.

The various methods of growth were attempted in order to determine the importance of each step. It is our hope that by changing as many growth variables as possible that the effects of choices at each step can be determined.

2.2. XAS Measurements

The measurements were taken at wiggler beamline 4–3 at the Stanford Synchrotron Radiation Lightsource using a Si(111) double-crystal monochromator, providing -8×10^{11} ph/s in a 2×12 mm beam spot with a nominal resolving power (*E*/ ΔE) of 10⁴. [33] The XAS measurements were performed in a standard X-ray fluorescence geometry (detected perpendicular to the incoming X-ray axis in the horizontal plane), where the partial S-*K* α emission line was resolved and collected using a four-element silicon drift detector. The measurements were taken at room temperature.

2.3. Calculated XAS Spectra

The method for calculating X-ray absorption spectra using the excited electron and Core-Hole (XCH) approach has been detailed previously. [34] In particular, we use the QUANTUM ESPRESSO electronic structure suite, within the plane-wave ultrasoft pseudopotential formalism, using orbital-occupancy constrained DFT employing the Perdew–Burke–Ernzehof (PBE) exchange-correlation functional. [35] The transition amplitudes are calculated according to Fermi's golden rule for X-ray absorption cross-sections:

$$\sigma(\omega) = 4\pi^2 \alpha_0 \hbar \omega \sum_f |M_{i \to f}|^2 \delta(E_f - E_i - \hbar \omega). \tag{1}$$

In this case, α_0 is the fine structure constant, $\hbar\omega$ is the energy of the absorbed photon and $M_{i \to f}$ are the transition amplitudes between the initial (*i*) and final (*f*) states, with a corresponding energy difference of $E_f - E_i$ We use the electric-dipole approximation, and approximate the transition amplitudes as effective single particle matrix elements:

$$M_{i \to f} = \langle \Psi_f | \hat{\varepsilon} \cdot \mathbf{R} | \Psi_i \rangle \approx S \langle \psi_f \hat{\varepsilon} \cdot \mathbf{r} | \psi_i \rangle \tag{2}$$

where $\hat{\varepsilon}$ is the polarization direction of the photon electric field vector, \boldsymbol{R} and \boldsymbol{r} are the many-body and single-particle position operators, respectively. The single particle Kohn-Sham eigenstates are represented as ψ_i and ψ_f . For the present work, the initial state is always the 1s orbital of the excited S atom and the final states are the unoccupied Kohn-Sham eigenstates derived from a selfconsistent field calculation within the excited electron and Core Hole (XCH) approximation for the electronic final state. [36] With this approach the excited-state electron density is computed self consistently within a supercell (multiple crystal primitive cells) with the replacement of the ground state pseudopotential of one core-excited atom in the system with that derived from a similarly core-excited isolated atom (for the S K-edge, we assume the configuration of $1s^{1}2s^{2}2p^{6}3s^{2}3p^{5}$) to model the hole, and with the addition of one extra (excited) electron to the total number of ground state valence electrons in the system. The supercell is large enough such that the spectrum has converged with system size (a good rule of thumb is $\sim 1 \text{ nm a side}$).

Calculated spectra were convoluted with a Gaussian of 0.3 eV standard deviation to match the instrumental broadening. We have not further broadened the spectra (e.g. mimicking final state lifetimes, vibrational broadening, etc.) to help emphasize and interpret the spectral contributions to the measured features. The sum over final states includes both electronic band indices and wave vectors. Typically, this will require several *k*-points, and we reduce the computational cost by exploiting an efficient numerical scheme from which the entire Brillouin zone can be generated based only on band information from the zone center. [37] To interpret X-ray transitions, we also examine isosurfaces of the electronic component of the excited state, approximated as a Kohn–Sham eigenstate in the unoccupied eigenspace of the XCH

self-consistent field with electron wave vector k=0. By doing this we are approximating the *K*-edge excitonic excited states to be factorizable into a product of the *1s* hole state and the corresponding electronic response to the core-hole perturbation. This method has produced accurate results in the past, comparable with the accuracy of BSE in certain cases. [38,39] We plot representations of these electronic isosurfaces in 3D using VESTA. [40] This allows us to correlate specific spectral changes with the character of specific states.

The X-ray absorption spectra are aligned relative to a theoretical standard defined by the isolated excited and ground state atom under the same periodic boundary conditions. [34] This is equivalent to computing a difference in formation energies between the excited and ground states, and formation energies are numerically well defined within a pseudopotential framework. We then shifted the computed excitation energies for all calculated spectra based on alignment to one experimentally well-defined system (Li₂S). This constant shift is valid for all further calculations using the same excited state pseudopotential. [41] In certain cases a stretch can be applied to correct for DFT underestimating the band gap, but this was not necessary here. The electronic density of states was calculated within Quantum-ESPRESSO. [42]

We also calculated spectra using the OCEAN package, a Bethe-Salpeter equation (BSE) approach that utilizes DFT as a basis. [39] The electronic structure was calculated within the local-density approximation using the QUANTUM ESPRESSO code [42], and sampling of the Brillouin zone was improved through use of a *k*-point interpolation scheme. [37] For the final states we included the first 500 conduction bands, and the screening of the core-hole potential included 2000 bands. For the BSE calculations we used $5 \times 5 \times 5$ k-point sampling and down-sampled the wave functions to a $10 \times 10 \times 10$ real-space mesh from a DFT planewave cut-off of 100 Ry (as required by the harder norm-conserving pseudopotentials).

2.4. Structural Models

Typically, for our DFT-XCH XAS simulations, we are limited, due to computational effort, to structural models with length scales ranging up to 1–2 nm and numbers of atoms less than – 500. The structural parameters of all crystalline phases considered in this work were taken from the literature. [43] Point defects were embedded in supercells (multiple primitive cells) and the atomic structure was then relaxed by minimizing forces to within 10^{-3} Rydberg/bohr. The spectral effects of allowing the lattice vector to relax was negligible in a few test cases. For the finite-temperature spectral estimates for CdS, first-principles molecular dynamics simulations were performed with VASP using the PBE functional [44]. The system was equilibrated for 5 ps and a single snapshot was used for spectral simulations, sampling all 108 S atoms to capture spectral variations due to structural disorder present at finite temperature.

3. Results and discussion

3.1. Pure crystalline phases

In Fig. 1, we outline the work presented in this study. A typical solar cell structure for a CIGS absorber is shown (left), where the CdS buffer layer is placed on top of a CIGS layer. We experimentally investigate the conduction bands in CdS using S 1s (*K*-edge) XAS, which maps out the partial density of states as defined by the dipole selection rule (i.e. only states with S *p*-character will contribute to the spectrum). We compare the S 1s XAS of various cadmium sulfide samples, including single crystals and thin films prepared by CBD and ALD. Comparison of the XAS for CBD CdS, ALD CdS and single crystal CdS gives us a platform to identify structure–property relationships that can be interpreted with theory. To analyze and interpret the experimental data we used density functional theory (DFT) [36], to allow us to explore the underlying origins of various features in the experimental spectra and evaluate the impact of disorder, defects and impurities.

In Fig. 2, we present experimental X-ray absorption spectra at the sulfur K-edge of: CBD CdS on CIGS (dark green) and on glass (light green); ALD deposited layers of CdS (blue) and CdS alternating with CdO (red); and single crystal cubic CdS (grey) as well as single crystal hexagonal CdS reproduced from the literature (red dashed) [45]. The dashed vertical grey lines highlight the locations of the first and second peak. The substrate makes no noticeable difference in the case of CBD, which is expected as the amount of Sulfur interacting with the surface should be very minor (>2%)for the amount of CdS deposited here. The spectrum of the single crystal CdS (cubic) sample is very similar to that of the ALD sample in both peak positions and energies, which is not unexpected given previous results from different techniques comparing CBD to ALD [46]. However, when the CdS is grown by chemical bath deposition rather than by ALD the features at 2474 eV and 2476 eV are less well separated, and the feature at 2478 eV is less pronounced, highlighted in Fig. 2(a). The intensity of the second peak is enhanced in ALD and CdS (cubic) as compared to the chemical bath deposition. We also note very little spectral difference at the S K-edge when comparing different samples grown with ALD, either pure CdS or alternating CdS and CdO. This is not particularly surprising when one considers that XAS is largely a local probe and the nearest oxygen atom is expected to be at least 2 atomic coordination spheres away from a given sulfur atom (assuming no interlayer diffusion in the ALD process) as well as having a cubic crvstal structure.

By comparing first-principles simulations of the XAS of a static model (i.e., atomic nuclei clamped at their equilibrium positions) of the perfect cubic crystal (Fig. 2b, black) with the spectrum at room temperature (purple), one can tell that disorder leads to some spectral broadening that slightly blends the first two features together due largely to bond length changes being averaged instead of discrete. CdS is also found in two other crystal



Fig. 1. A schematic representation of a typical CIGS device, showing each of the layers and their typical thicknesses (left). The CdS layer is generally not larger than 100 nm. Various samples grown by different methods were compared with simulated data.



Fig. 2. (a) Experimental S K-edge X-ray absorption spectra. All experimental spectra are taken on glass except where noted. From the bottom, experimental spectra of an ALD grown sample of CdO alternated with CdS on a working device (red), an ALD grown sample of CdS on a working device (blue), a chemical bath grown sample of CdS on a working device (dark green) as well as a chemical bath deposition on glass (light green), a single crystal cubic sample of CdS (grey) and single crystal hexagonal sample of CdS (red dashed) from the literature (see text). 2(b) Theoretical spectra of pure CdS are shown for comparison with the experimental crystal cubic spectrum (grey). The crystal structure seen in experiment (ZnS cubic) is simulated at room temperature (dark purple) as well as a 0 K (black). These are contrasted with the calculated CdS structure at in different forms at 0 K, the ZnS hexagonal structure (light green) and the NaCl structure (pink). The calculations are also compared with Bethe-Salpeter calculations from the OCEAN code, consisting of the CdS structure in the cubic (light blue) and hexagonal (yellow) structures. The locations of the first two transitions are highlighted with a grey dashed line. 2(c) Specific focus on the near-edge spectral region in the experimental data highlighting peak-shifts. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 Table 1

 Characteristic bond lengths and angles for various CdS/CdO structures.

X=S or O	CdS–ZnS (cubic)	CdS-ZnS (hexagonal)	CdS-NaCl	CdO-NaCl	CdO-ZnS (hexagonal)
Cd–X Bond length	2.519	2.527	2.725	2.348	2.168/2.181
# nearest neighbors	4	4	6	6	4
X–X bond length	4.114	4.136	3.854	4.696	3.507/3.582
Cd–X–Cd Bond Angle	109.5	109.1/109.9	90	90	107.5/111.4
Cd–X–Cd–X Dihedral Angle	- 60/60/180	- 60.5/59/180	0/-90/90/-180	0/-90/90/180	0/55/62.5/120/180



Fig. 3. Images of the LUMO and LUMO+1 of the three CdS structures studied within this paper. While the ZnS(cubic) and ZnS(hexagonal) have similar LUMO's, the NaCl LUMO is significantly less localized on the excited atom. However, the ZnS (hexagonal) LUMO+1 has significantly more p-type character, leading to a stronger intensity. The NaCl structure has very different LUMO characteristics. The images are discussed in more detail in this paper.

structures, and it is worth mentioning that the computed XAS of the high pressure NaCl-phase (pink) does not at all agree with the measured spectrum. However, the XAS of the zincblende wurtzite structure (green) agrees quite well with the corresponding single crystal experiment (red dashed), although less with the ALD deposited films. It is important to note that the nuclear motion causes spectral differences from the static cases. Primarily, in the calculated spectrum, the peaks at just below 2475 eV and at 2476 eV exhibit lower intensity with respect to the first peak.

It is also interesting to note the effect of the method used to calculate the X-ray absorption spectrum. The 0 K structure of CdS the cubic (light blue) and hexagonal (yellow) are shown for comparison calculated by solving the Bethe-Salpeter equation (BSE). This method appears to do a better job of capturing the transition energies and also of obtaining the large peak width found in experiments. As with the XCH calculation, the cubic calculation is made up of many transitions, but the BSE calculation generates different transitions with a closer match to experiment. Even though the underlying DFT is identical, the different methods yield this difference. Neither method exactly captures the experimental spectrum, but both methods reproduce all the observable features. In all calculated cases, a better visual fit could be obtained using a larger numerical broadening, closer to what would be experimentally found. It is also possible disorder in the nominally perfect crystal is improperly treated.

The differences in the crystal structure found in CdS and CdO lead to significant differences in properties like bond lengths and angles, as summarized in Table 1. In particular, the NaCl crystal structure has a significantly shorter Sulfur–Sulfur bond length and higher coordination. The CdO crystals are notably different from their CdS counterparts primarily in bond length, as the oxygen is a smaller atom. The CdO ZnS (hex.) differs from the CdS ZnS(cubic) in terms of bond angles also. The shorter NaCl crystal bond length leads to the drastic splitting of the first two peaks of the CdS spectrum. The other more similar crystal structures also exhibit significant differences in the energies and intensities of the first two spectral peaks, demonstrating that these two peaks will be sensitive

to the local environment. The higher energy spectral features (energy > 2490 eV) are roughly similar between all of the spectra.

Since these first two peaks are so sensitive to the crystal structure it is worth investigating qualitatively what causes these features to arise. For this reason specific states were imaged for the CdS primary crystal structure, shown in Fig. 3. In both the ZnS (cubic) and the ZnS(hex.) the first two available XCH excited states (labeled as LUMO and LUMO +1) are the strong transitions giving rise to the first peak. The high pressure NaCl crystal structure behaves fundamentally differently, with the first excited state (LUMO) being an almost completely dark state, appearing as a small bump -3 eV before the first strong transition. This is consistent with what has been seen in other octahedral structures. [41] The LUMO+1 and higher transitions are largely delocalized due to the short interatomic distances induced by the high pressure. While both zincblende LUMOs appear largely similar in character (both have three density lobes symmetrically centered about the atom of interest), it is apparent that the LUMO+1 in the ZnS(hex.) structure has significantly more p-character than the LUMO+1 in ZnS(cubic), leading to the stronger transition in the ZnS(hex.) for this calculated crystal. It also indicates that while nearest neighbor effects will be important, the wave function does not extend strongly beyond the first coordination sphere, indicating that XAS will be insensitive to changes at large distance from the defect. The shorter anion-anion distance as well as the vastly different symmetry certainly factors into why the highpressure structure has such a different character of states compared to the lower pressure structures.

4. Signatures of impurities

The CBD of CdS is performed in basic solution (NH₄OH) using CdSO₄ and thiourea as precursors, and thus has the potential to introduce defects and impurities into the CdS, such as vacancies, oxygen, hydroxyl, and sulfate contamination. In the following we systematically investigate specific defects in our theoretical framework and how these defects would manifest themselves in the S 1s XAS. A series of potential defects are shown in Fig. 4. The average listed in the figure is not a real average, but rather an average over several neighbors. The overall average would see much smaller effects due to most of the S atoms being unaffected by the defect. The effects of having a sulfur vacancy in the CdS (ZnS cubic) lattice causes a new low energy feature -1.5 eV below the main transition (a). A Cd vacancy leads to a redshift with respect to the perfect structure for neighboring S atoms (b). The effects of substitution of similarly charged ions are also shown, including Se for S (c) and Cu for Cd (d). The effect of selenium is minor, and the low energy feature found in Cu should be spread spectrally in energy by thermal motions given past studies. [41] Another possible defect, oxygen replacing a sulfur atom also yields only a very minor effect (e) and finally the effect of a sulfur defect embedded in Cd-O or Cd-OH spectrum was investigated (f) because ALD was performed with large amounts of both CdO and CdS in a single film. In this case, the effect generates an entirely different spectral



Fig. 4. Representative changes in the calculated S K-edge XAS spectra due to defects. The largest change is shown in blue, the other calculated atoms are shown in red and the effective 'average' is shown in black. The defects shown in otherwise pure CdS (ZnS cubic) are (a) S Vacancy, (b) Cd Vacancy (c) Se replace S, (d) Cu replace Cd, (e) O replace S, (f) S replacing an O in the CdO structure. The implications of this are discussed in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

shape for both Cd–O and Cd–OH. If –5% of the total S atoms were contained in such an oxygen rich environment, the effect would be visible in the experiment.

The low energy feature from a sulfur vacancy is only present in the neighboring sulfur atoms, as the sulfur atoms farther away do not possess such a feature. This means, that one would need a very large number of sulfur defects for the effect to be noticeable in the pre-edge tail of the experiment (at least a few percent) and at these levels we can state that S vacancies are not present. While the effect of a missing Cd is large for the nearest neighbors, the second nearest sulfur atoms have spectra that are largely unchanged from the bulk indicating that a large concentration of Cd defects would be needed to create a noticeable shoulder as compared to the perfect crystal. This is not found experimentally, also permitting us to eliminate the possibility of large concentrations of Cd vacancies in the CdS layer. Other defects including atom replacement, such as substituting Se for S as well as other substitutions (not shown) have only slightly different spectral onsets, indicating that XAS is quite insensitive to this kind of defect at low concentration. Certainly this will be true at the defect level found in actual devices, which is often below 10^{-3} at%. Based on imaging

of excited state orbitals, the state at the lowest energy due to copper defects is related to *d*-shell mixing, similar to what was seen in water. [47] The anti defect (i.e. Se replacing Cd) has a large effect (not shown) but these defects are known to be unstable. The oxygen substitution effect is too minor for the S *K*-edge XAS to determine oxygen contamination. Finally, while the simulated spectrum of a sulfur atom embedded in CdO indicates that the XAS spectrum should be sensitive to sulfur intercalation into the CdO layers, very little change is found experimentally; the spectra with and without CdO are almost identical. This indicates that ALD layers of CdO and CdS do not tend to mix in a manner that causes a noticeable amount of sulfur (–5%) to be embedded in a CdO like environment.

Perhaps the most likely form of sulfur contamination in the CIGS layer is sulfur exchanging for selenium in addition to being found in the CdS layer. As shown in Fig. 5, no matter what selenium in the crystal structure of CIGS is replaced with S the result is roughly the same spectrum. This is expected as the coordination around a S atom remains similar. As the specific identity of the mixture leading to the experimental S *K*-edge is difficult to determine based on X-ray absorption, the changes calculated here

would be consistent with -10% of the signal in experiment being due to S replacing Se in CIGS. Even then, it would be difficult to definitively assign S replacing Se in CIGS as the cause of the changes. Below this level, due to the high absorption onset energy of the sulfur contaminated CIGS the XAS spectrum would largely blend into the background of the bulk CdS spectrum. There also could be other sulfur containing compounds that are present in CIGS devices, and these are discussed here. [14,15,26–28,48] Cd₂SSe, Cd₂GaS₄, Cd₂Ga₂S₂Se₂, Cdln₂S₄ and CdlnS₂ calculated spectra are shown in Fig. 6 part (a). Shown in Fig. 6 part (b) is CdSO₄ hydrate, CdSO₄, CuGaS₂, CuS, Ga₂S₃, GaS and InS. The spectra of CdSO₄ hydrate and CdSO₄ are compared to experiment.



Fig. 5. Representative calculated CIGS S K-edge spectra determined by replacing a Se atom with a S atom. The site of the S that the Se replaces appears to be of minimal importance.



Fig. 6. Calculation of a large variety of potential impurity compounds found in CIGS devices at the S *K*-edge at 0 K. Calculated compounds include in a) Cd₂SSe(yellow), Cd₂Ga₂S₄ (blue), Cd₂Ga₂S₂Se₂(black), Cdln₂S₄ (green), CdlnS₂ (yellow) and b) CdSO₄ hydrate (black)CdSO₄ (yellow), CuGaS₂ (red), CuS (blue), Ga₂S₃ (green), GaS(purple), InS (orange). CdSO₄ hydrate and CdSO₄ are compared to experiment (dashed black and yellow lines respectively). The implications of these calculated spectra are discussed in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Current density vs voltage plots for a series of devices grown in a similar manner to this paper, all showing efficiencies between 14-17%. Of particular note is device 2, which is grown in a manner identical to CdS described in this work, but on CIGS. The overall efficiency is 17.2%.

The spectra of Cd₂GaS₄, Cd₂Ga₂S₂Se₂, CdIn₂S₄ and Cd₂SSe are all largely consistent with that of CdS, although contamination would change the locations and intensity of the peaks found in pure CdS. All of the features present would occur under the main peak of CdS, thus determining the amount and identity of each material is not presently possible. Cd₂SSe and CdInS₂ can be determined as not being present above 1% in the experimental CIGS device. The absorption onset of CdInS₂ is too low in energy as compared to experiment and thus must not be present in a sizeable amount. The oscillator strength at high energy of CdSO₄ due to its formal charge and the low energy for GaS as well as the low onset energy of InS preclude any noticeable presence in the CIGS devices studied here. It is however possible that CuGaS₂, Ga₂S₃ and InS are present in concentrations of -20%.

These methods do ultimately yield reasonably efficient devices, as shown in Fig. 7. The data originate from five devices fabricated on a CIGS film that received the same CBD CdS as the sample from Fig. 2. Efficiencies ranged from 14–17% where the device 2 performed the best at 17.2%. The device data is included to demonstrate that the CBD CdS in the study would produce reasonable device performance. Given that the XAS shown in Fig. 2a for CBD CdS grown on CIGS versus FTO does not differ appreciably and reasonable device performance is obtained, we conclude that our investigation is relevant to devices. This points to the notion that the CIGS surface does not produce any substrate-controlled growth for CBD. The local atomic structure of the CdS is the same for CdS grown on CIGS as well as substrates such as FTO. This underscores the importance the CBD CdS layer provides in carrier transport and formation of the interface.

Finally, we note that the S *K*-edge is not intrinsically insensitive to the effects of cations. ZnS, ZnMnS and ZnFeS all have very different S *K*-edges. [49] This supports that as probed by S 1s XAS, the overall conduction band structure in CdS is not very sensitive to defects and distortions, and that states that alter the buffer layer in cell devices are inferred to be local in character. Thus, the bulk properties of S in CdS are not critical to device performance. The differences in experimental XAS for CBD CdS with respect to the compounds are likely due to long-range effects, grain structure, and other factors not affecting device performance. Local, element-specific probes such as

X-ray absorption and X-ray Emission are well suited to address these issues in future studies.

5. Conclusions

An investigation of the electronic structure of CdS in the buffer layer of CIGS solar cells has been undertaken using S K-edge X-ray absorption fine structure spectroscopy. It is contrasted experimentally by comparing the spectra from pure crystals of CdS with that of CBD deposited CdS and ALD deposited CdS and Cd(O,S). Certain defects such as Cd vacancies can be ruled out as being present in large numbers. Furthermore, we can rule out any significant presence (beyond 1%) of certain compounds in CdS layers of the CIGS devices studied here, notably CdSO₄. The underlying characteristics of the S K-edge spectrum were investigated theoretically, and it was determined that the S 3p derived band, as probed by XAS, is not significantly altered in the CdS architecture by a large variety of defects. We infer that any effects of these defects to the overall transport properties are local in character. CBD CdS does not have as well-defined long-range structure as measured by XAS but nevertheless has the necessarily electronic structure to enable high performance solar cells. We hypothesize that the transport properties across this part of the PV architecture is mainly related to the CdS interface to CIGS and the detailed band energy alignment.

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References

- [1] J.F. Guillemoles, L. Kronik, D. Cahen, U. Rau, A. Jasenek, H.W. Schock, Stability issues of Cu(In,Ga)Se₂-based solar cells, J. Phys. Chem. B 104 (2000) 4849–4862.
- [2] A. Eicke, T. Ciba, D. Hariskos, R. Menner, C. Tschamber, W. Witte, Depth profiling with SNMS and SIMS of Zn(O,S) buffer layers for Cu(In,Ga)Se₂ thin-film solar cells, Surf. Interface Anal. 45 (2013) 1811–1820.
- [3] R.N. Bhattacharya, K. Ramanathan, Cu(In,Ga)Se₂ thin film solar cells with buffer layer alternative to CdS, Sol. Energy 77 (2004) 679–683.
- [4] W. Witte, S. Spiering, D. Hariskos, Substitution of the CdS buffer layer in CIGS thin-film solar cells, Vak. Forsch. Prax. 26 (2014) 23–27.
- [5] N. Naghavi, D. Abou-Ras, N. Allsop, N. Barreau, S. Bucheler, A. Ennaoui, C.H. Fischer, C. Guillen, D. Hariskos, J. Herrero, R. Klenk, K. Kushiya, D. Lincot, R. Menner, T. Nakada, C. Platzer-Bjorkman, S. Spiering, A.N. Tiwari, T. Torndahl, Buffer layers and transparent conducting oxides for chalcopyrite Cu(In,Ga)(S, Se)2 based thin film photovoltaics: present status and current developments, Prog. Photovolt. 18 (2010) 411–433.
- [6] D. Hariskos, S. Spiering, M. Powalla, Buffer layers in Cu(In,Ga)Se₂ solar cells and modules, Thin Solid Films 480 (2005) 99–109.
- [7] S. Siebentritt, Alternative buffers for chalcopyrite solar cells, Sol. Energy 77 (2004) 767–775.
- [8] P. Jackson, D. Hariskos, R. Wuerz, W. Wischmann, M. Powalla, Compositional investigation of potassium doped Cu(In,Ga)Se₂ solar cells with efficiencies up to 20.8%, Phys. Status Solidi (RRL) – Rapid Res. Lett. 8 (2014) 219–222.

- [9] R.W. Johnson, A. Hultqvist, S.F. Bent, A brief review of atomic layer deposition: from fundamentals to applications, Mater. Today 17 (2014) 236–246.
- [10] C.S. Lee, S. Kim, E.A. Al-Ammar, H. Kwon, B.T. Ahn, Effects of Zn Diffusion from (Zn,Mg)O Buffer to CIGS Film on the Performance of Cd-Free Cu(In,Ga)Se₂ Solar Cells, ECS J. Solid State Sci. Technol. 3 (2014) Q99–Q103.
- [11] J.N. Alexander, S. Higashiya, D. Caskey, H. Efstathiadis, P. Haldar, Deposition and characterization of cadmium sulfide (CdS) by chemical bath deposition using an alternative chemistry cadmium precursor, Sol. Energy Mater. Sol. Cells 125 (2014) 47–53.
- [12] J.R. Mann, N. Vora, I.L. Repins, In Situ thickness measurements of chemical bath-deposited CdS, Sol. Energy Mater. Sol. Cells 94 (2010) 333–337.
- [13] C. Heske, D. Eich, R. Fink, E. Umbach, T. van Buuren, C. Bostedt, L.J. Terminello, S. Kakar, M.M. Grush, T.A. Callcott, F.J. Himpsel, D.L. Ederer, R.C.C. Perera, W. Riedl, F. Karg, Observation of intermixing at the buried CdS/Cu(In, Ga)Se₂ thin film solar cell heterojunction, Appl. Phys. Lett. 74 (1999) 1451–1453.
- [14] L. Weinhardt, M. Bar, S. Pookpanratana, M. Morkel, T.P. Niesen, F. Karg, K. Ramanathan, M.A. Contreras, R. Noufi, E. Umbach, C. Heske, Sulfur gradientdriven Se diffusion at the CdS/Culn(S,Se)₂ solar cell interface, Appl. Phys. Lett. 96 (2010) 3.
- [15] L. Weinhardt, M. Bar, S. Pookpanratana, M. Morkel, T.P. Niesen, F. Karg, K. Ramanathan, M.A. Contreras, R. Noufi, E. Umbach, C. Heske, Sulfur gradientdriven Se diffusion at the CdS/CuIn(S,Se)(2) solar cell interface, Appl. Phys. Lett. 96 (2010) 182102.
- [16] J. Stöhr, NEXAFS Spectroscopy, Springer, Berlin, 1992.
- [17] B. Eckert, R. Steudel, Molecular spectra of sulfur molecules and solid sulfur allotropes, in: R. Steudel (Ed.), Elemental Sulfur and Sulfur-Rich Compounds li, Springer-Verlag Berlin, Berlin, 2003, pp. 31–98.
- [18] F. Jalilehvand, Sulfur: not a "silent" element any more, Chem. Soc. Rev. 35 (2006) 1256–1268.
- [19] P.L. Wincott, D.J. Vaughan, Spectroscopic studies of sulfides, in: D.J. Vaughan (Ed.), Sulfide Mineralolgy and Geochemistry, Mineralogical Soc Amer, Chantilly, 2006, pp. 181–229.
- [20] S.M. Babu, A. Meeder, D.F. Marron, T. Schedel-Niedrig, M. Havecker, A. Knop-Gericke, M.C. Lux-Steiner, Thermal stability and environmental effects on CuGaSe₂ thin film solar cells, J. Cryst. Growth 275 (2005) E1235–E1240.
- [21] M. Han, Y. Luo, J.E. Moryl, R.M. Osgood, J.G. Chen, A near-edge X-ray absorption fine structure study of atomic layer epitaxy: the chemistry of the growth of CdS layers on ZnSe(100), Surf. Sci. 415 (1998) 251–263.
- [22] M.W. Murphy, Y.M. Yiu, M.J. Ward, L. Liu, Y. Hu, J.A. Zapien, Y.K. Liu, T.K. Sham, Electronic structure and optical properties of CdS_xSe_{1-x} solid solution nanostructures from X-ray absorption near edge structure, X-ray excited optical luminescence, and density functional theory investigations, J. Appl. Phys. 116 (2014) 10.
- [23] C. Yan, F.Y. Liu, N. Song, B.K. Ng, J.A. Stride, A. Tadich, X.J. Hao, Band alignments of different buffer layers (CdS, Zn(O,S), and In₂S₃) on Cu₂ZnSnS₄, Appl. Phys. Lett. 104 (2014) 4.
- [24] Y.L. Soo, W.H. Sun, S.C. Weng, Y.S. Lin, S.L. Chang, L.Y. Jang, X. Wu, Y. Yan, Local environment surrounding S and Cd in CdS: O thin film photovoltaic materials probed by X-ray absorption fine structures, Appl. Phys. Lett. 89 (2006) 3.
- [25] M. Bar, I. Repins, M.A. Contreras, L. Weinhardt, R. Noufi, C. Heske, Chemical and electronic surface structure of 20%-efficient Cu(In,Ga)Se₂ thin film solar cell absorbers, Appl. Phys. Lett. 95 (2009) 3.
- [26] D. Eich, U. Herber, U. Groh, U. Stahl, C. Heske, M. Marsi, M. Kiskinova, W. Riedl, R. Fink, E. Umbach, Lateral inhomogeneities of Cu(In,Ga)Se₂ absorber films, Thin Solid Films 361 (2000) 258–262.
- [27] C. Heske, U. Groh, L. Weinhardt, O. Fuchs, B. Holder, E. Umbach, C. Bostedt, LJ. Terminello, S. Zweigart, T.P. Niesen, F. Karg, Damp-heat induced sulfate formation in Cu(In,Ga)(S,Se)₂-based thin film solar cells, Appl. Phys. Lett. 81 (2002) 4550–4552.
- [28] L. Weinhardt, O. Fuchs, D. Gross, G. Storch, E. Umbach, N.G. Dhere, A.A. Kadam, S.S. Kulkarni, C. Heske, Band alignment at the CdS/Cu(In,Ga)S₂ interface in thin-film solar cells, Appl. Phys. Lett. 86 (2005) 3.
- [29] M.A. Contreras, M.J. Romero, B.T.E. Hasoon, R. Noufi, S. Ward, K. Ramanathan, Optimization of CBD CdS process in high-efficiency Cu(In,Ga)Se₂-based solar cells, Thin Solid Films 403 (2002) 204–211.
- [30] J.R. Bakke, H.J. Jung, J.T. Tanskanen, R. Sinclair, S.F. Bent, Atomic Layer Deposition of CdS Films, Chem. Mater. 22 (2010) 4669–4678.

- [31] M.A. Contreras, J. Tuttle, A. Gabor, A. Tennant, K. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, J. Scofield, R. Noufi, leee, High efficiency Cu(In,Ga) Se2-based solar cells: Processing of novel absorber structures, in: 1994 leee First World Conference on Photovoltaic Energy Conversion/Conference Record of the Twenty Fourth leee Photovoltaic Specialists Conference – 1994, Vols I and Ii, I E E E, New York, 1994, pp. 68-75.
- [32] A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, R. Noufi, A.M. Hermann, High-Efficiency CulnxGa_{1-x}Se₂ Solar Cells Made From (In_x,Ga_{1-x})2Se₃ Precursor Films, Appl. Phys. Lett. 65 (1994) 198–200.
- [33] P. Kennepohl, E.C. Wasinger, S.D. George, X-ray spectroscopic approaches to the investigation and characterization of photochemical processes, J. Synchrot. Radiat. 16 (2009) 484–488.
- [34] A.H. England, A.M. Duffin, C.P. Schwartz, J.S. Uejio, D. Prendergast, R.J. Saykally, On the hydration and hydrolysis of carbon dioxide, Chem. Phys. Lett. 514 (2011) 187–195.
- [35] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [36] D. Prendergast, G. Galli, X-ray absorption spectra of water from first principles calculations, Phys. Rev. Lett. 96 (2006) 4.
- [37] D. Prendergast, S.G. Louie, Bloch-state-based interpolation: An efficient generalization of the Shirley approach to interpolating electronic structure, Phys. Rev. B 80 (2009) 10.
- [38] J.S. Uejio, C.P. Schwartz, R.J. Saykally, D. Prendergast, Effects of vibrational motion on core-level spectra of prototype organic molecules, Chem. Phys. Lett. 467 (2008) 195–199.
- [39] J. Vinson, J.J. Rehr, J.J. Kas, E.L. Shirley, Bethe-Salpeter equation calculations of core excitation spectra, Phys. Rev. B 83 (2011) 7.
- [40] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (2011) 1272–1276.
- [41] T.A. Pascal, U. Boesenberg, R. Kostecki, T.J. Richardson, T.C. Weng, D. Sokaras, D. Nordlund, E. McDermott, A. Moewes, J. Cabana, D. Prendergast, Finite temperature effects on the X-ray absorption spectra of lithium compounds: First-principles interpretation of X-ray Raman measurements, J. Chem. Phys. 140 (2014) 13.
- [42] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, QUANTUM ESPRESSO: a modular and opensource software project for quantum simulations of materials, J. Phys. – Condes. Matter 21 (2009) 19.
- [43] G. Bergerhoff, R. Hundt, R. Sievers, I.D. Brown, The Inorganic Crystal-Structure Data Base, J. Chem. Inf. Comput. Sci. 23 (1983) 66–69.
- [44] G. Kresse, J. Hafner, Abinitio molecular-dynamics for liquid metals, Phys. Rev. B 47 (1993) 558–561.
- [45] C. Sugiura, Y. Gohshi, I. Suzuki, Sulfur K Beta X-ray emission spectra and electronic structures of some metal sulfides, Phys. Rev. B 10 (1974) 338–343.
- [46] K. Aryal, Y. Erkaya, G. Rajan, T. Ashrafee, A. Rockett, R.W. Collins, S. Marsillac, leee, Comparative Study of ZnS Thin Films Deposited by CBD and ALD as a Buffer Layer for CIGS Solar Cell, 2013 leee 39th Photovoltaic Specialists Conference (Pvsc), (2013) 1101–1104.
- [47] LA. Naslund, M. Cavalleri, H. Ogasawara, A. Nilsson, L.G.M. Pettersson, P. Wernet, D.C. Edwards, M. Sandstrom, S. Myneni, Direct evidence of orbital mixing between water and solvated transition-metal ions: An oxygen 1s XAS and DFT study of aqueous systems, J. Phys. Chem. A 107 (2003) 6869–6876.
- [48] M. Bar, I. Repins, M.A. Contreras, L. Weinhardt, R. Noufi, C. Heske, Chemical and electronic surface structure of 20%-efficient Cu(In,Ga)Se-2 thin film solar cell absorbers, Appl. Phys. Lett. 95 (2009) 3.
- [49] K. LawniczakJablonska, R.J. Iwanowski, Z. Golacki, A. Traverse, S. Pizzini, A. Fontaine, I. Winter, J. Hormes, Local electronic structure of ZnS and ZnSe doped by Mn, Fe, Co, and Ni from X-ray-absorption near-edge structure studies, Phys. Rev. B 53 (1996) 1119–1128.