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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 first-principles 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 co-adsorbing 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) structure–property relationships of CdS and the interface with the absorber. CdS layers have previously been investigated by other techniques including XPS, X-ray emission spectroscopy, 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 ~50 nm. CdSO₄ hydrate and CdSO₄ (purchased from Sigma-Aldrich) were placed on low sulfur tape.

CIGS thin films were prepared on molybdenum-coated soda-lime 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 ($E/\Delta E$) of 10^4 . [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–Ernzerhof (PBE) exchange–correlation functional. [35] The transition amplitudes are calculated according to Fermi's golden rule for X-ray absorption cross-sections:

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

In this case, α_0 is the fine structure constant, $\hbar\omega$ is the energy of the absorbed photon and $M_{i \rightarrow f}$ 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:

$$M_{i \rightarrow f} = \langle \Psi_f | \hat{\epsilon} \cdot \mathbf{R} | \Psi_i \rangle \approx S \langle \psi_f | \hat{\epsilon} \cdot \mathbf{r} | \psi_i \rangle \quad (2)$$

where $\hat{\epsilon}$ is the polarization direction of the photon electric field vector, \mathbf{R} and \mathbf{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 self-consistent 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 ~ 1 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

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