

XAFS Investigations of the Local Structure of Cadmium in CuInSe₂-Based Materials

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Introduction

High-efficiency thin-film CuInSe₂ (CIS)-based solar cells have been demonstrated in small area (18.8%) and large area (12%) devices. One critical step is junction formation. The best results today have been based on the deposition of a thin CdS layer by a chemical bath deposition (CBD) process. Considerable effort has been directed toward explaining the mechanism responsible for the dramatic improvement in cell performance that has been observed for this process. Two hypotheses were proposed to account for the beneficial effects of the CBD CdS process. One proposes that the Cd diffuses into the CIS-lattice-forming Cd_{Cu} (Cd on Cu sites) donor and induces a type conversion (p to n) [1]. The other suggests that the Cd reacts with the CIS-surface-forming CdSe (or CdIn_xSe_y), which produces a graded interface structure [2]. More recently, Soo et al. [3] performed Cu K-edge EXAFS on CdS-deposited CuInSe₂ single-crystal samples. This source suggests that the Cd atoms sit next to Cu atoms as first nearest neighbors on the basis of a least squares fitting of Cu K-edge EXAFS data. However, no direct evidence has been provided to reveal the crystallographic position of the diffused Cd ions in the CuInSe₂ lattice host. XAFS is the technique most suited for this study. By looking at the Cd atomic local environment, we could assess whether the diffused Cd ions sit on the Cu site (serve as donors), the In site (serve as acceptors), or interstitial sites.

Methods and Materials

Cd-K edge Fluorescence EXAFS were performed on the thin film Cu(In,Ga)Se₂ samples deposited by physical vapor deposition at National Renewable Energy Laboratory. The thin film sample was first chemically treated in an aqueous bath solution consisted of CdCl₂ and NH₄OH at two different concentration level, 1.5 M (15PE) or 0.015 M (0.0015M). This partial electrolyte treatment of these thin film samples were conducted for 10 minutes at 80°C heating and dried with N₂ gas. Similar to the thin film samples described above, fluorescent measurements of the Cd *K-edge* for the powder samples were performed in the same manner. These were used as reference samples for comparison analysis to the thin films. Powder standards of CdO and CdSe compounds

were spread over a transparent tape, taking care to uniformly distribute the powder to avoid pinholes. Pure standard compounds of 99.9999% were purchased from Alfa Aesar.

The EXAFS measurements were performed at the Materials Research Collaborative Access Team (MR-CAT) beamline, which uses an APS undulator-A. The beamline optics incorporate a Si(111) double-crystal monochromator and an Rh-coated harmonic-rejection mirror, which was set to reject the second- and higher-order harmonics. The fluorescent x-ray intensities were monitored by using a multi-element solid state detector. The thin film sample was positioned 45° to the incident x-ray beam, with the multi-element fluorescent x-ray detector positioned 90° to the incident beam.

Results and Discussions

The first shell EXAFS spectra were analyzed using the *ab initio* multiple-scattering code FEFF8 [4] along with the WinXAS package [5]. Comparing the spectra of these transformed data with CdSe and CdO standards suggests these peaks may be Cd-Se and Cd-O bonds. Figure 1 superimposes the EXAFS spectra of CdSe standard with the two PE treated samples. The main peaks at ~2.1 Å of the PE treated samples are consistent with the Cd-Se bonds. The intensities however are noticeably dissimilar in all three samples, indicating that there is a difference in the average of the nearest neighbor numbers between these samples. Figure 4 superimposes the EXAFS spectra of CdO standard with the two PE treated samples. The peak at ~1.9 Å in Figure 2 for the CdO spectrum (green) corresponds to the Cd-O bonds, which matches well with the shoulder peak. This suggests that the shoulder peak represents Cd-O bonds. Cd local structure models were constructed and used for the least-square analysis of the spectra. Employing FEFF8 with WinXAS software package, experimental data was theoretically fitted to the first shell single-scattering paths of the Cd atom in the (PE) treated Cu(In_{0.7}Ga_{0.3})Se₂ thin film samples. The main peak observed in the data represents the Cd-Se bonds and the shoulder corresponds to the Cd-O bond. A two-phase model that includes both Cd-Se tetrahedron and Cd-O octahedron was constructed. The fitting using this model agrees very well with the

experimental data, and the total first nearest neighbor number is consistent with the two phase model at $NN=4.2$. The fitting results for Cd 15PE is given in table 1. This study indicates the surface of Cd partial electrolyte treated $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$ thin films contains both CdSe and CdO.

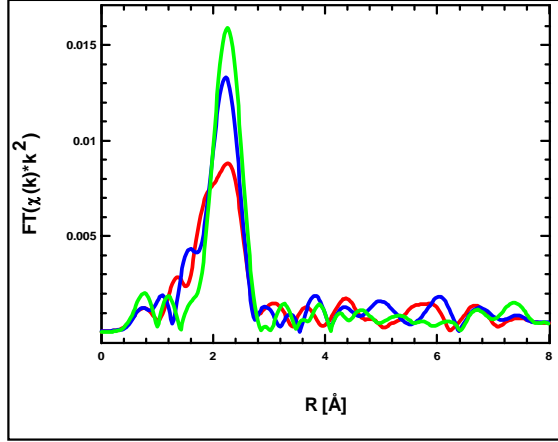


FIG.1. Fourier transforms of Cd K-edge EXAFS $\chi(k)$ functions on CdSe and treated samples of CIGS thin films (green line represents CdSe, blue line is CIGS/Cd 0015PE, and the red line is CIGS/Cd 15PE)

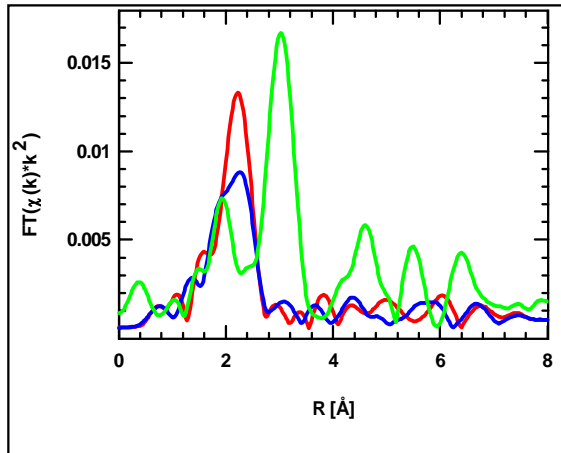


FIG. 2. Fourier transforms of Cd K-edge EXAFS $\chi(k)$ functions on CdO and treated samples of CIGS thin films (green line represents $\text{Cd}(\text{OH})_2$, blue line is CIGS/Cd 0015PE, and the red line is CIGS/Cd 15PE).

	CIS:1.5 M Cd	Standards
S_0^2 :	0.94	0.94
	Cd-Se	Cd-Se
NN:	2.3	4
$R_{\text{Cd-Se}}(\text{\AA})$:	2.63	2.63
$\sigma^2(\text{\AA}^2)$:	5.50E-03	5.51E-03
	Cd-O	Cd-O
NN:	1.9	6
$R_{\text{Cd-O}}(\text{\AA})$:	2.33	2.33
$\sigma^2(\text{\AA}^2)$:	5.50E-03	8.20E-03

Table 1. Least square fitting results of the one-phase model.

Summary

EXAFS analysis of CIGS thin films treated with two differing concentrations of the Cd partial electrolyte is consistent with a two-phase model. The model used in this study was generated from crystal structures consisting of CdSe tetrahedron and CdO octahedron in the CIGS lattice. Cd-Se and Cd-O bonds were found to be the main interaction of the Cd atom in the CIS/Cd PE treated samples. This was determined by comparing the CIGS/Cd PE EXAFS spectra to the EXAFS spectra of CdSe and CdO standards. The higher concentrated treatment has more Cd-O first nearest neighbors, while the lower concentrated sample has more Cd-Se nearest neighbors.

Acknowledgments

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