XAFS Investigations of the Local Structure of Cadmium in $CuInSe_2$-based Materials

G.N. Ma, C.-H. Chang
Department of Chemical Engineering, Oregon State University, Corvallis, OR, U.S.A.

Introduction

High-efficiency thin-film $CuInSe_2$-based (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 $CuInSe_2$ 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 extended x-ray absorption fine structure (EXAFS) data. However, no direct evidence has been provided to reveal the crystallographic position of the diffused Cd ions in the $CuInSe_2$ 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 spectroscopy was performed on the thin-film $Cu(In,Ga)Se_2$ samples deposited by physical vapor deposition at the National Renewable Energy Laboratory. The thin-film sample, labeled 1852, was first chemically treated in an aqueous bath solution consisting of 1.5 M $CdCl_2$ and 1.5 M NH_4OH. The partial electrolyte treatment of these thin-film samples was conducted for 10 minutes at 80°C heating, and the samples were dried with N_2 gas.

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

Results

The first-shell EXAFS spectra were analyzed by using the *ab initio* multiple-scattering code FEFF8 [4] along with the WinXAS package [5]. Two structural models were employed to explore the local environment of Cd atoms. The first model employed incorporation of cadmium and oxygen atoms into the $CuInSe_2$ lattice. A crystallographic structure of this model is shown in Fig. 1a.

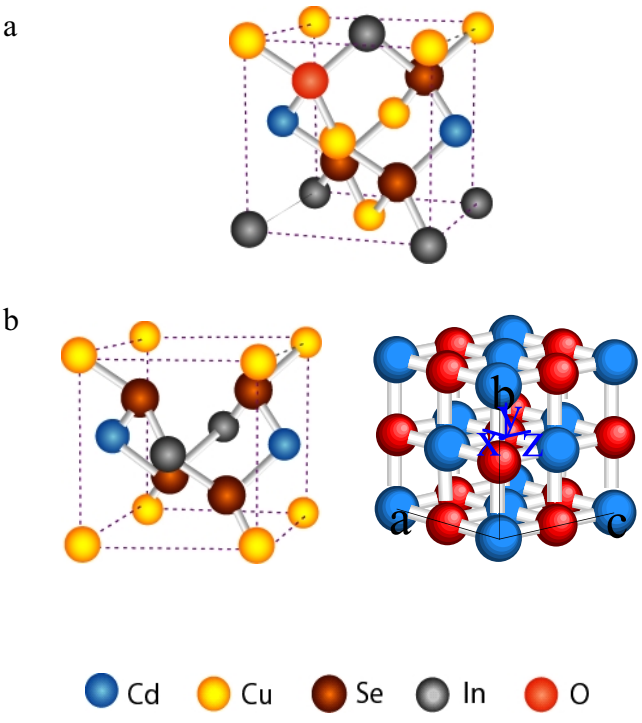

FIG. 1. a) Crystal structure of the one-phase model. b) Two-phase model consisting of CIS and CdO phases.

The least square analysis based on the first model is given in Table 1. This model results in reasonable bond

lengths for both Cd-Se and Cd-O. The first nearest numbers, however, appear to be too high for tetrahedral bonding.

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

Coord. No.	Bond Length (Å)	σ^2 (Å^2)	S_0^2
5.41	$R_{Cd\text{-}O}$ 2.33	2.83×10^{-2}	0.94
4	$R_{Cd\text{-}Se}$ 2.62	8.43×10^{-3}	0.94

This analysis led us to construct the second model, which consists of two-phases, as shown in Fig. 1b. One phase incorporates Cd into the $CuInSe_2$ lattice. The second phase is an octahedrally bonded CdO phase. The least square fit, which uses the calculated phase shifts and amplitude functions from FEFF8, and the experimental data are given in Fig. 2. The blue line represents the experimental data, and the red line is the least square fitting. The fitted results are given in Table 2. The S_0^2 value was obtained from the EXAFS spectrum of a CdSe reference sample. The second model results in reasonable nearest neighbor numbers and bond length values for both Cd-Se and Cd-O bonds. Further data analysis is still underway.

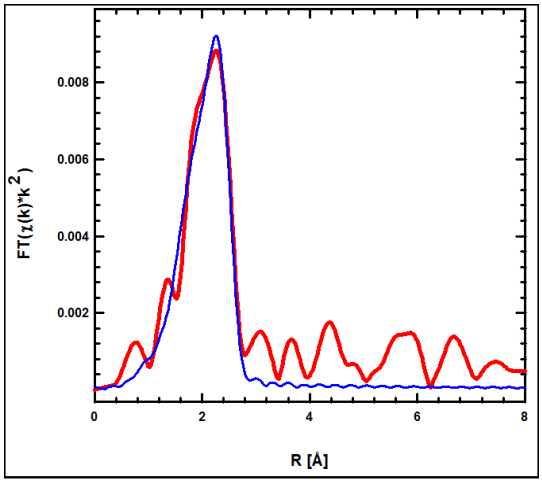

FIG. 2. Cd K-edge EXAFS in real space for CIS:Cd sample fit to two-phase model.

TABLE 2. Least square fitting results of the two-phase model in CIS:Cd shown with CdSe standard.

	CIS:1.5 M Cd	CdSe Standard
S_0^2	0.94	
	Cd-Se	Cd-Se
N	3.52	4
$R_{Cd\text{-}Se}$ (Å)	2.63	2.63
σ^2 (Å^2)	7.89E-03	5.51E-03
	Cd-O	
N	2.77	
$R_{Cd\text{-}O}$ (Å)	2.3	
σ^2 (Å^2)	1.38E-02	

Summary

Cd-K edge EXAFS data were collected for Cd partial-electrolyte-treated thin-film $Cu(In,Ga)Se_2$ samples. The EXAFS data were analyzed by using the *ab initio* multiple-scattering code FEFF8 along with the WinXAS package against two structural models. The preliminary analysis suggested that the Cd atoms were incorporated into the CIGS lattice along with a secondary CdO [or $Cd(OH)_2$] phase in the partial-electrolyte-treated CIGS thin films.

Acknowledgments

This work was supported by the National Renewal Energy Laboratory under Subcontract No. AD-2-30630-13. Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. The MR-CAT beamline is supported by DOE BES and member institutions. The authors would like to acknowledge the technical assistance from MR-CAT beamline scientists J. Terry and C. Segre.

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