

XAFS Investigations of the Role of Cadmium in High-efficiency CuInSe₂-based Solar Cells

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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. One important mechanism is thought to be the exchange reactions at the near-surface region with Cd or S ions, which chemically modify the surface. Secondary ion mass spectroscopy (SIMS) and x-ray photoelectron spectroscopy (XPS) have been used to establish the evidence for Cd diffusion into the CIS lattice [1]. 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

CuInSe₂ and CuIn₃Se₅ polycrystalline samples were prepared from powder Cu₂Se and In₂Se₃ (both from Alpha) in boron nitride (BN)-coated, evacuated quartz ampoules. CdIn₂Se₄ powders were prepared from powder CdSe (CERAC) and In₂Se₃ in BN-coated, evacuated quartz ampoules. The BN coating was used to prevent devitrification of the quartz at high temperature. These mixtures were then slowly heated to the melting temperature, gradually cooled to 700°C, and kept in a furnace at 700°C for a week to assure equilibrium. Then they were quenched in liquid nitrogen. Powder x-ray diffraction (XRD) and wavelength dispersive x-ray spectroscopy (WDS) were used to verify the formation of desired homogeneous single-phase materials. The CuInSe₂ and CuIn₃Se₅ were immersed in an aqueous solution containing 1 M CdCl₂ in 30% NH₄OH for 4 d.

The EXAFS measurements were performed on the Materials Research Collaborative Access Team (MR-CAT) beamline of the APS, which uses APS undulator A. The beamline optics incorporate a Si(111) double-crystal monochromator and a Rh-coated harmonic-rejection mirror, which was set to reject the

second- and higher-order harmonics. The samples sat in the sample box of an assembly of the fluorescent x-ray ion chamber detector (Lytle detector, The EXAFS Company) [2] oriented at 45° to the incident x-ray beam, with the fluorescent x-ray detector positioned at 90° to the incident beam. A Pd filter with a slit assembly was used to reduce the scattered x-ray background. The fluorescent x-ray intensities were monitored by using an x-ray ionization chamber filled with Kr gas.

Results

The collected EXAFS data were analyzed by standard procedure [3] by using the WinXAS package [4]. The experimental intensity data were first converted to absorption coefficients on the basis of the relationship $\mu(E) = I_f/I_0$, where μ = the x-ray absorption coefficient, E = the x-ray photon energy, and I_f and I_0 = the intensities of the incident and fluorescent x-ray, respectively. After removing the pre-edge background, the photon energy was converted to the photoelectron wave vector k by using the expression $k = \sqrt{2m(E - E_0)/\hbar^2}$, where m = the electron mass and E_0 = the K-edge energy. A normalized EXAFS spectrum was then obtained by subtracting the background $m_0(k)$ from the measured absorption coefficient $m(k)$ and normalizing by the edge jump $\Delta\mu_0(0)$:

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\Delta\mu_0(0)}$$

The resulting $\chi(k)$ oscillations were then Fourier transformed into r space with a k^2 weighting. The resulting Fourier-transformed Cd K-edge r -space data are shown in Fig. 1.

Discussion

The EXAFS results indicated that the first neighbors around Cd in CdSe and CdIn₂Se₄ are almost identical. However, the Cd-electrolyte-treated CuInSe₂ and CuIn₃Se₅ are not. 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, which induces a type conversion (p to n) [1]. The other suggests

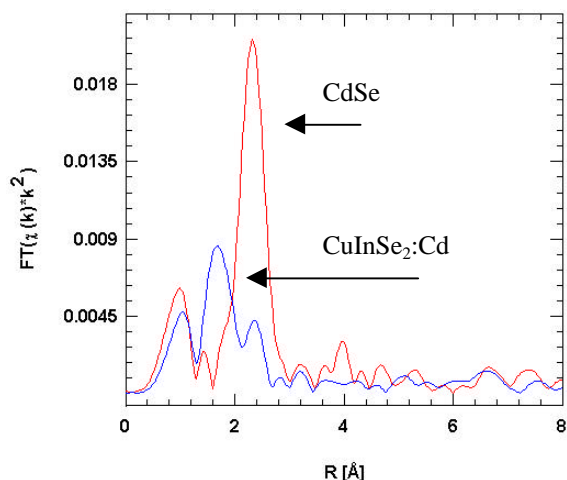


FIG. 1. Cd K-edge EXAFS in real space for CuInSe_2 treated in 1 M CdCl_2 in 30% NH_4OH aqueous solution compared with CdSe Cd-K EXAFS.

that the Cd reacts with the CIS-surface-forming CdSe (or CdIn_xSe_y), which produces a graded interface structure [5]. As clearly shown in Fig. 1, the current EXAFS results do not support these hypotheses. More recently, Soo et al. [6] 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 EXAFS data. A detailed quantitative least squares analysis of the EXAFS data by using

different Cd local structure models is currently underway to shed more light on this problem.

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