

The Chemical Environment about Cd atoms in Cd Chemical Bath Treated CuInSe₂ and CuGaSe₂

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Abstract

Recent reports in the literature have concluded that chemical bath deposited Cd (CBD-Cd) has beneficial effects on Cu(In, Ga)Se₂ solar cell performance. Before detailed mechanisms explaining why this is so can be proposed, a key question that must be answered is where in the lattice the Cd atoms reside. We have used near-edge x-ray absorption fine structure (XANES) to selectively investigate the local atomic environment about Cd atoms in CBD-Cd treated polycrystalline CuInSe₂ and CuGaSe₂ films. CBD-Cd treated CuInSe₂ and CuGaSe₂ layers grown on Mo-coated glass substrates using the three-stage method were excited by synchrotron radiation at the Cd L₃-edge (3537 eV) and the resulting XANES spectra were recorded. First-principles calculation using the code feff 8.10 show that the XANES spectra are consistent with Cd atoms being located in cation sites in the CuInSe₂

matrix. From the current data it is not possible to definitively state to what extent Cd resides on the group I or III sites, but it is clear that there is a contribution from both, not from only Cu sites as has been previously speculated in the literature. This is also found to be consistent with predictions for ion-exchange reactions which show that Cd is more likely to substitute for (surface) In than Cu.

Key words: x-ray absorption, CuInSe₂, CuGaSe₂, Cd, chemical bath deposition

1 Introduction

CdS buffer layers located between the p-type Cu(In, Ga)Se₂ (CIGS) absorber layer and the n-type ZnO window layer have become an integral part of high-efficiency polycrystalline CIGS solar cells. Experimentally it has been found that the highest conversion efficiencies occur in cells with chemical-bath deposited (CBD) CdS buffers. TEM observations have also shown that Cd interdiffusion is observable for distances on the order of 10 nm into the Cu(In, Ga)Se₂ matrix.(1) Even though the amount of Cd incorporated into the cells is minute, larger amounts of Cd compounds are used in the production process and as a consequence of this, an effort has been made to understand the reasons for the efficacy of the CBD-CdS buffer as a preamble to find alternative, less toxic substitutes. Several recent reports have concluded that treatment by CBD-Cd alone, or in combination with conventional CBD-CdS deposition results in improvement in either cell performance or reproducibility(2; 3; 4). An outstanding question that must be answered before detailed investigation of the underlying mechanism can begin is where in the CIGS matrix the CBD deposited Cd resides. We have used near-edge x-ray absorption fine structure (XANES) at the Cd-L₃ edge (3537 eV) to selectively

investigate the local atomic environment about Cd atoms in CBD-Cd treated polycrystalline CuInSe₂ and CuGaSe₂ deposited on Mo-coated soda-lime glass substrates.

For the L₃-edge, the electron is initially in a *p* state and in the dipole excitation approximation, the electron can be excited to states of either *s* or *d* symmetry in the conduction band. The cross section of an absorbing atom in XANES depends on the scattering of the generated photoelectron from neighboring atoms, thus yielding information on the local atomic environment of the absorbing atom. The XANES spectrum is also very sensitive to the relative arrangement of local atoms due to the strong contributions from multiple scattering effects. It is worth noting here that for the chalcopyrite structure, changes in the second coordination shell (12 atoms) must be detected to determine upon which cation site a Cd atom resides. As in the dilute limit, Cd substituting for an In(Cu) site has eight Cu(In) neighbors of twelve total, a measurable difference in the XANES signal can be expected.

Experimental XANES data were compared with *ab initio* calculations using the relativistic real-space scattering code feff 8.10 to determine the most likely local atomic environment of Cd.(5)

2 Experiment

Both the CuInSe₂ and CuGaSe₂ samples used in this study were deposited by the three-stage method onto Mo-coated soda-lime glass substrates. (6) The two endpoint compositions of the CuIn_{1-x}Ga_xSe₂ pseudobinary system were chosen to simplify the theoretical interpretation of the XANES data. The as-

grown samples were placed into a CBD-Cd chemical bath kept at a temperature of 40° for 40 minutes. The Cd precursor used was CdI_2 (0.7×10^{-3} mol/l) in an NH_4OH 0.5 mol/l solution. After deposition, the samples were then introduced into a vacuum chamber at beam line BL11B at the Photon Factory in Tsukuba, Japan. A linearly polarized x-ray beam was then introduced with the polarization vector perpendicular to the samples surface (glancing incidence geometry) to allow for excitation of more sample volume. The energy resolution was ~ 1.8 eV over the energy range used in the experiment. The Cd-L₃ edge (3537 eV) was excited and both total electron yield and fluorescence data were taken. No significant differences in the Cd – L₃ XANES signals were seen between the total electron yield (escape depth a few tens of nanometers) and fluorescence (escape depth about $3 \mu\text{m}$) samples implying that the Cd atomic environment was homogeneous. Identical CuInSe_2 and CuGaSe_2 were also fabricated into solar cells in the (glass/Mo/ CuInSe_2 /buffer/i-ZnO/ZnO/Al contact) configuration. Cells with no CdS buffer layer, a conventional CBD-CdS buffer layer, and only CBD-Cd treatment were fabricated and cell conversion efficiencies measured.

3 Results and Discussion

Fig. 1 show both experimental data for the Cd-L₃ edge taken for both CuInSe_2 and CuGaSe_2 CBD-Cd treated films in fluorescence mode. In addition to the experimental data the results of theoretical calculations done using the *ab initio* code feff 8.10 are shown for Cd residing in different places in the host matrix as well as Cd in metallic and oxide form. The feff calculations were performed using a self-consistent field approach as well as full multiple scat-

tering on a cluster of radius 0.8 nm. In addition to the calculations shown, additional calculations (not shown) were done for $\text{Cd}(\text{OH})_2$ as well as Cd in CuInSe_2 / CuGaSe_2 in tetrahedral and octahedral interstitial positions. These have been omitted from the plot for space reasons as they are a poor match to the experimental data and hence have been rejected as possible structural models. As XANES signals from different Cd sites combine incoherently, it is appropriate to consider the observed spectra to be an average of the XANES signals from individual, crystallographically unique Cd sites.

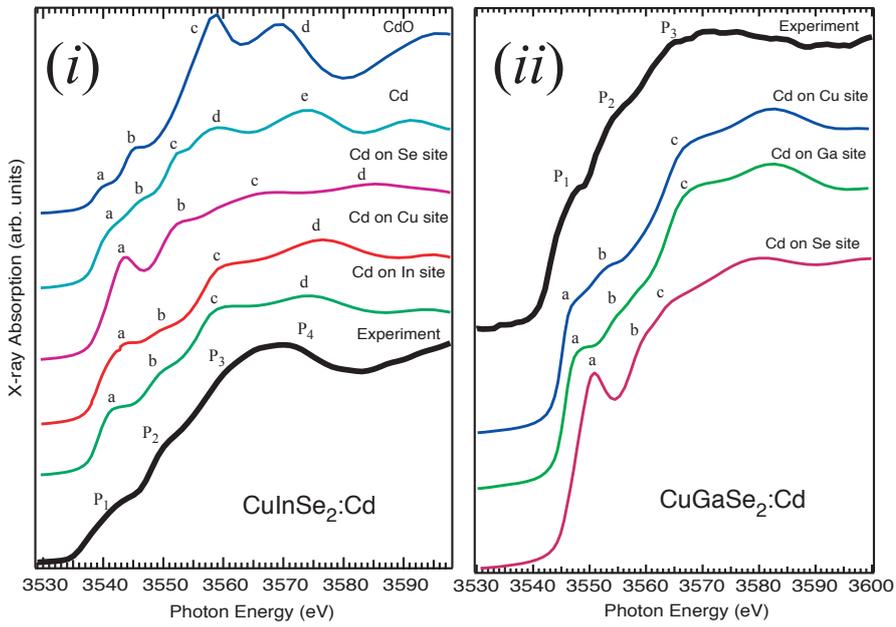


Fig. 1. Experimental and simulated Cd-L₃ XANES spectra for CBD-Cd treated CuInSe_2 (i) and CuGaSe_2 (ii) films

It is clear from Fig. 1(i) that metallic Cd and CdO, do not show good agreement with the CuInSe_2 :CBD-Cd experimental data and can be discarded as possible structural models. For the case of Cd incorporating substitutionally on a Se lattice site, the simulated data has a strong resonance at position (a) which is not reflected in the experimental data allowing rejection of the Se site as a possibility for Cd incorporation. The two remaining possibilities, Cd

incorporating on a Cu or In site, both show overall agreement with the experimental data. Although the current experiments cannot distinguish between these two possibilities, a set of experiments by Wada, however, show that Cu is also present in CBD-Cd solution after exposure to Cu(In, Ga)Se₂ while no significant concentration was detected. (7) The presence of Cu ions in the CBD-Cd solution is attributed to complexing with ammonia (a necessary condition). These results, however, were obtained for Cu(In, Ga)Se₂ powder samples exposed to CBD-Cd solutions for periods of up to two weeks (presumably to obtain measurable ion concentrations), making the well-known large mobility of Cu in Cu(In, Ga)Se₂ a significant factor. For the case of CuGaSe₂:CBD-Cd, as shown in Fig. 1(ii), a similar trend can be seen, with Cd apparently incorporation on both cation sites.

As earlier works (3; 2; 4) demonstrated that the use of CBD-Cd had beneficial effects similar to CBD-CdS, cells were fabricated from freshly prepared CuInSe₂ absorber layers with CBD-Cd, CdS, and no buffer layers. Consistent with earlier results, the conversion efficiency of the CBD-Cd sample was about two percent versus approximately zero percent for the cell fabricated without a buffer layer, and about 10% for a cell made with a conventional CBD-CdS buffer layer. It should be mentioned here that as EPMA analysis of the surface of the CuInSe₂ and CuGaSe₂ samples taken approximately six months after the XANES measurements showed a strong spatial correlation of O to Cd concentration, the reason for the improvement of the CBD-Cd treated layer may also be ascribable to the presence of an hydroxide/oxide of Cd on the uppermost surface.

4 Conclusion

We have measured the local structural environment of Cd in CBD-Cd treated CuInSe₂ and CuGaSe₂ polycrystalline samples using XANES at the Cd-L₃ edge and compared the experimental results to theoretical simulations. Similar results were found for both materials, namely that Cd most likely resides on the cation sites alone. The current experiments cannot distinguish between which of two cation sites the Cd ions reside upon. The presence of Cd on both cation sites also implies the near surface layer may be strongly electrically compensated.

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