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XPS AND UPS INVESTIGATION OF NH₄OH-EXPOSED Cu(In,Ga)Se₂ THIN FILMS

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ABSTRACT

Photoelectron spectroscopy was used to determine the compositional and electronic changes occurring in Cu(In,Ga)Se₂ thin films as a result of immersion in aqueous ammonia solution. We find that NH₄OH-treated CIGS surfaces are preferentially etched of indium and gallium, resulting in the formation of a thin layer of a degenerate Cu-Se compound that we tentatively identify as Cu₂Se. The work function of ammonia-treated samples is found to increase by 0.6 eV relative to as-grown CIGS thin films. The uniformity of chemical bath effects (etching & deposition) was found to be improved by the addition to the bath of a non-ionic surfactant. Initial device results show that the new surfactant-based chemical bath deposition (CBD) method may lead to better and thinner CdS buffer layers.

INTRODUCTION

To date, the most efficient thin film Cu(In,Ga)Se₂ (CIGS) based solar cells use an n-type "buffer layer" of a sulfide, usually CdS, which is deposited on the p-type absorber via an aqueous chemical bath. A typical CBD of CdS uses NH_{3(aq)}, (usually described as a cation complexing agent) CdSO₄ as the source for Cd, and thiourea to provide S²⁻. Although NH₃ is known to play an important role in controlling the formation of CdO, other effects attributed to the presence of this molecule include removal of Cu from the CIGS lattice and an increase in the rate of thiourea hydrolysis. Generally, the complex chemical reactions occurring both on the surface of the CIGS absorber and in solution are not well understood even though they can have large effects on the performance of finished devices. Even the basic question of whether CIGS/CdS devices are generally best represented as homojunctions or heterojunctions has not been settled. EBIC data indicate abrupt heterojunctions in these structures[1], yet SIMS and XPS and AES sputter profiling show diffusion of Cd deep into the CIGS absorber[2]. Recent scanning capacitance microscopy data[3] indicates a buried homojunction 80-90 nm from the CdS-CIGS boundary, but XPS data from Rockett et al. indicate that Cd was constrained to the first few atomic layers of a CIS single crystal film that had been exposed to Cd electrolyte [4]. In this paper we specifically address how ammonia and water affect the composition and electronic structure of the CIGS surface, and report initial results on a modification to water-based processes on CIGS that may lead to improved sulfide buffer layers.

EXPERIMENTAL

The CIGS thin films were grown by a three-stage process on Mo-coated soda-lime glass substrates and were stored in air for several days prior to the experiments described here. Surface analytical experiments were conducted in the NREL Surface Analysis Team's homemade cluster tool. The apparatus will be described in detail elsewhere [5], but briefly, the in-line cluster tool consists of a nitrogen-purged glove box, deposition chamber, photoemission system, and a field emission scanning Auger spectrometer, all interfaced to each other via a 24' long UHV transfer system. Photoemission data was obtained on a modified PHI 5600 XPS system. The binding energy scale of the photoemission system was calibrated according to the method of Powell[6] using the sharp Fermi edge observed in ultraviolet photoelectron spectra (UPS) of clean gold foil and with x-ray photoelectron spectroscopy (XPS) data covering the Au 4f_{7/2} and Cu 2p_{3/2} core levels. Aqueous chemical treatments reported here were conducted within the system's glove box, and were set up to emulate conditions that a CIGS surface would experience during growth of a typical CdS buffer layer. Aqueous reagents were purged with flowing N₂ prior to their insertion in the glove-box in an attempt to minimize effects of dissolved gases. Room temperature DI water and aqueous ammonia were added (1.8 M) to a stirred, double-walled beaker heated by flowing 65 °C water, followed immediately by the addition of the CIGS films. Films were treated as described, blown dry with N₂, and moved without air exposure into the UHV transfer system. Carbon content of the films was not quantified due to spectral interference between the C 1s photoelectron line and Ga and Se Auger transitions.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of surface composition as a function of film preparation. The shortest air exposure time is a conservative estimate of oxygen exposure within the cluster tool glove-box and corresponds to a film treated in the ammonia-only CBD bath and transferred directly into the UHV analysis system. The longest air exposure corresponds to the as-grown film which sat in the lab air for about five months. Air exposure times of 5, 60, and 1400 minutes were performed on ammonia-exposed CIGS. The data for this film show a trend observed in many different batches of CIGS of different composition: hot aqueous ammonia removes compounds of Na and O, as well as causes an increase in the relative concentration of Cu, similar to

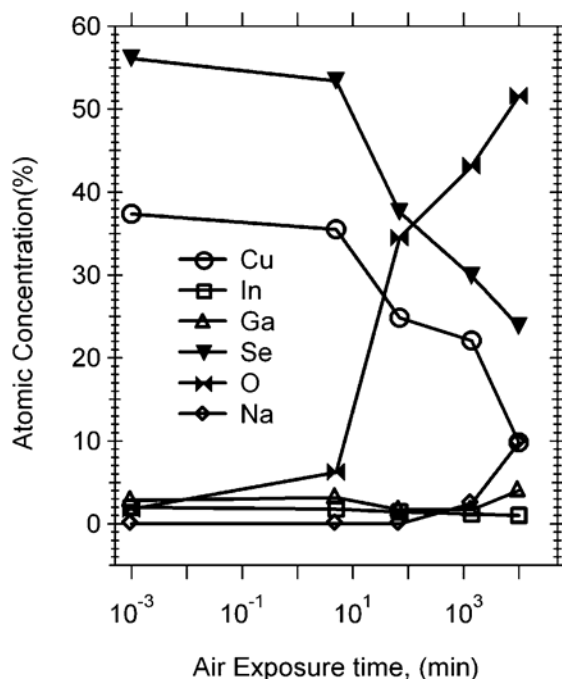


Figure 1. Effects of air and NH₄OH exposure on Cu(In,Ga)Se₂ composition

results on CuInSe₂ reported previously [7, 8]. This trend is more clearly observed in Table 1 and on the basis of the main constituents of the film, Cu, In, Ga, and Se. The data in Table 1 show the compositional changes as a result of the ammonia-only CBD bath on CIGS film M2737 starting from four different surface preparation conditions, as-grown, sputter-cleaned, Br₂-methanol etched, and a water-only chemical bath. It can be seen that the Group III elements, Ga in particular, are preferentially etched from the surface. In the case of the as-grown film, it is certain that some of the changes in stoichiometry are due to the

Table 1. NH₄OH effects on CIGS m2737

Surface Condition	Atomic Concentration, (%)			
	Cu	In	Ga	Se
as-grown	15.1	2.0	8.2	74.7
NH ₄ OH	39.0	1.9	3.1	56.0
% change	+160	-5	-62	-25
sputter-cleaned	18.4	22.1	4.1	55.4
NH ₄ OH	18.0	20.3	0.7	61.1
% change	-2	-8	-83	+10
Br ₂ /methanol	8.0	19.5	5.0	67.5
NH ₄ OH	23.2	12.0	1.1	63.6
% change	+190	-38	-78	-6
water	25.7	2.9	1.6	69.8
NH ₄ OH	27.7	3.2	2.5	66.5
% change	+8	+9	+60	-5

removal of oxides that have Cu, In, Ga, and Se concentrations different from the bulk of the CIGS absorber. Of interest is that even in the case of the sputter-cleaned, oxide-free surface, gallium is preferentially removed from the surface. A similar result is

seen for the clean Br₂-methanol etched surface. These two results demonstrate that removal of surface oxides cannot explain all of the chemistry seen to occur between Cu(In,Ga)Se₂ and NH₄OH. The implications for CIGS device finishing are that indium and gallium vacancies on the surface are available for substitution by Cd or Zn, a doping situation that is at odds with the generally accepted picture of Cd substituting for Cu, but is consistent with XANES data unambiguously showing that at least some V_{In} and V_{Ga} are populated by Cd atoms[9]. Another important point can be seen in the last three rows of Table 1. Water alone is seen to bring about the majority of the changes that have previously been attributed to NH₃[7, 8]. Ammonia was found to effect important changes in the relative position of the valence band maximum and the Fermi energy, as seen in Figure 2.

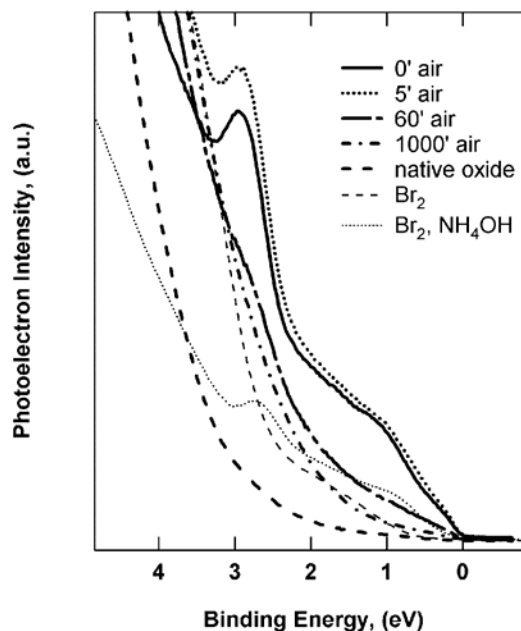


Figure 2. UPS data near E_F on Cu(In,Ga)Se₂ films with different surface preparations

Figure 2 shows UPS data taken with 21.2 eV He I excitation in the vicinity of the Fermi level of films that have undergone various treatments. Films having a native oxide were exposed to the NH₄OH bath for 15', a typical time for completion of a CdS buffer layer, and were then studied with UPS. After ammonia etching, some films were removed from the analysis chamber, exposed to air, and again studied with UPS and XPS. UPS spectra of the NH₄OH-treated CIGS films (0' air) show distinct features at 1.0 and 2.9 eV below the Fermi level. These spectral features were observed in all ammonia-treated films studied, including CuGaSe₂, and most importantly, CIGS that had been initially heavily etched with Br₂/methanol and subsequently exposed to NH₄OH. The fact that the spectral features were not observed for films etched only Br₂/methanol, sputtered, or mechanically cleaned, yet appear in CIGS films that have undergone both Br₂/methanol etching and NH₄OH-exposure strongly implies that the spectral features are the signature of a

specific surface structure that results from NH_4OH -treatment. Theoretical [10] and experimental [11] investigations of chalcopyrite valence band density of state structure have attributed these two spectral features to Cu 3d and Se 4p hybridized bonding. Photoemission data taken on well-characterized Cu_2Se thin films showed similar features[12], including the degenerate p-type surface that is implied by the coincidence of E_F and the valence band maximum (VBM) of the NH_4OH -etched samples. The position of the VBM, the presence of the 1.0 and 2.9 eV features, and the large increase in the Cu concentration all point towards the generation of a thin layer of a Cu_2Se compound on the surface as a result of hot NH_4OH treatment of $\text{Cu}(\text{In,Ga})\text{Se}_2$.

Figure 3 shows how the work function of $\text{Cu}(\text{In,Ga})\text{Se}_2$ changes as a result of exposure to the NH_4OH bath. The general trend for this and other films is that the work function was increased by the bath, as one would expect with the removal of alkali metals and other

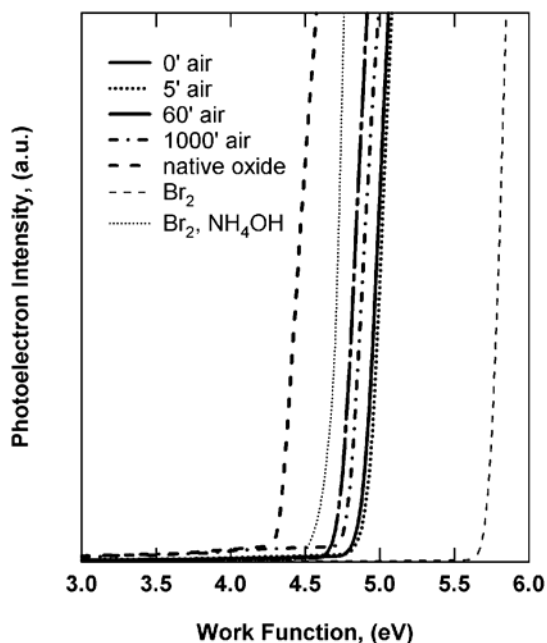


Figure 3. Secondary electron cutoffs of UPS data from CIGS m2737 after different chemical treatments

contaminants. Curiously, exposure to air of ammonia-etched samples for different lengths of time did not result in linear changes to the work function values. It should be noted here that work function values determined via photoemission generally are determined by the region within the analysis area having the lowest work function, unlike a Kelvin probe which spatially averages a heterogeneous surface, and that the experiments detailed in this paper necessarily involved sample movements that may have resulted in an analysis being conducted in a slightly different area than desired. During the course of experiments with aqueous reagents on $\text{Cu}(\text{In,Ga})\text{Se}_2$, it was observed that the heated solutions evolved dissolved gases. It was postulated that bubbles adhering to the

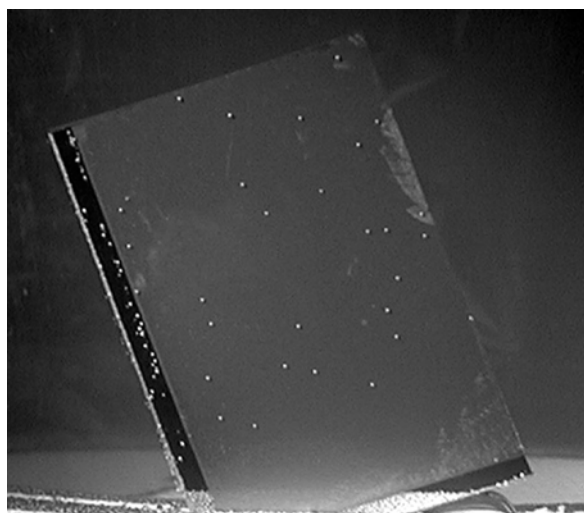


Figure 4. Formation of adherent bubbles during standard CdS CBD

absorber surface inhibited both the effects of the ammonia as well as the deposition of CdS, that this was contributing to the non-uniformity of work function values, and that a wetting agent, or surfactant might increase the uniformity of both ammonia-etching as well as the deposition of CdS.



Figure 5. Elimination of adherent bubbles upon addition of surfactant to bath

Figures 4-5 are photos showing the effects of the addition (0.7 mM) of Triton X-100, a common non-ionic surfactant, to the standard NREL CdS chemical bath. It can be seen that the number of large bubbles adhering to the absorber surface is greatly reduced by the surfactant. Smaller, non-adherent bubbles were seen to sheet up the absorber surface during CdS deposition, a process that should minimize spots of leftover Na compounds and pinholes in the CdS layer. Initial scanning Auger and XPS compositional results indicate that the CdS purity and deposition rate are not affected by the surfactant. To test the idea that the surfactant could improve the quality of

thin CdS buffer layers, CIGS/CdS devices were constructed using CdS thin enough such that the effects of pinholes and poor CdS coverage (i.e. a low Voc) could be observed. Another set of cells was made with surfactant added to the bath. Table 2 shows that the surfactant-modified CBD method led to a large (23%) increase in the overall efficiency of the devices, almost all of that coming from the increased Voc.

Table 2. Comparison of device performance using standard CBD (cells 1-5) and using surfactant-modified CBD (cells 6-10)

Cell	Voc (V)	Jsc (mA/cm ²)	Fill Factor	Efficiency
1	0.460	-29.9	63.69	8.75
2	0.450	-30.73	63.35	8.767
3	0.461	-32.26	63.79	9.479
4	0.469	-32.56	64.32	9.816
5	0.480	-32.41	67.02	10.416
Avg.	0.464	-31.57	64.43	9.446
6	0.187	-27.66	24.97	1.292
7	0.612	-29.78	66.16	12.054
8	0.577	-31.46	67.82	12.301
9	0.533	-31.67	68.05	11.482
10	0.505	-31.79	67.38	10.825
Avg.*	0.557	-31.18	67.35	11.666

*Average without bad cell #6

SUMMARY

XPS data show that Group III elements are preferentially removed from CIGS surfaces as a result of NH₄OH and that water is responsible for many but not all of the compositional changes. UPS shows a VBM within a few kT of the Fermi level, indicating that freshly NH₄OH-etched CIGS surfaces are degenerate and p-type. These data are consistent with the formation of a Cu-Se compound that we tentatively identify as Cu₂Se. The thickness of this layer is < 30 Å based on the fact that In and Ga core-level signals from the underlying substrate are still observable. The Cu-Se layer produced by NH₄OH-etching has a distinctive feature in He I ultraviolet photoelectron spectroscopy (UPS) data at 1.0 and 2.9 eV that disappears with brief air exposure. Work functions determined by extrapolating the secondary electron cutoff in UPS spectra to the energy axis show that the work function of ammonia-treated samples increases by 0.6 eV relative to as-received CIGS thin films covered with a native oxide. Lateral uniformity of chemical bath effects was found to be affected by the formation of bubbles adhering to the absorber surface. Addition of a common non-ionic surfactant, Triton X-100, was found to aid the wetting of CIGS surfaces during aqueous chemical treatments and eliminate adhering bubbles. Initial results obtained using the new surfactant-modified CBD method show that a surfactant can greatly improve the performance of devices made with thin CdS buffer layers.

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