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XPS and UPS Studies of Thin Film PV Materials Modified by Reactions in Liquids

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ABSTRACT

Water-based processing steps are ubiquitous in the semiconductor industry, and the field of photovoltaics (PV) is no exception. During chemical bath deposition (CBD) of CdS, complex chemical reactions occurring at surfaces and in solution are poorly understood, yet have been shown to have powerful effects on the performance in terms of reliability and efficiency of finished PV devices. In the past, electron spectroscopic studies of these reactions have been hampered by the conflicting requirements of ultra-high vacuum and exposure of samples to liquid water. In this paper we present initial results from a new tool at NREL that allows one to conduct atmospheric pressure, liquid phase chemical processes on thin film PV materials and subsequent examination via core and valence level electron spectroscopies without exposing samples to air contamination.

1. Objectives

The objectives of this work were to increase the understanding of CdS deposition-bath chemical effects on CIGS surfaces, with the ultimate goal of improving PV device performance in terms of efficiency and reliability. In addition, this work addresses the Measurements and Characterization goal in the five year PV technical plan to "validate the surface analysis test platform for process integration".

2. Technical Approach

A number of different approaches have been taken to study liquid-phase reactions with ultra-high vacuum (UHV) surface analytical techniques. Our initial approach, with goal of maximizing system flexibility, has been to integrate a commercially available glovebox with a homebuilt cluster tool. Details of the cluster tool will be published elsewhere, but briefly, the system consists of a photoemission system, a scanning Auger microscope, a deposition system, a glovebox, and an 8 m long UHV trolley-based sample transfer system that links all four stations.

3. Results and Accomplishments

Several different material systems have been investigated in the glovebox portion of the NREL Surface Analysis Team's new cluster tool. Preliminary investigations with sputter-cleaned metal foils were carried out to understand how well reactive surfaces could be kept clean under "real use" conditions. Experiments probing CdTe and chalcopyrite surface chemistry involving common etchants such as Br_2/methanol have been conducted. As an example of the kinds of experiments that the new apparatus makes possible, we present initial results on experiments designed to probe aspects of the aqueous chemistry occurring during CBD of CdS on chalcopyrite-based thin film absorber layers.

Figure 1 shows how the surface composition of a $Cu(In,Ga)Se_2$ thin film changes as a function of immersion time in a dilute solution of ammonium hydroxide. Although it is commonly held that aqueous ammonia preferentially removes copper from this type of film, x-ray photoelectron spectra (XPS) demonstrate that indium, and to a lesser extent gallium, are preferentially leached from the CIGS surface and that the copper content of the surface layer actually increases. Figure 1 hints at the fact that under proper conditions, the oxygen content of an ammonia-cleaned CIGS film approaches the limits of detection for XPS (< 0.5 %), much less than the 30 at. % commonly observed on films exposed to atmosphere (data not shown).

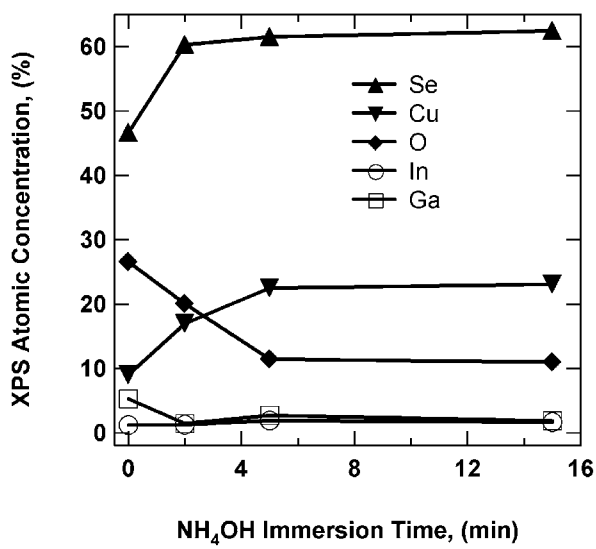

Figure 1. XPS-derived surface composition as a function of immersion in aqueous ammonia.

Valence band ultraviolet photoelectron spectroscopic (UPS) data on NH_4OH-exposed CIGS films are shown in Fig. 2. The position of the upper valence band edge with respect to the Fermi energy (E_F=0 eV) may be determined by extrapolating the valence band edge to its intersection with the background signal at negative binding energies. These results confirm the work of others in that they show that CIGS films that have been exposed to atmosphere have on their surface a high bandgap n-type layer. Of interest is

that ammonia-exposed films have a valence band edge close to the Fermi energy, indicating that the surface has become p-type. Because convention holds that the production of highly efficient CIGS-based cells is dependent on the surface retaining the type inversion afforded by surface-specific phases and because ammonia exposure is inevitable during CBD growth of CdS buffer layers, this type conversion is of direct relevance to understanding junction formation in CIGS-CdS devices.

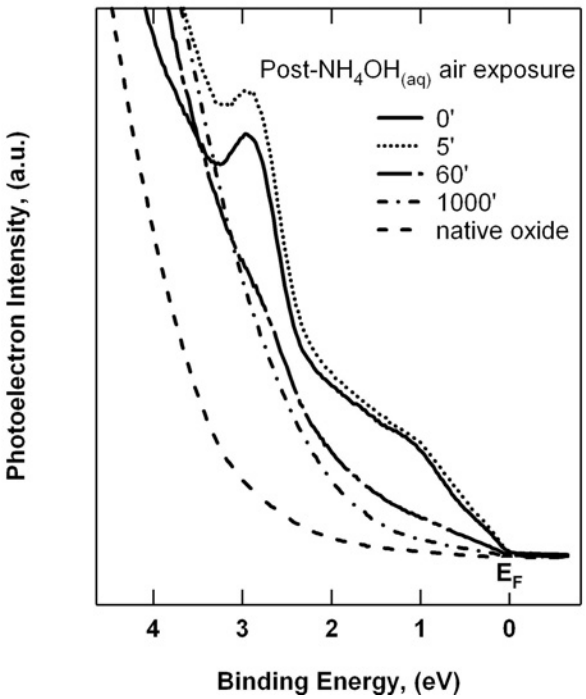

Figure 2. Ultraviolet photoelectron spectra of $Cu(In,Ga)Se_2$ valence bands in films exposed to NH_4OH, and subsequently exposed to air.

Figure 2 also demonstrates that ammonia-exposure causes the formation of a unique feature at 2.9 eV below the Fermi energy, and that this feature rapidly disappears upon exposure to air. Previous workers have identified peaks near 2.9 eV in UPS data taken on bulk Cu_2Se films as stemming from Cu 3d – Se 4p hybridized bonding.

Additional information about the species generated at CIGS surfaces as a result of aqueous ammonia exposure is found in Fig. 3, a series of high-resolution XPS spectra covering the Cu 2p core level. The Cu 2p spin-orbit doublet of the ammonia-cleaned CIGS surface had peaks at 932.44 eV (Cu $2p_{3/2}$) and 952.29 eV (Cu $2p_{1/2}$), whereas films that had been first cleaned in ammonia then exposed to air had additional peaks centered on ~ 943 eV and ~ 962 eV. These additional peaks are shake-up satellites indicating that the copper atoms in air-exposed films are paramagnetic, i.e., are in a Cu^{2+} configuration, most likely the result of oxide formation. That ammonia immersion causes the disappearance of these peaks is consistent with the presence of stoichiometric $Cu(In,Ga)Se_2$ and also with the formation of a thin layer of Cu_2Se, because both compounds have Cu in the 1+ oxidation state. A determination that ammonia-exposure causes the formation of a thin layer of Cu_2Se would be significant because the 0.4 eV conduction band discontinuity between bulk Cu_2Se and CdS represents a large barrier to charge flow in a CIGS-CdS solar cell.

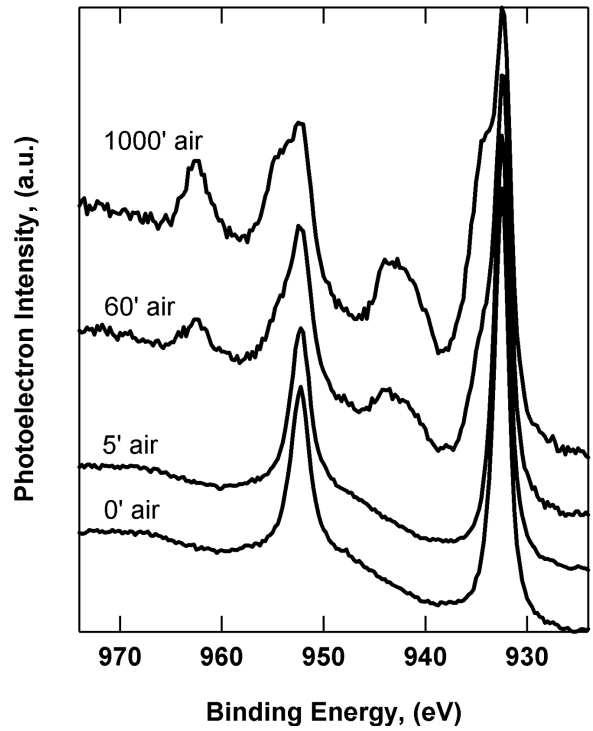

Figure 3. High resolution XPS data covering the Cu 2p core level. Data were taken on CIGS films initially exposed to NH_4OH (0' air) and on films exposed increasingly to air.

The results presented here call for further work to determine the exact nature of the Cu_2Se-like thin layer that is created on CIGS surfaces as a result of exposure to aqueous ammonia.

4. Conclusions

The NREL Surface Analysis Team has constructed a new and unique tool that integrates atmospheric pressure processes with ultra-high vacuum surface characterization tools. Initial experiments making use of this new tool have been conducted on CdTe, $Cu(In,Ga)Se_2$, and CdS. Example results presented in this paper on chemistry related to the aqueous deposition of CdS reveal several new phenomena: aqueous ammonia causes preferential loss of Group III elements from CIGS, type conversion of the surface, and reduction of Cu^{2+} to Cu^{1+}. These results are consistent with the formation of a thin layer of a material similar to Cu_2Se, a material detrimental to the functioning of CdS-CIGS solar cells.

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15. SUBJECT TERMS
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