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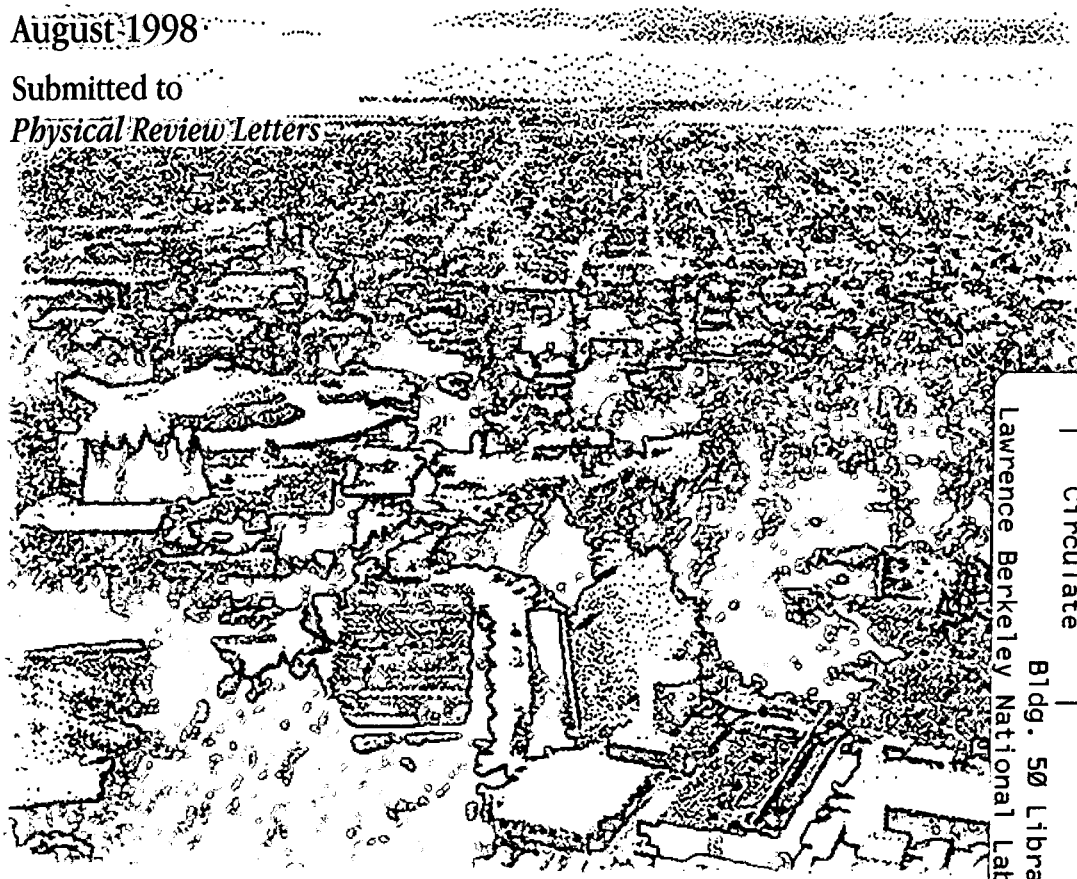

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Localization of impurities at a buried interface: Na and the $CdS/Cu(In,Ga)Se_2$ heterojunction

C. Heske*[1], D. Eich[2], R. Fink[2], E. Umbach[2], S. Kakar[3], M.M. Grush[4], T.A. Callcott[4], T. van Buuren[5], C. Bostedt[5], L.J. Terminello[5], F.J. Himpsel[6], D.L. Ederer[7], R.C.C. Perera[8], W. Riedl[9], and F. Karg[10]

[1] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

[2] *Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

[3] *Department of Applied Science, University of California at Davis/Livermore, Livermore, California 94551*

[4] *University of Tennessee, Knoxville, Tennessee 37996*

[5] *Lawrence Livermore National Laboratory, Livermore, California 94551*

[6] *Department of Physics, University of Wisconsin at Madison, Madison, Wisconsin 65500*

[7] *Tulane University, New Orleans, Louisiana 70118*

[8] *Lawrence Berkeley National Laboratory, Berkeley, California 94720*

[9] *Siemens AG Corporate Research and Development, Domagkstr. 11, D-80807 München, Germany*

[10] *Siemens Solar GmbH, Domagkstr. 11, D-80807 München, Germany*

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Abstract

A combination of Photoelectron Spectroscopy and X-ray Emission Spectroscopy has been employed to investigate the buried interface between a $Cu(In,Ga)Se_2$ thin film solar cell absorber and a CdS buffer layer. The experiments reveal that Na impurities from the sodalime glass substrate are localized at the buried interface and that intermixing of some of the major constituents occurs. These findings demonstrate a general approach to identify electrically

important impurities localized at buried interfaces and shed new light on the influence of Na on the electrical performance of CdS/Cu(In,Ga)Se_2-based solar cells.

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The investigation of interfaces in layered systems is one of the most important and challenging fields of solid state physics. This is true from a basic physics point of view such as the investigation of quantum interference effects in multilayer systems [1], as well as from a device-oriented point of view, e.g. for systems prepared by various chemical deposition or reaction methods. Nearly all electronic devices such as integrated circuits, light-emitting devices, and solar cells are based on, or contain, buried interfaces. Consequently, a detailed knowledge about the atomic and electronic structure at buried interfaces is extremely important. This calls for an experimental probe sensitive to the location of the interface, sensitive to the electronic and chemical structure at the interface, and atom-specific to discern the various elements involved. In addition, the probe should be non-destructive to rule out any obscuring influence of the measurement technique on the information that is being obtained.

Unfortunately, no single such probe exists today. Several techniques such as X-ray diffraction and scattering, X-ray standing waves, X-ray absorption, electron microscopy, second-harmonic and sum-frequency generation, Raman spectroscopy, and surface photovoltage spectroscopy have been used to address a few of these demands. It is the purpose of this letter to demonstrate that the complementary techniques X-ray Emission Spectroscopy (XES) and Photoelectron Spectroscopy (PES) can be combined to unambiguously identify the localization of a particular atomic species (example: Na) at a buried interface. We show that this can be done for a fraction of a buried monolayer in a non-destructive and atom-specific way and that this approach can be utilized to understand the electronic properties of an industrially prepared semiconductor device (example: $Cu(In,Ga)Se_2$ thin film solar cell).

X-ray Emission Spectroscopy has previously been employed to study buried layers [2], multilayers [3] [4] [5], and buried thin films [6]. The information depth is determined by the attenuation lengths of the incoming and outgoing photons (about 100 nm - 2 μm in the present study). Hence, XES is not per se interface-sensitive, but rather a bulk-sensitive probe. However, by either increasing the number of interfaces within the information volume or by reducing the thickness of a single buried layer to one or two monolayers, atom-specific

information about the electronic structure in the vicinity of an interface can be obtained [3] [5] [6]. This assumes a "well-behaved" interface, i.e. an abrupt junction and no interdiffusion, and requires that the interfaces or buried layers can be prepared as necessary for this approach. Both assumptions are probably not valid for many systems, and in particular not for the present case. Photoelectron Spectroscopy has generally been the method of choice to determine the electronic structure of a solid. However, the information depth is determined by the inelastic mean free path of the outgoing electron (about 0.5 - 2 nm in the present study), which makes it a highly surface sensitive probe. The common approach of subsequently removing layer-by-layer by ion-sputtering to probe interface properties is questionable because of the alterations of the system induced by the impinging ions, leading to a significantly changed stoichiometry and the formation of a Fermi edge in the present case [7].

The CIGS material chosen here as an example is of high interest since it yielded solar cell conversion efficiencies of up to 17.7 % [8], which makes this system a prime candidate for cost-efficient thin film solar cells. Moreover, the CdS/CIGS heterojunction and in particular the potential role of Na at this interface is poorly understood and hence it is ideally suited for the investigation of impurity localization at a real, buried interface [9]. The two common preparation techniques for the CIGS absorber are Rapid Thermal Processing (RTP) of elemental precursor layers on a Mo-coated sodalime glass substrate and co-evaporation of individual or multinary constituents. Both rely on high-temperature steps during which Na diffuses from the glass substrate, through the Mo back electrode, and into the forming polycrystalline CIGS layer. It is generally accepted that Na impurities have an extremely beneficial influence on the solar cell performance over a wide range of Na concentration [10], and several chemical models have been proposed [10] [11] [12]. To date, however, the enhancing mechanism and the microscopic Na location during the various stages of the solar cell production process have not been fully understood. There is good evidence that for thermally treated CIGS films the Na is mostly located at the surface [13], but it has been assumed that Na at CIGS surfaces does not play a role for the complete solar cell device,

because a CdS buffer layer is deposited onto the CIGS film by a short dip in an aqueous solution, and because water can remove Na from the CIGS surface [12] [14]. It is the purpose of this letter to demonstrate that Na is in fact not only located on the free CIGS surface, but that a significant fraction of the Na atoms also remains localized at the CdS/CIGS interface for CdS overlayer thicknesses generally employed in solar cell devices.

The experiments were performed at the undulator Beamline 8.0 of the Advanced Light Source employing the Soft X-Ray Fluorescence spectrometer and the Ellipsoidal Mirror Analyzer. The samples were prepared by RTP technology from elemental layers of Cu, In, Ga, and Se deposited on Mo-coated sodalime glass substrates. CdS was deposited using chemical bath deposition (CBD) in aqueous solution. The CdS overlayer thicknesses were controlled by the duration of immersion; the absolute thickness values are accurate only within 30 %, the relative values within about 10 %. Immediately after preparation, the samples were sealed under dry-nitrogen ambient conditions in over-pressurized and moisture-free containers. Unless otherwise mentioned, no additional in-situ preparation was performed so that the experiments relate as much as possible to the actual solar cell production process. One CIGS film was treated by ion-sputtering to remove the Na surface content. A single sputter step was performed on this sample with 2 keV Ar^+ ions at about 1 μAmp/cm^2 for 30 minutes.

Fig. 1 shows the PES valence spectra obtained for two incident photon energies and different sample treatments. Spectrum a) was recorded for the pristine CIGS surface at a photon energy of hν=800 eV (moderate surface sensitivity). All other spectra were recorded at hν=208 eV (increased surface sensitivity). In detail, spectrum b) shows the signal from the pristine CIGS surface, c) after a short sputter treatment to remove the Na surface content, and d) and e) after deposition of 5 nm and 200 nm CdS on *non-sputtered* CIGS, respectively. In addition to the In 4d (as marked) and Cu 3d peaks (in the valence band region, VB), a small (spectrum a) and large (spectrum b) Na signal for the pristine CIGS surface is detected [15]. The increase in peak intensity is due to both the increased surface sensitivity as well as the increased photoionization cross section (by a factor of 50 [16]) for

Na 2p in spectrum b). As known from a previous investigation, the Na surface content can be entirely removed by a short ion-sputtering treatment (spectrum c) [13]. Note the influence of the ion-sputtering on the shape of the valence band region and on the peak height of the In 4d doublet, indicating significant changes in the CIGS surface composition due to the ion-sputtering treatment as mentioned above. Upon deposition of a 5 nm CdS layer (onto the pristine sample) the Na signal is drastically reduced by a factor of about 170. For thicker CdS overlayers (15 to 200 nm), no Na peak is detected with PES. Note that the In 4d signal is not nearly as much reduced as the Na signal. Both the In 4d and the In $3d_{5/2}$ peaks are merely attenuated by a factor of 6, which is in disagreement with a simple exponential attenuation model that would predict a decrease by a factor of about 150 for an overlayer thickness of 5 nm and an inelastic mean free path of 1 nm. This clearly indicates that In atoms diffuse into the CdS overlayer. The attenuation of the Na signal is a first indication that the number of detected Na atoms is slightly less, but close to the number expected for the pristine surface coverage buried underneath a CdS overlayer of 5 nm.

In Fig. 2, XES spectra of the Na K_α transition (2p→1s), corresponding to the previous PES experiments, are presented. The excitation photon energy was set to $h\nu$=1075 eV in order to maximize the Na signal. The spectra were normalized and energy calibrated with respect to the Cu L_α transition ($3d \rightarrow 2p_{3/2}$) which was measured simultaneously with the Na signal. The entire spectrum for the pristine CIGS surface is shown in the inset of Fig. 2. The location of the Na signal under investigation is marked as well. The main part of Fig. 2 shows the Na 2p→1s and the Cu 3p→2s transitions for the pristine CIGS surface (spectrum a), after the same short ion-sputter treatment as described previously (spectrum b), and after deposition of 5 nm CdS (spectrum c) and 100 nm CdS (spectrum d) on the pristine CIGS film. The Na peak for the pristine CIGS surface is completely removed by the sputter treatment. This demonstrates that Na is, within the detection limits of XES, entirely located at the CIGS surface. Note that the Na saturation content at RTP-produced CIGS surfaces was previously determined to be about 1 % of a monolayer [14], so that the peak in spectrum a) corresponds to about a hundredth of a surface monolayer. Consequently, even

fractions of an atomic percent of Na, if present, should be resolvable in the CIGS bulk (i.e., in the ion-sputtered sample).

Remarkably, the Na content of the pristine CIGS surface (spectrum a) is only slightly reduced upon deposition of 5 nm CdS (spectrum c). In fact, we were able to observe Na signals for overlayer thicknesses up to 50 nm, well beyond the common buffer layer thicknesses in CIGS solar cell devices. Apparently, the Na content is reduced but not removed by the aqueous CdS dip. Note that due to the normalization with the Cu signal (which remains localized in the CIGS film [17]), all influences due to the differences in X-ray attenuation from the buried regions are removed. We do detect a reduction of the Na content due to an interaction between water and Na, as reported previously [14]. However, significant amounts of Na remain present and are localized at the CdS/CIGS interface. A diffusion of Na into the CIGS bulk can be ruled out because of the presence of a Na signal in the PES spectrum for a 5 nm CdS overlayer. Only for very thick overlayers (100 nm and more) does the Na signal in the XES spectra become hardly discernible from the spectral noise (spectrum d).

Our results are summarized in a schematic block diagram in Fig. 3. The combination of the two complementary techniques PES and XES, together with ion-sputtering, revealed that, within the XES detection limit, all Na atoms are located at the surface of the pristine CIGS film, as depicted in the upper left hand region of Fig. 3. Both, PES and XES, detect Na on the pristine surface. After the ion-sputter treatment (bottom of Fig. 3), neither technique detects Na. Combining the PES and XES results for CdS/CIGS interfaces with a simple attenuation analysis, we were able to deduce that some of the Na surface content is removed by the CdS dip but that a significant fraction is incorporated and localized at the interface. Also, we find that indium diffuses into the CdS overlayer, which is conceivable considering the possibility of forming In- and S-containing compounds such as In_2S_3. Moreover, we find direct evidence of a S/Se exchange by analyzing the S VB→2p emission and the S and Se PES peak intensities upon interface formation, which will be presented elsewhere [17]. Hence, we propose an intermixed region at the buried interface, as denoted by the hatched area in

Fig. 3. Note that the intermixed region is extending much further than the interface region in which the Na is localized, as derived from the attenuation behaviour of the PES signals. Both findings - the localization of Na at the buried interface as well as the formation of an intermixed zone - shed new light on the role of Na for the improvement of the CdS/CIGS solar cell device, as well as on the understanding of interfaces in general and of the CdS/CIGS interface formation in particular.

In summary, we have demonstrated that a combination of Photoelectron Spectroscopy (PES) and X-ray Emission Spectroscopy (XES) can be employed to investigate the localization of an electronically important impurity species at a real buried interface. The availability of such a methodical approach will be a key ingredient in understanding and optimizing the electronic structure of heterojunctions in general. In particular, it opens up new possibilities for investigating complex and non-ideal interfaces such as the CdS/Cu(In,Ga)Se_2 heterojunction.

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* Address after Jan 1999: Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. e-mail: heske@physik.uni-wuerzburg.de

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FIGURES

FIG. 1. Photoemission spectra at various stages of the CdS/Cu(In,Ga)Se_2 interface formation: pristine Cu(In,Ga)Se_2 surface (CIGS) excited with (a) hν=800 eV and (b) hν=208 eV photons; (c) after sputter treatment (hν=208 eV); after chemical-bath deposition of (d) 5 nm CdS and (e) 200 nm CdS (both hν=208 eV). The binding energy scale is referenced to the Fermi energy. Spectra (b) - (e) are normalized by the exciting photon flux and spectrum (a) is normalized to give the same In 4d peak height as spectrum (b).

FIG. 2. X-ray emission spectra at various stages of the CdS/Cu(In,Ga)Se_2 interface formation excited with hν=1075 eV: (a) pristine Cu(In,Ga)Se_2 surface (CIGS); (b) after short sputter treatment; and after chemical bath deposition of (c) 5 nm CdS and (d) 100 nm CdS. The spectra are energy calibrated and normalized with the simultaneously measured Cu 3d$\rightarrow$2$p_{3/2}$ emission line (Cu L_α, 929.7 eV), as shown in the inset for spectrum (a). The presence of the Cu 3p$\rightarrow$2s peak is ascribed to an excitation with X-rays produced by higher harmonics of the undulator and higher orders of the beamline monochromator.

FIG. 3. Schematic diagram of the CdS/Cu(In,Ga)Se_2 interface formation, summarizing the photoemission (PES) and X-ray emission (XES) results. "PES: Na" denotes detectability of Na with PES, while for "PES: no Na" no Na signal is found in the PES spectrum (analogous for XES). The hatched area in the CdS-dipped sample represents an intermixed region with In segregation and S/Se intermixing. This region includes the buried Na localization region. The layer thicknesses are not drawn to scale.

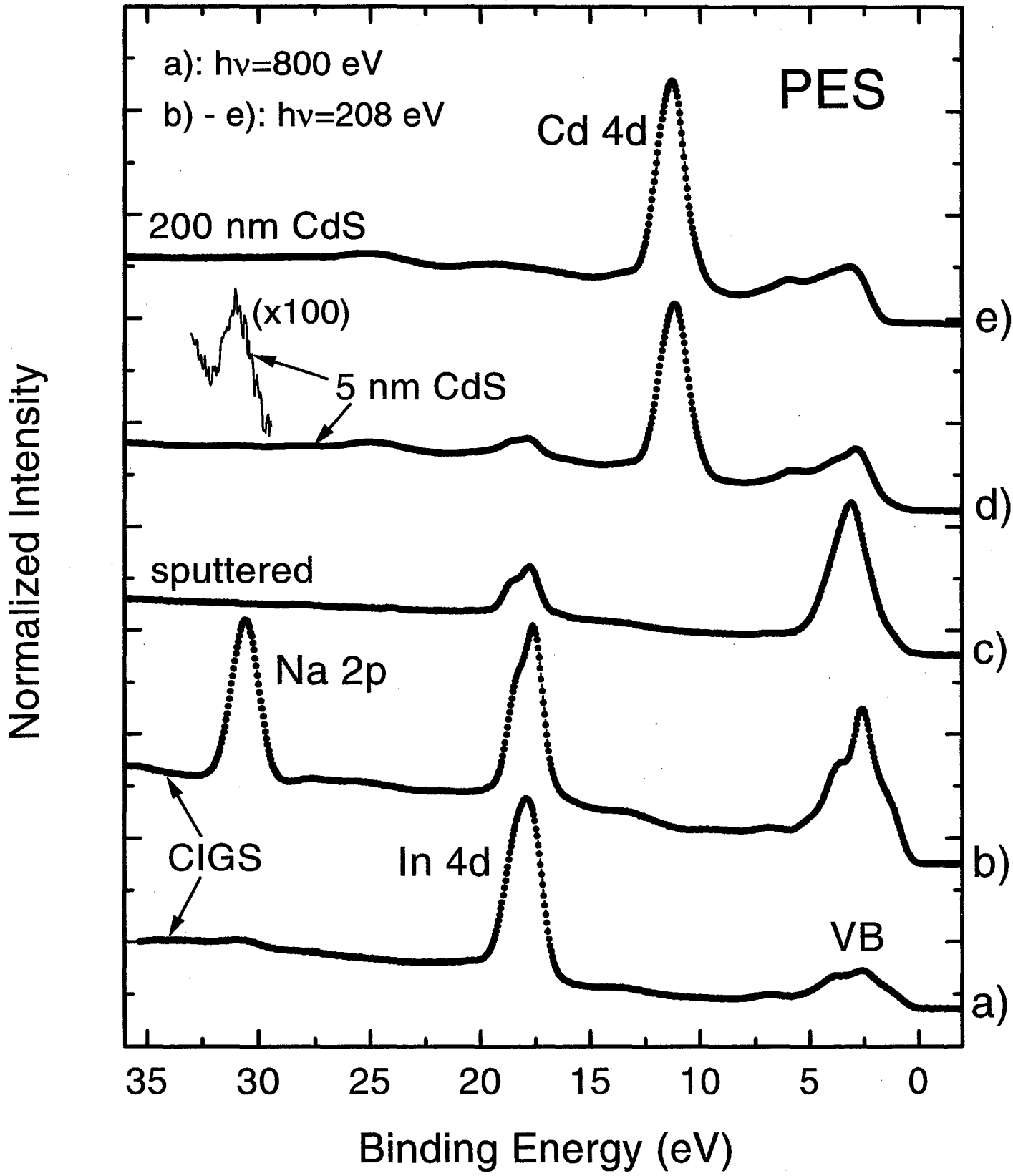
a): hν=800 eV
b) - e): hν=208 eV
PES
Cd 4d
200 nm CdS
(x100)
5 nm CdS
sputtered
Na 2p
CIGS
In 4d
VB
e)
d)
c)
b)
a)
Normalized Intensity
35
30
25
20
15
10
5
0
Binding Energy (eV)

Figure 1

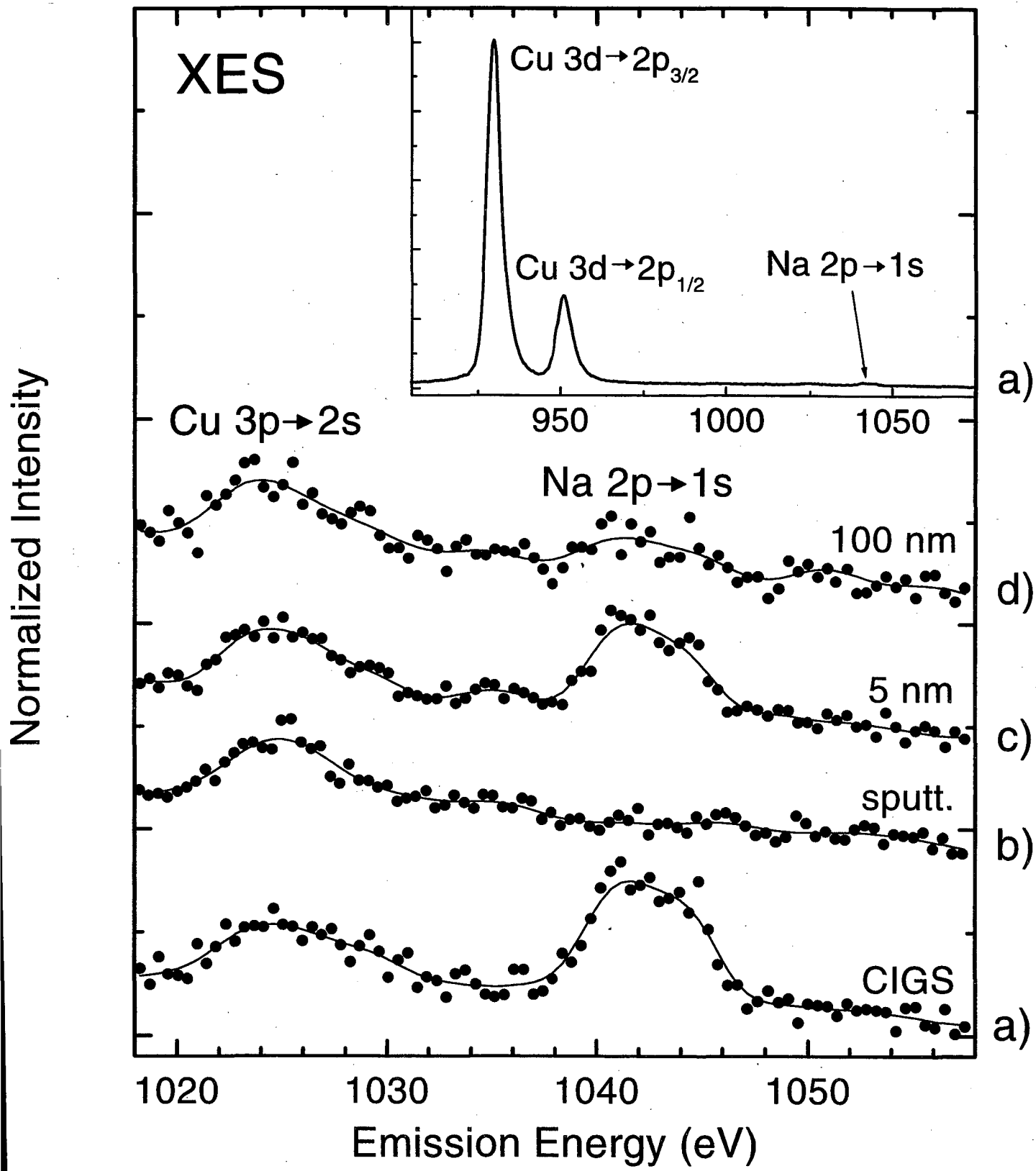
XES
Cu 3d→2p3/2
Cu 3d→2p1/2
Na 2p→1s
950
1000
1050
a)
Cu 3p→2s
Na 2p→1s
100 nm
d)
5 nm
c)
sputt.
b)
CIGS
a)
1020
1030
1040
1050
Emission Energy (eV)
Normalized Intensity

Figure 2

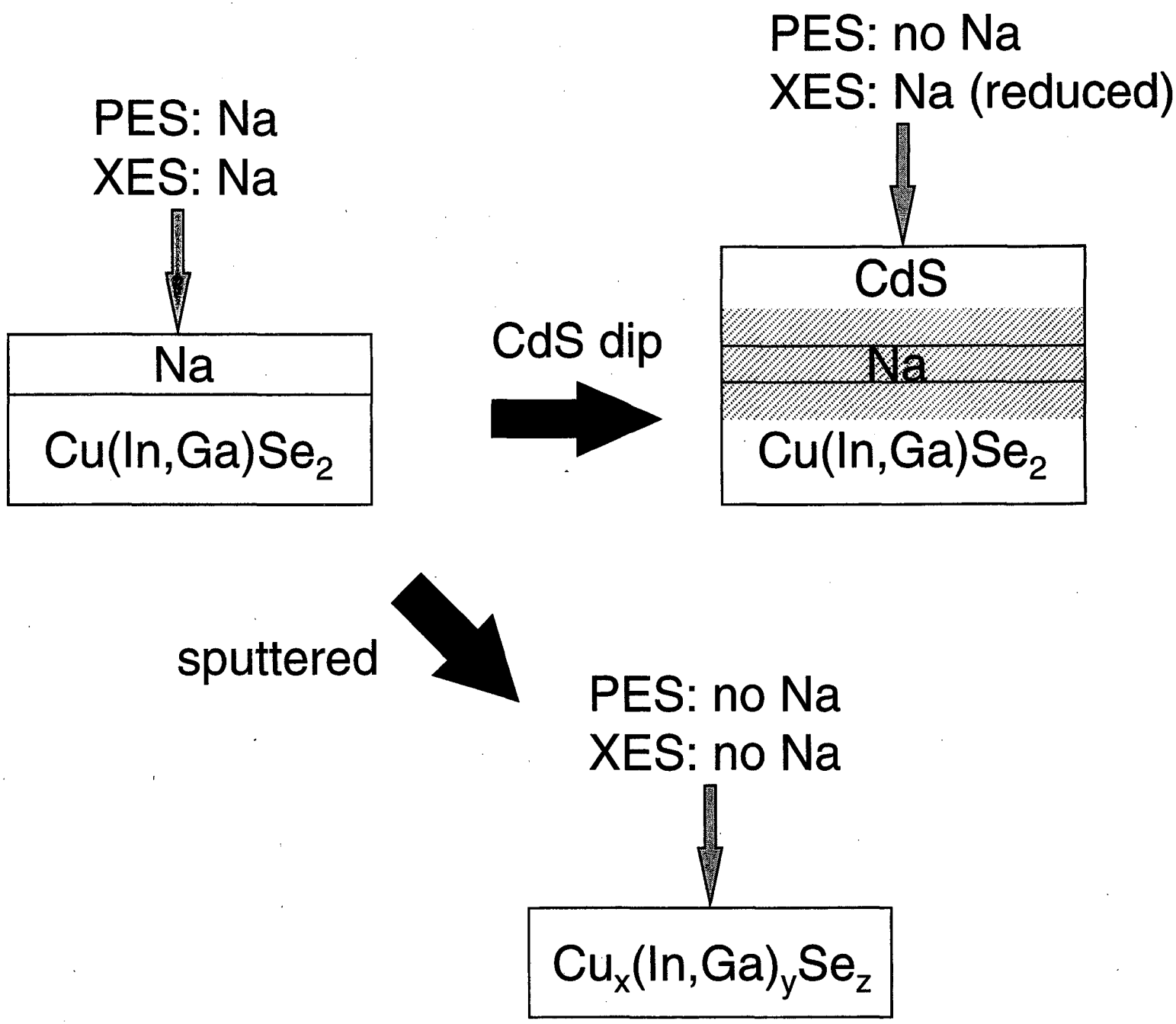
PES: Na
XES: Na
Na
Cu(In,Ga)Se2
CdS dip
PES: no Na
XES: Na (reduced)
CdS
Na
Cu(In,Ga)Se2
sputtered
PES: no Na
XES: no Na
Cux(In,Ga)ySez

Figure 3

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ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720

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