Self-limited Na content at the buried CdS/Cu(In,Ga)Se_2 solar cell heterojunction

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INTRODUCTION

Thin film solar cells based on Cu(In,Ga)Se_2 (CIGS) have, over the past few years, attracted considerable attention due to their high conversion efficiency (18.8 % [1]), due to the advantages of cost-efficient preparation methods, and due to low material input. One of the most interesting questions regarding the optimization of CIGS-based thin film solar cells is the role of Na "impurities" (originating from the glass substrate) and their surprising positive influence on the electronic and morphological properties of the solar cell device.

By employing a combination of photoelectron spectroscopy (PES) and X-ray emission spectroscopy (XES) we were recently able to show that for CIGS films, the Na impurities are solely located at the external surface (within the sub-ppm sensitivity of XES). Furthermore, we could show that this surface coverage of Na is not entirely removed by the aqueous CdS-chemical bath commonly employed in device fabrication, but that a significant fraction of the initial surface coverage is localized at the CdS/CIGS interface [2].

Having thus identified a method to non-destructively, semi-quantitatively, and atom-specifically study the localization of Na atoms at the buried interface (and also to study the intermixing at buried interfaces [3]), we have then investigated the possibility to "design" the electronic structure of the buried interface by forming interfaces of *Na-rich* CIGS with CdS. Here, the aim was to test whether the pristine Na surface coverage of the CIGS film can be used to control the amount of Na which is localized at the interface.

EXPERIMENTAL

The present data were obtained by utilizing the ellipsoidal mirror analyzer and the soft X-ray fluorescence spectrometer at Beamline 8.0. CdS/CIGS samples with different Na content were prepared by rapid thermal processing (RTP) of the CIGS films from elemental precursor layers and by chemical bath deposition (CBD) of the CdS buffer layer.

RESULTS

Fig. 1 (left) compares a series of photoemission spectra obtained for the extended valence region of differently prepared samples (hν = 208 eV), both with *nominal* Na content (i.e., a Na content pertaining to efficiency-optimized devices) and with *high* Na content, respectively. In the case of the Na-rich CIGS sample (b), the Na 2p / In 4d peak ratio is enhanced (by a factor of about 1.7) as compared to the nominal-Na CIGS sample (a), as expected. Upon deposition of CdS (30 nm, spectrum c), a Cd 4d peak is observed, the In peaks are entirely removed, and the Na peak is strongly reduced but still significant. This observation is markedly different from that in our previous study of CdS deposition on CIGS with *nominal* Na content, where no Na could be observed on the CdS surface for film thicknesses of more than 5 nm. Even in the 5 nm case (spectrum e) the observed Na peak was substantially smaller (reduced by a factor of 170 with respect to spectrum a). In the present case of a high Na content the Na atoms responsible for the PES Na 2p peak (spectrum c) are localized at the CdS surface. This can be derived from the fact that the Na 2p peak can be drastically reduced by a short Ar$^+$ sputter treatment (spectrum d).

Note that in spectrum e) we still detect a substantial In 4d peak. This is not due to an incomplete coverage for the 5 nm CdS layer, but is rather interpreted as an intermixing at the CdS/CIGS interface [2,3]. This conclusion is derived from the attenuation behavior of the Na 2p and Cu 3d photoemission signals and from an a-posteriori Auger/SEM investigation both in Auger mapping mode and in small-spot Auger spectroscopy mode.

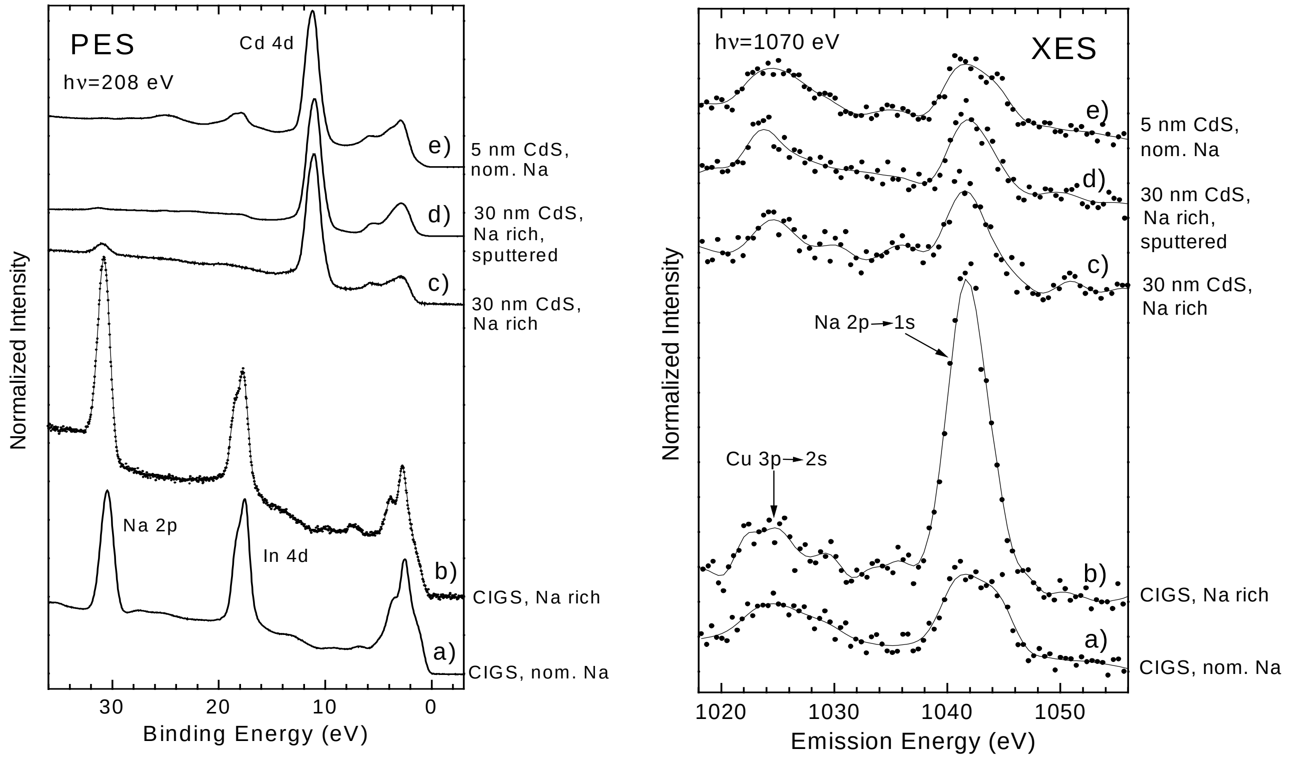

Fig. 1. Photoemission (hν=208 eV) and X-ray emission (hν=1070 eV) spectra at various stages of the CdS/Cu(In,Ga)Se$_2$ interface formation.

X-ray Emission spectra for the Na K_α transition are presented in Fig. 1 (right) for the same set of samples. The spectra were calibrated and normalized with the simultaneously measured Cu L_α ($3d \rightarrow 2p_{3/2}$) transition (929.7 eV, not shown). This normalization removes all attenuation effects due to the different overlayer thicknesses from the spectra. Apart from a dominant Na peak, the Cu 3p → 2s transition is also observed, due to excitation with higher-order light from the beamline and undulator. Again, spectra a) and b) compare data obtained from CIGS films with *nominal* Na content and with *high* Na content, respectively. As in the case of the photoemission spectra, we find a sizeable peak for the sample with nominal Na-content (a) and a significantly increased peak (by a factor of 3.7) for the Na-rich sample (b). The different factors for the peak increase in PES and XES can be explained on the basis of some residual surface contamination and the different information depths of PES and XES. Additionally, lateral inhomogeneities of the Na content on the Na-rich CIGS sample cannot be entirely ruled out.

Upon deposition of 30 nm CdS on the Na-rich sample the Na peak is strongly reduced, albeit not totally removed. A similar behavior was found for the previously recorded nominal-Na series, where some of the Na on the surface of the CIGS film was removed, but the larger fraction was incorporated and localized at the buried interface [2]. Spectrum e) is taken from that series. Remarkably, the peaks in spectra c) and e) are comparable in size, even though the peak intensities of spectra a) and b) (as-introduced CIGS films) are very different. In order to determine the influence of the residual Na surface content of the 30 nm CdS/Na-rich CIGS sample (see Fig.1 left, spectrum c), we have also investigated the sputter-treated sample by XES and found only a slight decrease of the XES Na peak intensity.

The experimental results can be interpreted in terms of a *self-limitation* of the Na content at the buried CdS/CIGS interface. For the series with nominal Na content, we observe that most of the Na is localized at the interface. For the Na-rich series, however, we observe that indeed some of the Na surface content of the CIGS remains upon CdS deposition, but that a much larger fraction of Na atoms is removed. A remnant of these Na atoms is possibly observed as the residual Na signal on the CdS surface. The amount of Na localized at the buried interface is comparable for both the Na-rich series and the nominal-Na series. This can be interpreted such that only a certain maximal amount of Na atoms can be incorporated at the interface, and that additional Na atoms are either washed off by the CdS bath, or segregate to the surface of the growing CdS overlayer, perhaps due to a reaction with the constituents of the CBD-bath and/or a Coulomb-repulsion between the Na alkali atoms.

Our experimental results and the model of a self-limited Na content can thus contribute to explain the large process window for employable Na concentrations. In particular on the Na-rich side the system appears to "stabilize" itself by "choosing" the right amount of Na to be incorporated at the buried interface. However, this also means that the deliberate addition of Na atoms to the CIGS film does not represent a good parameter for influencing the Na content localized at the buried interface, i.e., that it is not easily possible to "tailor" the electronic structure of the buried interface, at least not in the Na-rich regime.

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