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Transient and modulated charge separation at $CuInSe_2/C_{60}$ and $CuInSe_2$/ZnPc hybrid interfaces

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ABSTRACT

Spectral dependent charge transfer and exciton dissociation have been investigated at hybrid interfaces between inorganic polycrystalline $CuInSe_2$ (untreated and Na-conditioned) thin films and organic C_{60} as well as zinc phthalocyanine (ZnPc) layers by transient and modulated surface photovoltage measurements. The stoichiometry and electronic properties of the bare $CuInSe_2$ surface were characterized by photoelectron spectroscopy which revealed a Cu-poor phase with n-type features. After the deposition of the C_{60} layer, a strong band bending at the $CuInSe_2$ surface was observed. Evidence for dissociation of excitons followed by charge separation was found at the $CuInSe_2$/ZnPc interface. The Cu-poor layer at the $CuInSe_2$ surface was found to be crucial for transient and modulated charge separation at $CuInSe_2$/organic hybrid interfaces.

1. Introduction

$CuInSe_2$ is investigated as an absorber material in thin film solar cells due to its band gap of ~1.0 eV, its p-type conductivity with an optimum charge carrier concentration in the range of 10^{16}–10^{17} cm^3, its high absorption coefficient of >10^5 cm^{-1}, and its high chemical stability [1–3]. In addition, $CuInSe_2$ can be easily alloyed by $CuGaSe_2$ and thereby the absorber band gap can be increased from ~1.0 eV for $CuInSe_2$ to ~1.7 eV for $CuGaSe_2$ [4]. By tuning the absorber band gap in this way, highest efficiencies of 22.3% were achieved for solar cells with polycrystalline $Cu(In,Ga)Se_2$ absorbers with a Ga/(Ga + In) ratio of about 0.33–0.38 [5,6]. Nevertheless, $CuInSe_2$ is most suitable as an absorber in the bottom cell of a two junction tandem device because of its band gap of about 1.0 eV [7]. Early research on two junction tandem solar cells with a polycrystalline $CuInSe_2$ bottom cell and an epitaxial GaAs top cell for spacecraft applications showed efficiencies of 25.8% [8]. Note that the band gap of GaAs of 1.4 eV is not optimum for a two junction solar cell. Theoretical maximum efficiencies of 42% could be achieved by using an absorber with a band gap of about 1.9 eV in the top cell [7]. However, the choice of inorganic materials with such a band gap as well as appropriate electronic properties and low cost manufacturing is limited. The rather new field of hybrid photovoltaic devices enables a wide branch of combinations of inorganic and organic semiconductors, opening the possibility to tune the needed properties for the desired application.

In this work, we investigate the combination of the inorganic p-type $CuInSe_2$ semiconductor with the small organic molecules of fullerene C_{60} acceptor and zinc phthalocyanine (ZnPc) donor semiconductors. ZnPc has the first optical transition at approximately 1.9 eV, which coincides with the optimum required absorber band gap in the top cell of the tandem device. In addition, ZnPc has a high absorption coefficient of about $5{\cdot}10^4$ cm^{-1} [9,10]. C_{60} has a band gap of about 2.1–2.4 eV [11–13] showing a good transparency in a wide range of the visible spectrum and thus opening the possibility of its use as a buffer or a window layer in solar cells with $CuInSe_2$. Additionally, C_{60} is favorably used and already well investigated for the application in organic bulk heterojunction solar cells including those with ZnPc [14–17].

Our investigation is focused on the surface properties of polycrystalline $CuInSe_2$ thin films and their influence on the electronic processes taking place at the $CuInSe_2/C_{60}$ and $CuInSe_2$/ZnPc inorganic/organic interfaces. We investigate the influence of differently conditioned $CuInSe_2$ thin films (as-prepared and Na-treated) on the dissociation of the high binding energy excitons generated in organic layers. Note that in $CuIn(Ga)Se_2$ absorber layers, sodium is a standard ingredient to increase its p-type conductivity [18]. Thus, different band bendings and band alignments can be expected

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Table 1
Specification of samples and investigation methods. CIS denotes $CuInSe_2$.

1 untreated	2 Na-treated	3 analysis
CIS	CIS:Na	XPS, UPS, SPV
CIS/C_{60}	CIS:Na/C_{60}	SPV
CIS/ZnPc	CIS:Na/ZnPc	SPV

at organic/inorganic interfaces with non- and Na-treated $CuInSe_2$ surfaces. The surface chemistry and electronic properties of the $CuInSe_2$ thin films were investigated by x-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), respectively. The electronic processes at these interfaces, i.e., spectral dependent charge transfer and exciton dissociation at $CuInSe_2/C_{60}$ and $CuInSe_2$/ZnPc interfaces were investigated by transient and modulated surface photovoltage (SPV) measurements.

2. Experimental

The $CuInSe_2$ layers were deposited by a conventional three stage physical vapor deposition process (PVD) which is described elsewhere [19]. Soda lime glass coated with a sodium diffusion barrier and a 300 nm thick molybdenum layer was used as substrate. Prior to the $CuInSe_2$ deposition, half of the substrates were coated with a 12 nm thick NaF layer serving as a sodium source for the $CuInSe_2$ layer [20]. The deposited $CuInSe_2$ layers (thickness: 1.7 μm) were slightly copper poor and of p-type conductivity [19].The deposition of C_{60} (MER, purity > 99%) and ZnPc (Alfa Aesar, additionally purified in house by two step sublimation) layers (thickness: 45 nm) was performed by organic vapor phase deposition (OVPD, Aixtron) [21]. In addition, reference layers of C_{60} and ZnPc were deposited on indium tin oxide (ITO)/glass substrates. Six differently prepared $CuInSe_2$ samples were analyzed. The samples were sorted in two groups: untreated and Na-treated, as shown in Table 1. The stoichiometry, the surface work function, and position of the valence band edge were determined for bare $CuInSe_2$ samples. The SPV spectra were measured for each sample. After the deposition of $CuInSe_2$, the samples were transferred into a N_2-filled glovebox for storage. The prepared samples were transferred from the glove box to the measurement set-ups in a specially designed transfer box.

XPS spectra were recorded upon excitation using a Mg Kα radiation source (energy 1253.6 eV) without a monochromator. As reference for the peak position, the Au 4f peak was measured for a gold foil and set to 84 eV [22].Detailed spectra of the Se 3d, In 3d, Cu 2p, O 1s, C 1s and Na 1s lines were measured with a step width of 0.05 eV. The resolution was related to the band width of the excitation beam of 0.8 eV. The stoichiometry of the $CuInSe_2$ layers near the surface was obtained by using the following equation [23]:

$$N_A = I_A/\sigma_A \cdot \lambda(E_{kin}) \cdot T(E_{kin}) \cdot K, \quad (1)$$

where N_A is the amount of element A, I_A is the area of the peak of the core level A fitted by a Voigt function, σ_A is the cross section of the core level A taken from Ref. [23], $\lambda(E_{kin})$ is the mean free path of the photoelectrons (which defines the information depth ID: ID = 3 $\lambda(E_{kin})$) with the kinetic energy E_{kin} obtained by the software QUASES-IMFP-TPP2M [24], $T(E_{kin})$ is the transmission function of the analyzer, and the constant parameter K considers the photon flux of the excitation beam, the angle of the photoelectron emission, and the area of excitation.

The work function and the difference between the valence band edge and the Fermi energy of the $CuInSe_2$ layers has been determined from UPS measurements with an excitation energy of 21.2 eV (He I radiation). The Fermi level of gold was set to the binding energy of zero. The work function was obtained by subtracting the binding energy at the secondary electron cutoff from the excitation energy.

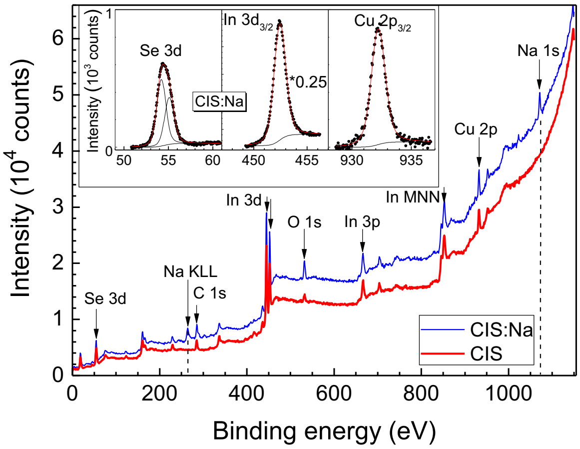

Fig. 1. Overview XPS spectra of $CuInSe_2$ thin films conditioned by sodium (CIS:Na) and without sodium (CIS). The peak at 1072 eV originates from photoelectrons of the Na 1s shell. In the inset, the core level Se $3d_{3/2}$ and $3d_{5/2}$, In $3d_{5/2}$ and Cu $2p_{3/2}$ XPS spectra and their Shirley background and Voigt fits of the CIS:Na thin films are presented.

For investigation of the charge transfer at the hybrid interface, modulated SPV spectroscopy in a fixed capacitor arrangement [25] was performed for all samples. In this configuration, the capacitor plates were given by the sample and a transparent SnO_2:F coated quartz electrode with a diameter of 6 mm. The sample and the electrode were separated by a thin mica sheet (~30 μm). The transparent electrode was connected to a high impedance (500 MHz) buffer. A quartz prism monochromator (SPM2) with a halogen lamp was used for illumination. The light was chopped at a frequency of 8 Hz. The SPV-signal was recorded by a lock-in amplifier (EG&G5210). In a simplified model, the separated charges are considered on the two plates of a parallel plate capacitor. Thereby the SPV signal can be expressed by the following equation [26]:

$$SPV = Q(t) \cdot d(t)/\varepsilon r \varepsilon 0. \quad (2)$$

Thus, the SPV signal depends on the time dependent charge $Q(t)$, the distance $d(t)$ between charges, and the dielectric constant ε_r of the sample. SPV is well suitable for our study because it is contactless, sensitive to charge distances up to a scale of few nanometers [27] and thereby sensitive to charge transfer processes and the type of charge states [28]. All SPV measurements were performed in vacuum < $1 \cdot 10^{-2}$ mbar.

3. Results and discussion

3.1. Stoichiometry of the $CuInSe_2$ surface by XPS

Fig. 1 shows the survey XPS spectra of the two $CuInSe_2$ layers with (blue line) and without (red line) sodium treatment. Compared to the untreated CIS sample, the CIS:Na sample shows two additional peaks with binding energies at 1072 eV and 266 eV (corresponding to a kinetic energy of 987 eV), which are attributed to the photoelectron signal Na 1s and Auger signal Na KLL [29], respectively, indicating the presence of sodium at the surface. The peaks In 3d (445 eV), Se 3d (55 eV), Cu 2p (933 eV), Se 3p (162 eV), Cu LMM (336 eV), In 3p (665 eV) and In MNN (853 eV) are assigned to photoelectron or Auger processes from the elements Cu, In and Se. The additional peaks O 1s (530 eV) and C 1s (285 eV) arise from oxygen and carbon containing adsorbates. The analysis of the chemical shifts in the high resolution spectra of the C 1s and O 1s peaks (not shown here) have revealed the presence of compounds with binding energies corresponding to In_2O_3, $In(OH)_3$ and Na_2CO_3 as well as other compounds with chemical bonds between oxygen and car-

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