Thin-film ZnO/CdS/CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells: Anomalous Physical Properties of the CuIn$_{1-x}$Ga$_x$Se$_2$ Absorber

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Thin-film ZnO/CdS/CuIn$_{1-x}$Ga$_x$Se$_2$ solar cells are manufactured with ~20% solar-cell conversion efficiency. The CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) absorber exhibits rather different physical properties compared with conventional semiconductors (e.g. Si, GaAs and ZnSe). For instance, (*i*) the valence-band maximum in CIGS consists of cation-*d*–anion-*p* hybridized states. (*ii*) Cation vacancies have low formation energies and high mobility at room temperature. (*iii*) The most stable surface of CuIn$_{1-x}$Ga$_x$Se$_2$ is the reconstructed, and otherwise polar, (112) surface. (*iv*) Solar cells with absorbers containing grain-boundaries outperform cells with crystalline absorbers. In this work, the fundamental physical properties of CIGS, like the electronic structure, the defect formation energies, as well as surface properties are discussed from a theoretical perspective.

Keywords: Solar cells; Photovoltaic; Absorbers; CuInSe$_2$; Surface; Interface; Defects

I. INTRODUCTION

Thin-film photovoltaic (PV) technologies (or "solar cells") are being developed by the means of substantially reducing the cost of the PV systems, owing to reducing material, growth and processing energy, and handling [1].

By alloying the group I-III-VI$_2$ chalcopyrites CuInSe$_2$ (CIS) and CuGaSe$_2$ (CGS) one can tune the fundamental band-gap energy of CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) from 1.0 to 1.7 eV, varying the Ga content x = [Ga]/([Ga]+1[In]) from 0 to 1. Today's high-quality thin-film ZnO/CdS/CIGS solar cells have the world record of the solar-cell conversion efficiency of ~20% [2], using Cu-poor ([Cu] $\approx$ 22.5–24.5%) high off-stoichiometric polycrystalline CIGS absorber with ~1-2μm size grains with Na-rich and extremely Cu-poor grain interfaces. The best PV cells have a Ga content of ~ 28% (i.e., x = 0.28), but the band-gap energy of the CIGS alloys suggests that the optimum cell performance should be obtained with x = 0.5–0.7. The PV cell comprises an absorber (e.g. CIGS) that converts light to electron-hole pairs, and a built-in electrical potential at the CdS/CIGS interface that separates the photo-generated electrons and holes. The built-in electric potential is the key factor of the open-circuit voltage V_{oc} of the device. The CdS buffer is *n*-type doped, and the CIGS absorber is grown *p*-type with energetically higher valence-band (VB) and conduction-band (CB) edges, denoted E_v and E_c. For best PV cell performance, the *pn*-junction should be buried inside the CIGS absorber [1].

Several anomalous physical properties of the CIGS absorber are not fully understood [1]. For instance: (*i*) experiments reveal that cell efficiency does not increase in the Ga-rich composition regime ($x > 0.30$), although the increased band gap should improve V_{oc}. The reason for this limitation of cell efficiency is not known. (*ii*) Whereas CIS can be grown *n*-type under Se-poor/In-rich conditions, CGS seems to resist all kinds of *n*-type character, both from intrinsic and extrinsic doping. (*iii*) It is not clear why introduction of Na improves the solar cells. (*iv*) Polycrystalline materials with grain boundaries (GB) and grain interior (GI) outperform the crystalline films in a CIGS-based PV device, which is in contrast to conventional semiconductors.

In this work, the electronic structure of bulk and reconstructed (112) surfaces of CIS and CGS are discussed from a theoretical perspective [3-5]. The impacts due to doping and surface reconstruction on the PV device performance are discussed. The first-principles calculations are based on the local density approximation (LDA) within the density functional theory (DFT) with an on-site Coulomb self-interaction-like correction (SIC) in the LDA+U$^{\text{SIC}}$ approach [6]. The defect transition and formation energies are obtained from total energies $E(\alpha,q)$ of defect α in charge state q, the chemical potentials μ_α, and defect formation energies: $\Delta H_f(\alpha,q) = E(\alpha,q) - E(0,0) + \Sigma_\alpha n_\alpha \mu_\alpha + q(E_v + E_F)$ and the Boltzmann statistics for the defect concentration: $[N(\alpha,q)] = \exp(-\Delta H_f(\alpha,q)/k_B T)$.

II. ELECTRONIC STRUCTURE

The LDA+U$^{\text{SIC}}$ calculations of the electronic structures [Fig. 1(a)] and the density-of-states (DOS), see Fig. 2 in next section, reveal that the VB states of CIGS is composed primarily of Cu 3*d* orbitals hybridized with Se 4*p* orbitals [Fig. 1(b)]. The lowest CB states consist mainly of In-*s* and Se-*p*. This is *a most significant difference* between the I-III-VI$_2$ structure compared to diamond group IV, and zinc-blende II-VI and III-VI semiconductors, which have *sp*-hybridized bonds [Fig. 1(b)]. The electronic VB structure of CIGS has been confirmed by x-ray photoelectron spectroscopy [7]. The Cu-*d*–Se-p hybridization forms an antibonding-like VB maximum which implies weak Cu–Se bonds. This is the origin to the low formation energy of Cu vacancies: $\Delta H_f(V_{\text{Cu}}^0) \sim 0.8 + \Delta\mu_{\text{Cu}}$ eV in CIS, and $\sim 0.6 + \Delta\mu_{\text{Cu}}$ eV in CGS [5] and antisites: $\Delta H_f(\text{III}_{\text{Cu}}^0) \sim 0.90 - \Delta\mu_{\text{In}} + \Delta\mu_{\text{Cu}}$ eV, and $\sim 2.43 - \Delta\mu_{\text{Ga}} + \Delta\mu_{\text{Cu}}$ eV [5]. Therefore, as-grown CIGS thin films are often extremely Cu-poor [1,2,8].

LDA has been successful to describe electronic structures and total energies of various condensed matter structures, but it is well known that DFT/LDA underestimates the fundamental band-gap energy E_g of semiconductors by ~50%.

This failure has been attributed to missing the discontinuity in the exchange-correlation potential and a self-interaction error within the LDA. For CIS, the calculated LDA band-gap energy is zero, partly due to the repulsive Cu-d–Se-p interaction which pushes the antibonding $p - d$ VB states to higher energies, yielding somewhat smaller band gap. LDA fails to accurately describe this valence d-state localization in ZnO [9], where the LDA cation-anion $3d2p$-hybridization disagrees with soft x-ray emission spectra. This shortcoming was corrected by the LDA+U^{SIC} approach [6,9]:

$$V(LDA + U^{SIC}) = V(LDA) + \frac{U_l}{2}\left(1 - 2\sum_{m,\sigma} n_{m,\sigma}\right),$$

where $n_{m,\sigma}$ is the orbital occupancy of the l-orbital in question (i.e., $s-$, $p-$, and $d-$states) and σ is the spin component. The orbital dependency of the LDA+U^{SIC} potential has a capacity to be more asymmetric than LDA. Details of the computational methods can be found in Refs. 3-6, 9 and 10. LDA without SIC produces a potential of CIS with the lowest CB state $\sim$0.3 eV below the Γ-point VB maximum. Applying U_d(Cu) = 6 eV, the Cu-d valence electrons become more localized which reduces the pd-repulsion, and thereby lower the VB maximum. As a consequence the lowest CM state increases above VB maximum ($E_g \sim 0.05$ eV). By applying also U_s(Se) = 6 eV the band-gap energy of CIS opens up to E_g(LDA+U^{SIC}) = 0.9 eV [Fig. 1(a)]. Using the same SIC parameters also for CGS yields E_g(LDA+U^{SIC}) = 1.6 eV. Experimental values are 1.0 and 1.7 eV for CIS and CGS, respectively [1]. Thus, the band-gap energy of both CIS and CGS can be obtained from the similar SIC within LDA+U^{SIC}. We have found [6] that effective masses and optical properties are somewhat overcompensated by fitting the LDA+U^{SIC} band-gap energy to the exact experimental value. This can be a side effect of the energy-independent LDA+U^{SIC} approach, but it can also be an indication that one may not be able to extract the experimental band-gap energy from the single-particle DFT/Kohn-Sham eigenvalues. We have therefore chosen to fit the SIC band-gap energy to $\sim$0.1 eV smaller than the experimental value.

III.   CU-VACANCIES IN BULK CIGS

The CIGS absorber in the ZnO/CdS/CIGS solar cells should have p-type character deep inside the CIGS absorber, and n-type character (or at least, much less p-type) closer to the CdS/CIGS interface [1]. Both intrinsic bulk CIS and CGS can easily be grown p-type under Cu-poor conditions by an access of V_{Cu}^- which has low formation energy. However, it has been puzzling that whereas polycrystalline CIS can be grown lightly n-type doped under Se-poor/In-rich conditions, CGS seems to resist all kinds of n-type character, both from intrinsic and extrinsic doping.

We have in Ref. 5 calculated the ionization energy of various extrinsic divalent cation donors: Mg_{Cu}, Zn_{Cu}, Cd_{Cu}.
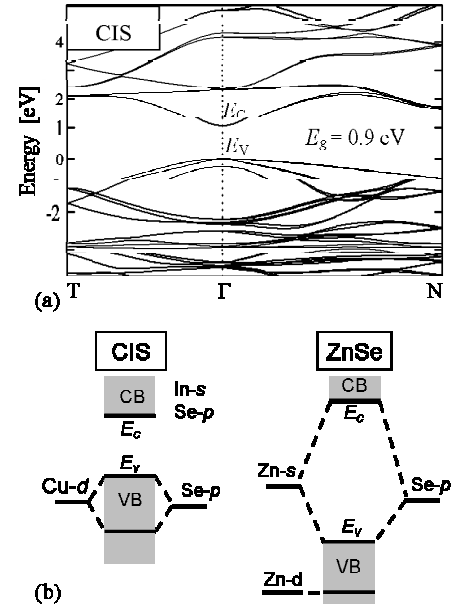

FIG. 1: (a) Electronic structure of CIS. (b) Schematic picture of VB and CB states in CIS, and in conventional sp-hybridized semiconductors (e.g., III-Vs and II-VIs).

The ionization energies for Cd_{Cu} is 0.05$\pm$0.05 eV in CIS and 0.12$\pm$0.06 eV in CGS, with relatively low formation energy, indicating that both CIS and CGS should be able to become n-type. (The error bar accounts multipole correction [5].) However, since CIGS has two different cation types (group-I and group III), the group II dopant will prefer to occupy the group III-site (creating II_{III} acceptors) if the Fermi energy E_F increase above mid-gap energy $E_g/2$ (as in n-type materials) and thereby compensate the n-type character [5]. Thus, group-II dopants are not efficient as donors in CIGS. Instead, one may use group-VII halogens (Cl, Br, and I) in order to form VII_{Se} donors. Also here the calculations yield relatively shallow donors (0.09 $\pm$0.04 eV for Cl_{Se} in CIS and 0.13$\pm$0.04 eV in CGS) with low formation energies [5]. Thus, neither the ionization energies nor the formation energies of the donors can explain the puzzling fact that it is difficult to n-type dope CIS, and impossible (to date, at least) to n-type dope CGS.

Instead, one needs to fully understand the behavior of CIGS under various growth conditions, especially the effects of native (neutral and charged) defects. Our calculations show [5] that the low formation energy of charged Cu vacancies (V_{Cu}^-) prevents E_F to increase above the mid-gap energy in CGS. For higher energies, the exothermic behavior of V_{Cu} [i.e., $\Delta H_f(V_{Cu}^-) = 0$] in CGS compensates all kinds of n-type doping, no matter what donor type is supplied. This behavior cannot be overcome under equilibrium conditions. Even with the Cu chemical potential $\Delta\mu_{Cu}$= 0 eV (i.e., the best conditions for achieving n-type), the formation energy of V_{Cu} becomes exothermic at $E_F = E_c - 0.09$ eV in CIS and $E_c - 0.92$ eV in CGS. This explains the experimental findings that CGS cannot be n-type. It also indicates that the n-type inversion layer at the CdS/CIGS interface will be suppressed by spontaneously

formation of V_{Cu}^- when the Ga-content is increased in CIGS. Thus, *Ga-rich CIGS may not be the proper wide-gap alloy for high-efficient solar cells.*

IV. CU-VACANCIES AT CIGS SURFACES

Unlike conventional binary semiconductors (e.g., GaAs), the most stable CIGS surfaces are the polar $(112)_{metal}$ and $(\bar{1}\bar{1}\bar{2})_{Se}$[11]. These polar surfaces are reconstructed via formation of V_{Cu} [at the (112) surface] or In_{Cu} [at the $(\bar{1}\bar{1}\bar{2})$ surface] to compensate the surface dipole. The relatively low energies for the reconstructions in CIGS are explained by the low formation energy of V_{Cu}.

Our model of GBs in CIGS is based on ideal surface-like behaviour [3,4]. In reality, one can separate between two types of GBs, one which has *abrupt change* in its crystallographic structure (or in the chemical composition), and the other which has a Cu-poor *composition gradient* over a wider space region. The former is expected to exist mainly deep inside the CIGS absorber [8], and the latter to exist more likely in the space-charge region (SCR) near the CdS/CIGS interface [8] where as-grown CIGS often show an additional strong Cu-poor gradient. Both types of GBs involve Cu vacancies, and we have in Refs. 3 and 4 modelled both (112) and $(\bar{1}\bar{1}\bar{2})$ surfaces/GBs as well as dislocations containing $(2V_{Cu}+In_{Cu})^0$ and Na_{Cu} defects. The calculations of these strongly Cu-poor structures show similar band offsets [3,4], and here we therefore present only the results for CIS and CGS (112) surfaces [Fig. 2].

Upper panel in Fig. 2 show the DOS of bulk/GI in CIS and CGS. Lower panels show the DOS at the (112) surface/GB. The calculations reveal that the VB maximum is depressed at the surfaces. The reason is that the surface lacks Cu-*d* electrons, and the repulsive Cu-*d*–Se-*p* repulsion is thereby not present at the surface, and thus the VB maximum is lowered (by ~0.2 eV in CIS and ~0.6 eV in CGS). This lowering of the VB maximum implies *hole barriers* at the surface/GB which are *charge neutral*. Moreover, for CGS (but not for CIS) the CB minimum is lowered (~0.5 eV) at the surface/GB, creating an *electron trap* there.

The electronic structure of the surface/GB VB and CB edges has a direct affect on the carrier transport in the polycrystalline CIGS-based solar cells. In Figs. 3(a) and (b), we show schematically the band profile of GI/GB/GI structure in CIS and CGS, which is compared to conventional semiconductors with positively charged GB defects [Fig. 3(c)], which is the normal origin for band-bending at GBs. In CIS, the GB barriers affect *only one carrier type* (the holes, which are majority carriers). The electrons can move freely in the absorber whereas the holes cannot move to the GB region. This separation of electrons and holes can (at least partly) explain [3,4] the puzzle of the superiority of polycrystalline CIGS solar cells over their crystalline counterpart. Notice, the *charge-neutral* GBs *do not imply additional recombination channels* in the band-gap region. However, at very *abrupt* GI/GB/GI
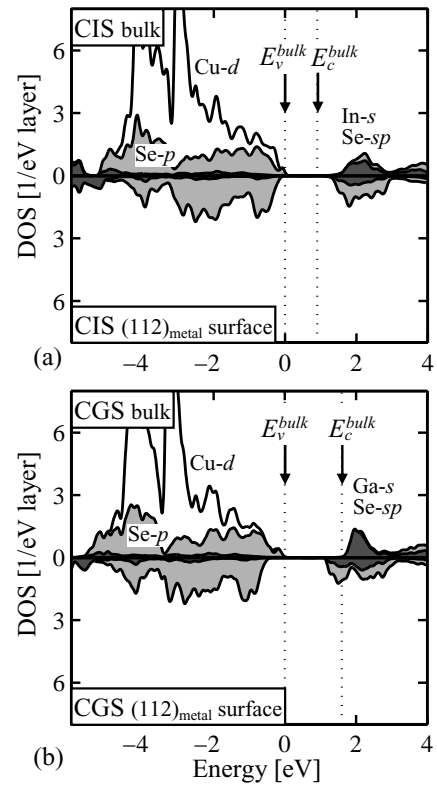

FIG. 2: Atomic resolved DOS of (a) CIS and (b) CGS. Upper panels show bulk/GI DOS and lower panels show DOS of reconstructed (112) surfaces/GBs. Black, grey, and white areas show s-, p-, and d-character, respectively.
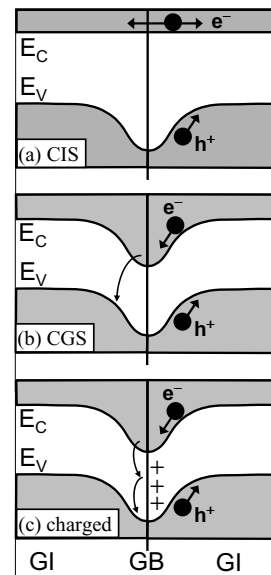

FIG. 3: Schematic picture of GI/GB/GI band profile in (a) CIS, (b) CGS with neutral reconstructed GBs, and in (c) conventional semiconductor with positively charged GBs.

dislocations, tunneling assisted GI→GB→GI transport can occur (just like in conventional semiconductors), restricted by the barrier width and depth.

Also in CGS the electrons and holes are separated due to carrier barriers. However, since the electrons (minority carriers) in CGS can be trapped in the GB region, additional recombinations may occur from the GB CB-minimum to the GI VB-maximum if the GB/GI interface is sufficiently abrupt. Thus, Ga incorporation can limit the cell performance.

In the SCR near the CdS/CIGS interface, the CB profile E_c restricts the open circuit voltage V_{oc} and thereby the cell performance. In CIS, the CB at the GB is not affected, thus not limiting V_{oc}. However, in CGS the strong downward band bending of E_c at the GB will affect V_{oc} negatively.

V. CONCLUSION

V_{Cu} and III_{Cu} are important native defects in CIGS due to their low formation energies. The origin for that is the Cu-d like VB states which form weak Cu-d–Se-p bonds. Therefore, as-grown CIGS is often Cu-poor. In bulk CIGS, the low formation energy of V_{Cu}^- limits the possibility of achieving electronic n-type character, especially in Ga-rich CIGS. At surfaces/GBs, the reconstructed $(112)_{metal}$ and $(\bar{1}\bar{1}\bar{2})_{Se}$ are Cu-poor which compensates the dipoles of these nominally (unreconstructed) polar surfaces. The lack of Cu d-states at the GBs creates hole barriers there. In contrast to CIS, the $(112)_{metal}$ surface of CGS has also a strong lowering of the CB which can limit V_{oc}, and result in recombinations at abrupt GB/GI interfaces.

Acknowledgement

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