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Limitation of the Open-Circuit Voltage Due to Metastable Intrinsic Defects in $Cu(In,Ga)Se_2$ and Strategies to Avoid These Defects

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LIMITATION OF THE OPEN-CIRCUIT VOLTAGE DUE TO METASTABLE INTRINSIC DEFECTS IN Cu(In,Ga)Se_2 AND STRATEGIES TO AVOID THESE DEFECTS

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ABSTRACT

Using first-principles defect theory, we investigate the role of intrinsic point defects in the limitation of the open-circuit voltage (V_{OC}) in Cu(In,Ga)Se_2 solar cells. We find that the intrinsic donors In_{Cu} (In-on-Cu antisite defect) and V_{Se} (Selenium vacancy) and their defect complexes with V_{Cu} (Cu vacancies) represent two independent mechanisms that are expected to cause saturation of V_{OC} around 1 eV, when the absorber band gap is increased towards Ga-rich compositions. Strategies to avoid these sources of V_{OC} limitation are discussed.

$CuIn_{1-x}Ga_xSe_2$ (CIGS) alloys cover a range of the fundamental band gap between 1.0 eV for pure $CuInSe_2$ (CIS) to 1.7 eV for pure $CuGaSe_2$ (CGS). Yet, the open-circuit voltage does not follow in proportion to the band gap increase [1], and reaches a maximum at 0.9 eV for pure $CuGaSe_2$ [2], hardly more that half the band gap. Overcoming the present limitations of V_{OC} is not only desired in order to achieve higher efficiencies of single-junction CIGS cells, but also it is a prerequisite to achieve any additional gain from a tandem structure, which in principle could considerably improve the efficiency of solar-cells within thin-film technology [3]. A fundamental understanding of the sources of V_{OC} limitation is essential to develop strategies to overcome the present bottlenecks.

Recent theoretical studies [4,5] on the behavior of the Se vacancy in $CuInSe_2$ and $CuGaSe_2$ revealed that the prominent light- and bias-induced metastability effects observed in Cu(In,Ga)Se_2 absorbers can be explained by the properties of the V_{Se}-V_{Cu} divacancy complex. The metastability occurs due to the existence of two different atomic configurations which are separated by energy barriers. Subsequent experimental studies [6,7,8,9] have confirmed this model, and provide evidence that this defect strongly affects the behavior of actual solar cell devices. Very recently, we predicted that also the intrinsic In_{Cu} and Ga_{Cu} donors exhibit two different stable atomic configurations [10], and can account for a specific type of metastability, i.e., the "red-on-bias" metastability [11], whose atomistic origin was not determined before.

In the present work, we analyze the implications of these metastable defects for the limitation of V_{OC}, and discuss how the densities of these defects could be minimized. First, we briefly review how the reconfiguration of the atomic structure affects the electronic properties of the metastable defect (for details about the respective atomic configurations, please see Refs. [5,10]).

(i) *The V_{Se}-V_{Cu} divacancy complex (Fig. 1).* For Fermi levels below E_F^{re} = E_{VBM} + 0.2 eV in CIS (0.3 eV in CGS), the complex acts as a compensating donor, and introduces a defect level (*a*) at 1.6 eV (1.9 eV in CGS) above the valence band maximum (VBM), i.e. inside the conduction band (Fig. 1). When the Fermi level rises above E_F^{re}, the complex undergoes an atomic reconfiguration, acting now as a shallow acceptor, but – importantly in view of the V_{OC} limitation (see below) – it also has a deep defect state (*b*) at 1.0 eV (CIS) and 0.9 eV (CGS) above the VBM in this configuration. Since, the energies of the (*a*,*b*) defect levels (with respect to the VBM) are very similar in CIS and CGS, the main effect of Ga-alloying into CIS is to change the positions of these levels relative to the conduction band minimum (CBM). Thus, for a typical CIGS composition $x \approx 0.3$ with a band gap of ~1.2 eV, Fig. 1 shows schematically the position of the critical Fermi level E_F^{re} where the atomic reconfiguration takes place, and the defects levels (*a*,*b*) in the respective configurations.

(ii) *The In_{Cu} (Ga_{Cu}) antisite donor (Fig. 2).* The intrinsic In_{Cu} and Ga_{Cu} donors introduce a defect level around 1.4 eV above the VBM, i.e. inside the conduction band of CIGS. If the Fermi level rises higher than E_F^{re} = E_{VBM} + 0.9 eV, the donors relax off their substitutional configuration, and capture free-electrons into a deep level located ~0.5 eV above the VBM. This transition is similar as in

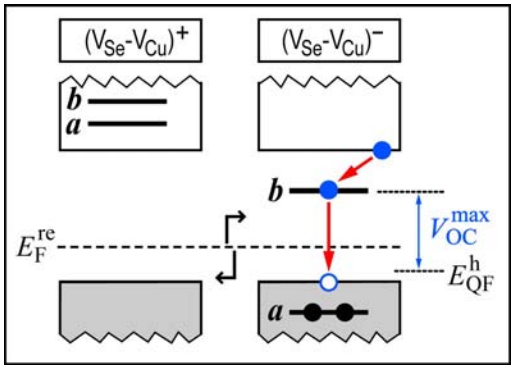

Fig 1. Defect levels (*a*,*b*) in the donor (+) and in the acceptor (–) configuration of the V_{Se}-V_{Cu} divacancy complex, being stable for $E_F > E_F^{re}$ and for $E_F < E_F^{re}$, respectively. The recombination of photo-excited electrons (blue) through the deep acceptor level (*b*) limits V_{OC}.

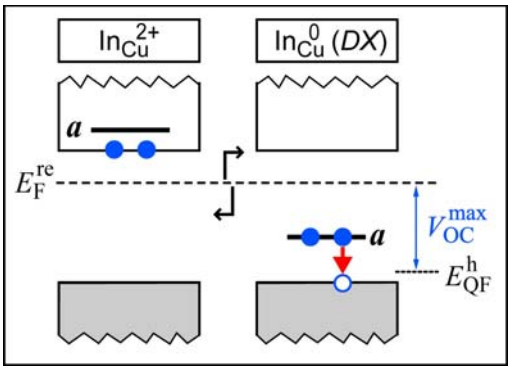

Fig 2. Defect level (*a*) of the In_{Cu} antisite donor in the shallow substitutional (2+) and the deep *DX*-like (0) configuration. The capture of photo-excited electrons (blue) into the deep *DX* level (*a*) and subsequent recombination with photo-excited holes limits V_{OC} .

case of the well-known *DX* centers in binary semiconductors [12,13]. The important difference here is that in CIGS, such deep levels can occur intrinsically, without any extrinsic dopant atoms [10]. The mechanism to form a deep state still exists when In_{Cu} or Ga_{Cu} donors form defect pairs with V_{Cu}, e.g., the (In_{Cu}-$2V_{Cu}$) complex. In this case, E_F^{re} moves to somewhat higher energies [10].

Limitation of V_{OC} due to metastable defects. (i) In case of the V_{Se}-V_{Cu} divacancy complex, the deep gap state occurs only in the acceptor-configuration which is stable for equilibrium Fermi levels above E_F^{re}, i.e., within a large fraction of the space-charge-region adjacent to the heterojunction (under equilibrium dark conditions). Far away from the junction, the donor-configuration is stable, which does not introduce any detrimental deep gap states (Fig. 1). When, under solar illumination, the quasi-Fermi level for electrons E_{QF}^{e} raises towards the energy of the deep gap level, it becomes thermodynamically favorable for the electrons to occupy the deep level instead to move in the conduction band, i.e., electrons become trapped, and recombine with photo-excited holes (see Fig. 1). Thus, the E_{QF}^{e} is pinned to deep acceptor level around 1.0 eV above the VBM [5]. As V_{OC} equals the difference $E_{QF}^{e} - E_{QF}^{h}$ between the quasi-Fermi levels for electrons and holes, this pinning implies a limitation of V_{OC} below 1.0 eV.

(ii) In case of the In_{Cu} and Ga_{Cu} antisite donors and their defect pairs with V_{Cu}, the mechanism of V_{OC} limitation is different from that of the divacancy, in that it is here the activated transition itself (associated with the atomic reconfiguration), occurring at $E_{QF}^{e} = E_F^{re}$, that leads to pinning of E_{QF}^{e}: When E_{QF}^{e} raises to about 0.9 - 1.3 eV above the VBM (the range is due to the different In_{Cu}/Ga_{Cu} + V_{Cu} defect pairs [10]), photo-excited electrons are captured into the defect state close above the CBM (see Fig. 2), which after the structural reconfiguration is located deep in the gap, closer to the VBM. Since the energy barrier for electron re-emission is large (about 0.6 eV [10,11]), the trapped electrons will finally recombine with photo-excited holes (Fig. 2).

How to avoid the V_{OC} limiting defects. The formation of the V_{OC} limiting defects during crystal growth is determined by their formation energies, which depend on the thermodynamic conditions during growth. Specifically, the defect formation energy is obtained (see, e.g., Ref. [14]) from first-principles calculations of supercell energies as

$$\Delta H_{D,q} = (E_{D,q} - E_H) + \sum_\alpha n_\alpha(\mu_\alpha^{elem} + \Delta\mu_\alpha) + qE_F$$

where $E_{D,q}$ and E_H are supercell energies with and without the defect in charge state q. Here $\mu_\alpha = \mu_\alpha^{elem} + \Delta\mu_\alpha$ is the chemical potential of the atom α added ($n_\alpha = -1$) or removed ($n_\alpha = +1$) from the crystal, given with respect to the energy μ_α^{elem} of the elemental phase, and E_F is the Fermi energy.

The chemical potentials of the elements, describing the growth conditions, have to fulfill a number of requirements: First, according to Gibb's phase rule, the sum of the $\Delta\mu_\alpha$ of the host atoms (e.g., Cu, In, and 2×Se for CIS) has to equal the heat of formation of the compound, e.g., $\Delta\mu_{Cu} + \Delta\mu_{In} + 2\,\Delta\mu_{Se} = \Delta H_f$(CIS). Second, additional constraints are imposed by formation of other phases. For example, if $\Delta\mu_{In} + \Delta\mu_{Se} > \Delta H_f$(InSe), InSe would form instead of CIS. Thus, only the shaded area in the phase diagram shown in Fig. 3 corresponds to growth conditions under which $CuInSe_2$ can be synthesized. Note that the respective diagram for CGS is qualitatively very similar (when considering the respective Ga compounds, like Ga_2Se_3). While it is difficult in experiment to determine exactly the chemical potentials under general conditions, the existence of secondary phases, e.g., Cu_3Se_2 or the Cu-poor ordered vacancy compound $CuIn_5Se_2$, indicates that an equilibrium with these phases was established during crystal growth, and that the present growth conditions correspond to the respective lines in Fig. 3.

Shown in the phase diagram (Fig. 3) are arrows indicating the direction under which the formation energy of the V_{OC} limiting defects increases, i.e., under which the respective defect densities decrease. We see that the

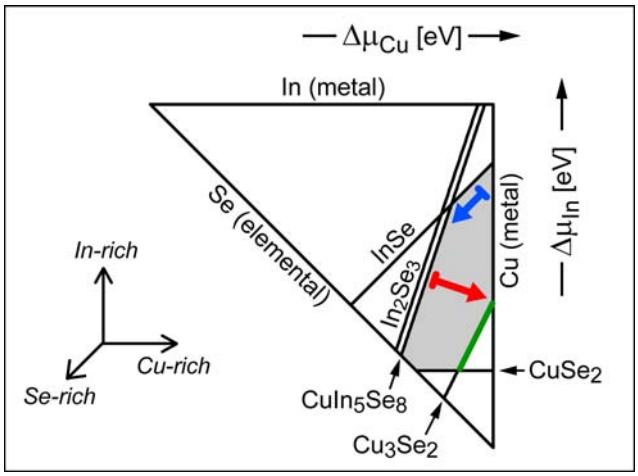

Fig 3. Phase diagram of $CuInSe_2$ (shaded area), elemental and secondary compound phases are indicated. The color arrows indicate the direction of growth conditions (chemical potentials) in which the formation energy of V_{OC} limiting defects increases (blue: V_{Se}; red: In_{Cu}). The green line indicates phase equilibrium between CIS and Cu_3Se_2.

optimal growth conditions are described as "Cu-rich" and "Se-rich". Relatively low densities of the V_{OC} limiting defects are expected, e.g., when phase equilibrium exists between CIGS and Cu_3Se_2 (green line in Fig. 3). We emphasize that these conditions are very different from those generally used for high-efficiency solar cells which are generally grown with considerable Cu-deficiency. Keeping in mind that the defects discussed here are relatively benign as long as the quasi Fermi level for electrons does not rise higher than 1 eV above the VBM, the growth parameters for present high-efficiency CIGS cells are apparently a trade-off between this V_{OC} limitation and other aspects, such as, e.g., the type inversion near the window/absorber interface which necessitates Se-poor conditions [15,16]. Thus, based on the present theoretical predictions, we suggest that any attempt to overcome the present limitations of V_{OC} will require a rather dramatic change in the growth parameters. At the same time, any other sources of V_{OC} limitation that may exist in parallel need to be addressed simultaneously. For example, CIGS alloys with high Ga-contents are expected to have a considerable negative band offset ("cliff") at the interface with the CdS buffer [17]. Since E_{QF}^{e} can not rise higher than the CBM of the buffer, such a cliff can also limit V_{OC}, even when the defects discussed here are minimized.

Conclusions. Theory predicts that intrinsic donors In_{Cu}, Ga_{Cu}, and V_{Se}, as well as their complexes with V_{Cu} limit the open-circuit voltage in CIGS solar cells. Minimizing the densities of these defects would require growth parameters that differ strongly from those currently used.

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