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Stephan Lany and Alex Zunger[a]
National Renewable Energy Laboratory, Golden, Colorado 80401

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exhibit metastable behavior that can lead to persistent photoconductivity. In Ref. 20 we discussed in detail the general defect physics that lead to metastability and PPC

dicating that meta table beha io of CIGS ola cell i ac-
companied b a potentiall det imental ecombination cente .

i needed to co ect fo the band- lling effect (Mo - B tein hift) e . lting f om the high defect den it of the act al calc lation. D e to the mall effecti e elect on ma in CIS and CGS, m_e^*/m_e=0.09 (Ref. 36), the e band- lling effect a e mo t t ongl p ono nced fo dono . Th , the e pecti e co ection fo ΔH of the int in ic In_C^0 do ble dono in CIS i a la ge a 1.5 eV. D e to the la ge effecti e hole ma , m_h^*/m_e=0.8 (Ref . 37 and 38) in CIS, the band- lling co ection fo the ingle-accepto tate of V_C^0 and of the $(V_{Se}\text{-}V_C)^0$ complex. (in the accepto con g ation) i onl abo t 0.1 eV. Note that the e band- lling effect o iginate f om the . e of . nite- i e . pe cell and not f om de - ciencie of the LDA.

(iv) Potential alignment correction for charged impurities. The . pe cell fo mali m de c ibe a pe iodic, in nite

band minim m,[42] the ange of po ible Fe mi le el in Fig. 2(a) (left) i ex.tended abo e the CBM of p e CIS, p to $E_F=E_V+1.25$ eV, app ox.imatel co e ponding to the CBM of C In$_{1-x}$Ga$_x$Se$_2$ allo ith compo ition p to $x \approx 0.4$, a ed fo high ef cienc CIGS ola cell . We ee in Fig. 2(a) (left) that in CIS, the *isolated* V_{Se} ha a deep, negati e-*U*-like, do ble dono t an ition $\varepsilon(2+/0)=E_v+0.05$ eV clo e to the VBM, and deep accepto t an ition high in the gap, i.e., $\varepsilon(0/)=E_v+0.85$ eV and $\varepsilon(/2)=E_v+1.14$ eV.[39] The e deep accepto le el e lt f om the occ pation of the antibonding *b* le el (Fig. 1), leading to the fo mation of V_{Se} (a^2b^1) and V_{Se}^2 (a^2b^2). Th , the i olated V_{Se} ex.hibit ampho-te ic beha io ha ing both deep dono and deep accepto le el , he e the al o de of the dono and accepto le el i in e ted, i.e., the accepto t an ition occ highe in the

shown in Fig. 4 (Ref. 44) for the acceptor configuration with the short In-In distance, along with the electronic orbital (isosurface plot of the wave function square) of the a and b defect level, which, in this configuration, lie below the VBM and in the band gap, respectively (Table I). The bonding and the antibonding character of the a and the b level, respectively, are clearly visible in Fig. 4.

The deep $\varepsilon(-/2-)$ and $\varepsilon(2-/3-)$ acceptor transition of the complex (Table II), which result from the occupation of the antibonding b level, occur at somewhat higher energy [Fig. 2(a)] compared to the respective $\varepsilon(0/-)$ and $\varepsilon(-/2-)$ level of the isolated V_{Se}. The position of the deep acceptor level around 1 eV above the VBM indicates that in a CIGS solar cell, the defect level can only be occupied near close to the CdS/CIGS heterojunction, where the Fermi level can rise to such high energies. Even though the occupation of the deep level is accompanied by considerable atomic relaxation, no energy barrier is involved. Consequently, the deep acceptor level are effectively instantaneous. Note, however, that the deep level appearance only in the acceptor configuration (short III-III distance), where the b level is located inside the band gap [Fig. 3(a)]. In contrast, no such deep transition level exists along the complex remains in the donor configuration (large III-III distance), because the b level is pushed outside the band gap, i.e., above the CBM, in this configuration [Fig. 3(a)].

In the acceptor-configuration of (V_{Se}-V_{Cu}), there exists additional optical transitions caused by the b level in the gap: The optical absorption energies due to photoexcitation of electrons from the VBM into the b level ($a^2b^0 \rightarrow a^2b^1+h$), and the photoluminescence energies due to recombination of electrons in the b level with holes at the VBM ($a^2b^1+h \rightarrow a^2b^0$), are given in Table II. Later in Sec. V, we compare these optical energies to experimentally observed absorption and PL energies. Unlike the $\varepsilon(-/2-)$ and $\varepsilon(2-/3-)$ acceptor transitions which are caused by occupation of a gap state, i.e., the b level, the activated $\varepsilon(+/0)$ transition inside the gap marks the demarkation the Fermi level at which the the model namically stable state of (V_{Se}-V_{Cu}) changes from the donor to the acceptor configuration. The single-particle state being occupied during this transition, i.e., the a level, is resonant inside the band gap before and well after the transition [Fig. 3(a)] and, therefore, does not cause an optical transition level within the gap.

Configuration coordinate model for the conversion between the donor and acceptor configurations. Figure 3(b) shows the calculated configuration coordinate diagram for the (V_{Se}-V_{Cu}) complex in CIS. Here, the distance $d_{In,In}$ between the In atoms serves as the reaction coordinate. As shown in Fig. 2(a), the (V_{Se}-V_{Cu})$^+$ state in the donor configuration with large $d_{In,In}$ [1 in Fig. 3(b)] has the lowest energy in p-type CIGS, where the Fermi level is close to the VBM.3.5 /F8 1 Tf

ι on $(a^1 \rightarrow a^2 + h)$, leading ιo a hole in ιhe hallo$_{\nabla}$ accepιo
le el (E_a in Fig. 3

o dinate diag am fo CGS [Fig. 5(b)]. Con e . ent l , the *n*-cond cti e meta table dono tate that ex.i t in CIS fo E_F □ □(+/) [da hed g een line in Fig. 2(a), CIS] doe not ex.i t in CGS [cf. Fig. 2(a), CGS]. In CGS, once E_F i e abo e the □(+/) t an ition le el, the po iti el cha ged complex. ill con e t ia E . (2) into the (V_{Se}-V_C) accepto con g ation, e en at lo tempe at e. Th , the dono con- g ation ith la ge Ga. Ga di tance ex.i t in CGS onl a a *compensating* dono fo E_F □ (□(+/). In cont a t, the meta- table hallo accepto tate [ed da hed line in Fig. 2(a)] ex.i t in CGS imila l like in lo e -gap CIS (cf. E_a in Table II). The onl diffe ence i the light l lo e ene g ba ie a ociated ith the hole capt e p oce of E . (3) and the ome hat la ge ene g ba ie fo hole emi ion b t an i- tion E . (3) in the back a d di ection, i.e., □E_2=0.28 eV and □E_3=0.92 eV in CGS [cf. Fig. 5(b)].

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(***V*** ***-V***)

Distribution between the donor/acceptor configurations of (V_{Se}-V_{Cu})*, determined from the Fermi level in thermodynamic equilibrium*. In o de to a e the change in the net accepto den it . pon ill mination o e e e-bia t eatment, e need to dete mine the di t ib tion bet een the dono and accepto con g ation of the (V_{Se}-V_C) complex. befo e the t eatment, i.e., in the ela.ed tate at e o bia . Since the e . ilib i m table cha ge tate of (V_{Se}-V_C) depend on the local Fe mi le el [cf. Fig. 2(a)], it ill change a a f nction of di tance *d* f om the CdS/CIGS hete oj nction in a ola

Dynamics of donor/acceptor conversion. The e ilib- i m di t ib tion bet een the dono and the accepto con- g ation ho ld be ega ded a a tead tate it ation ith e pect to the fo a d and back a d di ection of the t an i- tion E . (2) and (3). We no add e the t an ition d nam- ic , i.e., the t an ition ate of E . (2) and (3), ith hich a ne e ilib i m bet een the dono and accepto con g a- tion of (V_{Se}-V_C) i e tabli hed, once an ex.te nal pe t. ba- tion i applied, e.g., ill mination o bia . If the ex.te nal pe - t. bation c eate an ex.ce of f ee elect on , the complex. ill eact to thi pe t. bation b the elect on capt e, E . (2) in the fo a d di ection, and the con e ion into the accepto tate, the eb ed cing the elect on ex.ce acco ding to Le Chatelie ' p inciple. Simila l , if the ex.te nal pe t. bation

e pond to the dono -to-accepto con e ion of $(V_{Se}\text{-}V_C)$ d e to the capt e, E . (2), of photoex cited elect on . Thi p o-ce i de c ibed b the e ence **1**→**2**→**3**→**4** in the CCD of Fig . 3(b) and 5(b), and can take place onl he e the complex ex i ted, at lea t pa tl , a $(V_{Se}\text{-}V_C)^+$

diate distance from the junction drive the electron capture, Eq. (2), in the forward direction. Taking $n=10^{7}$ cm^{-3},[48] we find from Eq. (4) a time constant $\tau_{ec}=10^{-2}$ s at $T=300$ K. Second, due to hole depletion, the forward direction of the hole capture, Eq. (3), is suppressed, which drives Eq. (3) in the backward direction, i.e., hole emission, for which we find the time constant $\tau_{he}=10^{3}$ s at $T=300$ K. Thus, both electron capture and hole emission are expected to lead to an increased acceptor density at intermediate distance from the junction, at the time scale of reverse-bias experiments. These two processes may be discernible by their different energy barriers ΔE_1 and ΔE_3 (Table II), which should, to a large extent, determine the apparent activation energy of the bias-induced changes. Note, however, that the transitions, Eqs. (2) and (3), depend on the local electron and hole concentrations, which, in turn, depend on temperature due to a temperature dependent depletion width. This may lead to a contribution to the apparent thermal activation energy, in addition to the barrier height.

The recovery of the equilibrium state after reverse-bias treatment was investigated in Ref. 15 in a thermally stimulated capacitance experiment, by analyzing the (negative) capacitance step after which the increased capacitance of the metastable state relaxed back to the capacitance of the equilibrium state before reverse-bias treatment. In our $(V_{Se}$-$V_{Cu})$ model, this step is caused by the back transition from the acceptor into the donor configuration by the hole capture, Eq. (3). The activation energy of 0.32 eV measured in Ref. 15 for this transition compares well with our calculated energy barriers in Table II. Also, the measured frequency prefactor of $\nu_0=4\times10^{4}$ s^{-1} (Ref. 15) supports the $(V_{Se}$-$V_{Cu})$ model, as we find from Eq. (5) a similar value $\nu_{ph}P_{hc}^{2}=10^{3}$ ap.978 250.4789 36 0 9.1096 0 0 9.978 235.8143 347.5361 Tm0.1096 Tc1 7/F8 3842

Can the amphoteric (V_{Se}-V_{Cu}) *defect explain unusual capacitance transients*? E en tho gh the d namic of the acti ated □(+/) t an ition co e ponding to the dono /accepto con e ion of (V_{Se}-V_{C}) i diffe ent f om con entional t an ition (cf. Sec. IV), thi con e ion ma be in both di ection ob e ed di ectl in capacitance e pe iment , p opo ed the tempe at e, and f e enc indo a e app op iate. [Note that in the e pe iment cited abo e, the e idence fo the □(+/) t an ition of (V_{Se}-V_{C}) i onl indi ect and i manife ted b a change of the hallo accepto concent ation d e to ill mination o bia . The hallo accepto den it i all dete mined at lo tempe at e, he e the □(+/) t an ition it elf i not acti ated.] Recentl , Yo ng *et al.*[16] and Yo ng and C andall[17]

imila it ith o calc lated ab o ption le el of (

an o e e timated o e lap and, hence, inte action bet ee defect and ho t o bital , e ea the choice of the ex.pe imental (none . ilib i m) lattice con tant implie the p e ence of ome h d o tatic p e . e acting on the lattice in the calc lation. Fo t natel , the e a e . . all onl mino diffe - ence in the defect fo mation and t an ition ene gie . Since the la ge lattice ela . ation of the anion acancie in II-VI compo nd i pa tic la l en iti e to the lattice con tant (Ref. 20) the diffe ence can be mo e p ono nced, in the ca e of anion acancie , ho e e . Fo CIS and CGS, e con med b additional calc lation that ΔH change b not mo e than 0.2 eV hen . ing the LDA lattice con tant.

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[38] We dete mined m_h^*/m_e=0.8 f om . tting an effecti e-ma -like den it of tate (degene ac facto of 2) to the n me ical den it of tate , calc - lated in LDA incl ding pin-o bit co pling. The obtained al e i clo e to m_h^*/m_e=0.73 dete mined ex.pe imentall in Ref. 37.

[39] In Ref. 20, e dete mined ΔV f om the diffe ence of the ingle-pa ticle ene g of the In-*d* (Ga-*d*) o bital in the defect calc lation elati e to In-*d* (Ga-*d*) ene g in the p e ho t. The p e ent method appea to ield mo e con i tent e . lt and le . ncont olled catte compa ed to the fo me method. Acco dingl , the potential alignment ΔV fo the (V_{Se}-V_C) comple ex. dete mined he e diffe b . p to 0.2 eV f om that dete mined in Ref. 20. The mo t igni cant change i that e no . nd a hallo tate of the accepto con g ation of (V_{Se}-V_C), imila to the hallo tate of the i olated V_C.