Light- and bias-induced metastabilities in Cu (In , Ga) Se 2 based solar cells caused by the (V Se - V Cu) vacancy complex

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

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exhibit metatable beha io that can lead to pe i tent photocond cti it . In Ref. [20] w e di c ed in detail the gene al defect ph ic that lead to metatabilit and PPC dicating that meta table beha io of CIGS ola cell i accompanied b a potentiall det imental ecombination cente .

i needed to co ect fo the band- lling effect (Mo -B tein hifi) 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 □H of the int in ic $\mathrm{In}_{\mathrm{C}}^0$ 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 $(V_{\mathrm{Se}}\text{-}V_{\mathrm{C}})^0$ 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 extended abo e the CBM of p e CIS, p to $E_F = E_V + 1.25$ eV, app oximatel co e ponding to the CBM of C In$_{1\ x}$Ga$_x$Se$_2$ allo ith compo ition p to x 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 (2+/0)=E_v+0.05 eV clo e to the VBM, and deep accepto t an ition high in the gap, i.e., (0/)=E_v+0.85 eV and (/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} exhibit amphote 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

ho n in Fig. 4 (Ref. 44) fo the accepto con g ation ith the ho t In-In di tance, along ith the elect onic o bital (i o face plot of the a e f nction a e) of the *a* and *b* defect le el , hich, in thi con g ation, lie belo the VBM and in the band gap, e pecti el (Table I). The bonding and the antibonding cha acte of the *a* and the *b* le el , e pecti el , a e clea l i ible in Fig. 4.

The deep ε(/2) and ε(2 /3) accepto t an ition of the comple (Table II), hich e lt f om the occ pation of the antibonding *b* le el, occ at ome hat highe ene g [Fig. 2(a)] compa ed to the e pecti e ε(0/) and ε(/2) le el of the i olated V_{Se}. The po ition of the deep accepto le el a o nd 1 eV abo e the VBM indicate that in a CIGS ola cell, the e le el can onl be occ pied e clo e to the CdS/CIGS hete oj nction, he e the Fe mi le el can i e to ch high ene gie . E en tho gh the occ pation of the e deep le el i accompanied b con ide able atomic ela ation, no ene g ba ie a e in ol ed. Con e entl , the deep accepto le el a e e ilib i m t an ition . Note, ho e e , that the e deep le el a e p e ent onl in the accepto con g ation (ho t III-III di tance), he e the *b* le el i located in ide the band gap [Fig. 3(a)]. In cont a t, no ch deep t an ition le el e i t a long a the comple emain in the dono con g ation (la ge III-III di tance), beca e the *b* le el i o t ide the band gap, i.e., abo e the CBM, in thi con g ation [Fig. 3(a)].

In the accepto -con g ation of (V_{Se}-V_{C}), the e e i t al o optical t an ition ca ed b the *b* le el in the gap: The optical ab o ption ene gie d e to photoe ciation of elect on f om the VBM into the *b* le el ($a^2b^0 \rightarrow a^2b^1 + h$), and the photol mine cence ene gie d e to ecombination of elect on in the *b* le el ith hole at the VBM ($a^2b^1 + h \rightarrow a^2b^0$), a e gi en in Table II. Late in Sec. V, e compa e the e optical ene gie to e pe imentall ob e ed ab o ption and PL ene gie . Unlike the ε(/2) and ε(2 /3) accepto t an ition hich a e ca ed b occ pation of a gap tate, i.e., the *b* le el, the acti ated ε(+/) t an ition in ide the gap athe dema k the Fe mi le el at hich the the mod namicall table tate of (V_{Se}-V_{C}) change f om the dono to the accepto con g ation. The ingle-pa ticle tate being occ pied d ing thi t an ition, i.e., the *a* le el, i o t ide the band gap befo e a ell a afte the t an ition [Fig. 3(a)] and, the efo e, doe not ca e an optical t an ition le el ithin the gap.

Configuration coordinate model for the conversion between the donor and acceptor configurations. Fig e 3(b) ho the calc lated con g ation coo dinate diag am fo the (V_{Se}-V_{C}) comple in CIS. He e, the di tance d_{In-In} bet een the In atom e e a the eaction coo dinate. A ho n in Fig. 2(a), the $(V_{Se}\text{-}V_{C})^{+}$ tate in the dono con g ation ith la ge d_{In-In} [1 in Fig. 3(b)] ha the lo e t ene g in *p*-t pe CIGS, he e the Fe mi le el i clo e to the VBM.3.5 /F8 1 Tf

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

o dinate diag am fo CGS [Fig. 5(b)]. Con e entl , 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 lightl 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 elaxed 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 ilibi 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 ition E . (2) and (3). We no add e the t an ition d namic , 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 ation of (V_{Se}-V_{C}) i e tabli hed, once an ex te nal pe t bation 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}-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 v he e the complex. ex.i ted, at lea t pa tl , a (V_{Se}-V_{C})$^+$

diate di tance f om the j nction d i e the elect on capt e, E . (2), in the fo a d di ection. Taking $n=10^7$ cm ^{3},[48] e nd f om E . (4) a time con tant $\tau_{ec}=10^2$ at $T=300$ K. Second, d e to hole depletion, the fo a d di ection of the hole capt e, E . (3), i pp e ed, hich d i e E . (3) in the back a d di ection, i.e., hole emi ion, fo hich e nd the time con tant $\tau_{he}=10^3$ at $T=300$ K. Th , both elect on capt e and hole emi ion a e expected to lead to an inc ea ed accepto den it at inte mediate di tance f om the j nction, at the time cale of e e e-bia expe iment . The e t o p oce e ma be di ce nible b thei diffe ent ene g ba ie E_1 and E_3 (Table II), hich ho ld, to a la ge extent, dete mine the appa ent acti ation ene g of the bia - ind ced change . Note, ho e e , that the t an ition , E . (2) and (3), depend on the local elect on and hole concent ation , hich, in t n, depend on tempe at e d e to a tempe at e dependent depletion idth. Thi ma lead to a cont ib tion to the appa ent the mal acti ation ene g , in addition to the ba ie height.

The eco e of the e ilib i m tate afte e e e-bia t eatment a in e tigated in Ref. 15 in a the mall tim lated capacitance expe iment, b anal ing the (negati e) capacitance tep afte hich the inc ea ed capacitance of the meta table tate elaxed back to the capacitance of the e ilib i m tate befo e e e e-bia t eatment. In o (V_{Se}-V_C) model, thi tep i ca ed b the back t an ition f om the accepto into the dono con g ation b the hole capt e, E . (3). The acti ation ene g of 0.32 eV mea ed in Ref. 15 fo thi t an ition compa e ell ith o calc lated ene g ba ie in Table II. Al o, the mea ed f e enc p efacto of $\nu_0=4\times10^4$ ^{1} (Ref. 15) ppo t the (V_{Se}-V_C) model, a e nd f om E . (5) a imila al e $\sigma_{ph}P^2_{hc}=10^3$ 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 ex pe iment , p opo ed the tempe at e, and f e enc indo a e app o- p iate. [Note that in the ex pe iment cited abo e, the e i- dence 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 con- cent 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 v. ith o. calc. lated ab o ption le el of (

an o e e timated o e lap and, hence, inte action bet een defect and ho t o bital , he ea the choice of the e 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 elaxation 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 e 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 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