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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 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

ho w n in Fig. 4 (Ref. 44) fo the accepto con g ation w ith the ho t In-In di tance, along w ith the elect onic o bital (i o face plot of the w a e f nction a e) of the *a* and *b* defect le el , w hich, in thi con g ation, lie belo w 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 (/2) and (2 /3) accepto t an ition of the comple (Table II), w hich e lt f om the occ pation of the antibonding *b* le el, occ at ome w hat highe ene g [Fig. 2(a)] compa ed to the e pecti e (0/) and (/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, w 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 w 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), w 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 w ith hole at the VBM ($a^2b^1+h \rightarrow a^2b^0$), a e gi en in Table II. Late in Sec. V, w e compa e the e optical ene gie to e pe imentall ob e ed ab o ption and PL ene gie . Unlike the (/2) and (2 /3) accepto t an ition w hich a e ca ed b occ pation of a gap tate, i.e., the *b* le el, the acti ated (+/) t an ition in ide the gap athe dema k the Fe mi le el at w hich the the mod nami call 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 w 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 w ithin the gap.

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

ι on ($a^1 \rightarrow a^2 + h$), leading ιo a hole in ιhe hallo acceptιo
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 e i t in CIS fo E_F □ □(+/) [da hed g een line in Fig. 2(a), CIS] doe not e 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 comple 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 e 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)] e 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}) comple 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 equilibrium distribution between the donor and the acceptor configuration should be regarded as a steady state situation with respect to the forward and backward directions of the transitions Eqs. (2) and (3). We now address the transition dynamics, i.e., the transition rates of Eqs. (2) and (3), with which a new equilibrium between the donor and acceptor configurations of (V_{Se}-V_{Cu}) is established, once an external perturbation is applied, e.g., illumination or bias. If the external perturbation creates an excess of free electrons, the complex will react to this perturbation by the electron capture, Eq. (2) in the forward direction, and the conversion into the acceptor state, thereby reducing the electron excess according to Le Chatelier's principle. Similarly, if the external perturbation e pond to the dono -to-accepto con e ion of (V_{Se}-V_{C}) d e to the capt e, E . (2), of photoexcited 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 w 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 fow a d di ection. Taking $n=10^7$ cm ^{3},[48] w 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 fow a d di ection of the hole capt e, E . (3), i pp e ed, w hich d i e E . (3) in the backw a d di ection, i.e., hole emi ion, fo w hich w 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 tw o p oce e ma be di ce nible b thei diffe ent ene g ba ie ΔE_1 and ΔE_3 (Table II), w hich ho ld, to a la ge extent, dete mine the appa ent acti ation ene g of the bia -ind ced change . Note, how e e , that the t an ition , E . (2) and (3), depend on the local elect on and hole concent ation , w hich, in t n, depend on tempe at e d e to a tempe at e dependent depletion w 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 w 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 w hich the inc ea ed capacitance of the meta table tate elaxed back to the capacitance of the e i- lib 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 w ell w 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 w e nd f om E . (5) a imila al e $\nu_{ph}P_{hc}^2=10^3$ 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 ex pe iment , p opo ed the tempe at e, and f e enc indo a e app op iate. [Note that in the ex 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 y ith o calc lated ab o ption le el of (

an overestimated overlap and, hence, interaction between defect and host orbitals, whereas the choice of the experimental (nonequilibrium) lattice constant implies the presence of some hydrostatic pressure acting on the lattice in the calculation. Fortunately, there are usually only minor differences in the defect formation and transition energies. Since the large lattice relaxation of the anion vacancies in II-VI compounds is particularly sensitive to the lattice constant (Ref. 20) the differences can be more pronounced, in the case of anion vacancies, however. For CIS and CGS, we confirmed by additional calculations that ΔH changes by not more than 0.2 eV when using the LDA lattice constant.

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[38] We determined m_h^*/m_e=0.8 from fitting an effective-mass-like density of states (degeneracy factor of 2) to the numerical density of states, calculated in LDA including spin-orbit coupling. The obtained value is close to m_h^*/m_e=0.73 determined experimentally in Ref. 37.

[39] In Ref. 20, we determined ΔV from the difference of the single-particle energy of the In-*d* (Ga-*d*) orbitals in the defect calculation relative to In-*d* (Ga-*d*) energy in the pure host. The present method appears to yield more consistent results and less uncontrolled scatter compared to the former method. Accordingly, the potential alignment ΔV for the (V_{Se}-V_{Cu}) complex determined here differs by up to 0.2 eV from that determined in Ref. 20. The most significant change is that we now find a shallow state of the acceptor configuration of (V_{Se}-V_{Cu}), similar to the shallow state of the isolated V_{Cu}.