Metal-Dimer Atomic Reconstruction Leading to Deep Donor States of the Anion Vacancy in II-VI and Chalcopyrite Semiconductors

S e han Lan and Ale Z nge
National Renewable Energy Laboratory, Golden, Colorado 80401, USA
(Recei ed 13 A il 2004; bli hed 5 Oc obe 2004)

Fi - inci le o al-ene g calc la ion e eal a no el local a omic econ c ion mode a o nd anion acancie in II-VI and chalco i e com o nd e l ing f om he fo ma ion of me al dime . A a con e ence, he ne al Se acanc ha an ne ec ed lo mme in ZnSe an6.6410.5257 C5(of)-2Zn2(con)m 17eacla ic e

DOI: 10.1103/Ph Re Le .93.156404 PACS n mbe : 71.15.Mb, 71.20.N , 71.55.G

Vacancie a e he mo f ndamen al oin defec in olid , con olling mechanical o e ie in me al [1]

de o de e mine fo he anion acanc he a omic c e, he elec onic e (ingle- a icle defec el), defec fo ma ion ene g *H*

f (c . e.g., Ref. [10]), and o ical an i ion ene gie . The o al-ene g *E* and a omic fo ce e e calc la ed in he e do o en ial-momen m ace fo mali m [16] i hin he local den i a o ima ion (LDA) of den i f nc ional heo . We e he Ce e le -Alde LDA e change co ela ion o en ial a a ame e i ed b Pe de and Z nge [17] and o jec- o a gmen ed a e o en ial a im lemen ed in he VASP code [18]. The ene g c off in he lane- a e e an ion a 280 eV, and B illo in one in eg a ion e e e fo med on a $3 \times 3 \times 3$ me h ing he im o ed e ahed on me hod. In ca e of he cha ged acancie , he io in e ac ion of e iodic image cha ge i co- ec ed o $O(L^{-5})$ [19], he e L i he linea e cell dimen ion. We e he e e imen al la ice con an of

 0031-9007/04/93(15)/156404(4)$22.50

ZnSe and $CuGaSe_2$ [20]. The LDA band ga e i co ec ed b ackno ledging ha he ca ion *d* a e

e ing he ingle- a icle ene g of he $a_1(a)$ o bi al in ZnSe ($CuGaSe_2$) f om E_v + 1.1 eV (E_v + 0.2 eV), befo e ela a ion o E_v + 0.2 eV (E_v − 2.5 eV), af e ela a ion. Th , a ill a ed in he e anel of Fig. 1, af e ela a ion, he do bl occ ied a_1^2 le el i loca ed in ZnSe j abo e he VBM, he ea in $CuGaSe_2$ i i dee *inside* he alence band. When V_{Se}^0 i ioni ed ice, e fo m he a_1^0 con g a ion of V_{Se}^{2+} (Fig. 1), ho ing a b eak of he me al-me al dime (Table I), and a e n o he o iginal T_d la ice mme (Fig. 1, bo om). The ingle- a icle ene g le el of he a_1 a e in ZnSe mo e *up* f om E_v + 0.2 eV (V_{Se}^0) o E_v + 2.5 eV (V_{Se}^{2+}), he ea in $CuGaSe_2$ i mo e *up* f om E_v − 2.5 eV (V_{Se}^0) o E_v + 1.5 eV (V_{Se}^{2+}) [20]. Tha a omic ela a ion i he d i ing fo ce fo hi le el hif can be j dged f om he fac ha elec o a ic effec , i.e., he elief of in e elec onic Co lomb e l ion d e o he a_1^2 (V_{Se}^0) → a_1^0 (V_{Se}^{2+}) an- i ion, o ld ha e di laced he a_1 le el o a d *lower* ene gie . Beca e of he cha ge a e de enden hif of he defec le el f om *below* VBM o *above* he VBM, he Se acanc in chalco i e can a me a me a able con g a ion, in hich elec on a e an fe ed f om he VBM o he dee defec le el, elea ing f ee hole . Th , he Se acanc can e lain he e i en ho o-