

# Defect-induced nonpolar-to-polar transition at the surface of chalcopyrite semiconductors

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Received 9 May 2001; published 29 November 2001)

In zinc-blende semiconductors, the *nonpolar*  $\bar{1}10$  surface is more stable than all polar surfaces because the formation of the latter requires the creation of charge-neutralizing but energetically costly surface reconstruction. Our first-principles calculations on  $\text{CuInSe}_2$  reveal this in the double-zinc-blende (chalcopyrite) structure, the defect-induced reconstructions make the  $\bar{1}12$ -cation plus  $(\bar{1}\bar{1}\bar{2})$ -anion polar facets lower in energy than the nonpolar  $\bar{1}10$  plane, despite the resulting increased surface area. We show that this spontaneous faceting results from the remarkable stability of surface defects (Cu vacancy, Cu-on-In antisite) in chalcopyrites, and explains the hitherto puzzling formation of polar microfacets when one attempts to grow epitaxially a nonpolar chalcopyrite surface.

DOI: 10.1103/PhysRevB.64.241304

PACS number(s): 61.72.Ji, 68.35.Bs, 68.35.Md

Chemisorption, catalysis, film growth, and carrier transport on the surfaces of compound semiconductors (GaAs, InP, ZnSe,...) depend on the atomic structure of the surface.<sup>1-4</sup> Covalently bonded semiconductor surfaces fall into two basic types:  $AB_2$  and  $A_2B_3$  semiconductors.

$AB_2$  semiconductors are of the form  $B^{\text{III}}X_2^{\text{VI}}$  chalcopyrites<sup>12,13</sup> with  $A^{\text{I}}=\text{Cu,Ag}$ ,  $B^{\text{III}}=\text{Al,Ga,In}$ , and  $X^{\text{VI}}=\text{S,Se,Te}$ . Just like the II-VI or III-V binary zinc-blende semiconductors, chalcopyrites semiconductors are fourfold-coordinated adamantite structures,<sup>12</sup> except that instead of having a single-cation-type II-VIs (e.g.,  $\text{ZnTe}$ ), chalcopyrites have two cation types from neighboring columns in the Periodic Table (e.g.,  $\text{CuGaSe}_2$ ). This generalization of the binary zinc-blende structure—the availability of two, rather than one type of metal atom—leads in chalcopyrites to easily formed defects.<sup>14</sup> For example, Cu vacancy is nearly exothermic as is the complex between two negatively charged Cu vacancies ( $2V_{\text{Cu}}$ ) and positively charged In-on-Cu antisite ( $\text{In}_{\text{Cu}}$ ) in  $\text{CuInSe}_2$ . How would the greater propensity for defect formation affect the polar vs. nonpolar surface stability? It turns out that while there are calculations on *bulk defects*<sup>14</sup> in chalcopyrites, as well as a calculation on defect-free *ideal chalcopyrite surface*,<sup>15</sup> no calculations are available on surface defects in chalcopyrite semiconductors. We performed such pseudopotential LDA calculations, finding that the polar surface of  $\text{CuInSe}_2$  is considerably more stable than the nonpolar surface, thus reversing the commonly accepted order of stability in binary semiconductors.<sup>1-4</sup> We predict the polar  $\bar{1}12$  surface to be stabilized by Cu vacancies ( $V_{\text{Cu}}$ ) in Cu-poor conditions, and by Cu-on-In antisite defects  $\text{Cu}_{\text{In}}$  in In-poor conditions,  $(\bar{1}\bar{1}\bar{2})$  is stabilized by subsurface  $\text{In}_{\text{Cu}}$ . This explains the hitherto puzzling spontaneous formation of microfacets

*Geometry:* In CuInSe<sub>2</sub> CIS) the nonpolar (110) surface also called (220)] has zigzag chains of atoms Cu-Se-In-

The range of values for the defect-free slab reflects possible effects of LDA band-gap errors: A polar slab depolarizes itself by moving valence charges from the anion surface into conduction bands associated with the cation surface, and the energy cost of doing this should scale with the band gap. One possible correction for this would be to increase the supercell energy by the number of electrons transferred (two) times the difference between the computed and experimental bulk gaps, giving about 2 eV. For a second estimate, we calculated the ideal energies of the  $(110)$  and  $(111)/(\bar{1}\bar{1}\bar{1})$  surfaces of several zinc-blende II-VI semiconductors, extracted a component of the polar-nonpolar surface energy difference that scaled with the LDA band gap, then rescaled this component by shifting the gap to its experimental value, yielding a correction of about 1 eV in CIS. These error estimates were included in our results below.

*The Nonpolar (110) Surface of  $\text{CuInSe}_2$ :* We used a five-layer slab in which the top three atomic layers were allowed to relax and the bottom two were held fixed, with the number of vacuum layers equal to the number of occupied layers. Test calculations on thicker slabs showed only negligible changes in surface energy. We find that when fully relaxed, the CIS  $(110)$

ous formation of  $(112) + (\bar{1}\bar{1}\bar{2})$  microfacets of epitaxial polar surfaces, as shown schematically in Fig. 2, when one attempts to grow nonpolar surfaces.<sup>16</sup> Both results reflected the intrinsic thermodynamic stability of the polar surfaces.