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# Surface Science

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# Atomic structure of the (001) surface of CuGaSe<sub>2</sub>

# Leandro Liborio <sup>a,\*</sup>, Su Chuen Chew <sup>a</sup>, Nicholas Harrison <sup>a,b</sup>

<sup>a</sup> TYC, The London Centre for Nanotechnology, Imperial College London, London SW7 2AZ, United Kingdom

<sup>b</sup> STFC, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

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ABSTRACT

Hybrid exchange density functional theory is used to study the wide band gap chalcopyrite CuGaSe<sub>2</sub>. The formation energies of the experimentally observed  $(4 \times 1)$  and  $(1 \times 1)$  atomic scale reconstructions on the CuGaSe<sub>2</sub> (001) surface are calculated for different environmental conditions. The results suggest that a Serich  $(1 \times 1)$  reconstruction, and a Cu-poor, Se-rich  $(4 \times 1)$  reconstruction, are the only stable surfaces under all the studied environmental conditions. Two complementary mechanisms for the stabilisation of CuGaSe<sub>2</sub> surfaces are proposed, and it is suggested that the presence of Na stabilises the  $(4 \times 1)$  reconstructions, making them the stable terminations under Na-rich conditions.

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surface science

#### 1. Introduction

Ternary I-III-VI<sub>2</sub> chalcopyrite compounds (CuInSe<sub>2</sub>, CuGaSe<sub>2</sub> and Cu (In/Ga)Se<sub>2</sub>) are promising materials for photoelectronic devices such as solar cells [1,2]. These devices are usually multilayered thin-film heterostructures in which the absorber layer is made of a chalcopyrite thin film that is epitaxially grown. Efficiencies of the order of 20% -measured under the AM 1.5 global spectrum for 1000 W/m<sup>2</sup> irradiance- have been achieved in the lab for epitaxially grown  $CuIn_xGa_{(1-x)}Se_2$ -based solar cells [3,4], and solar cells whose absorber was grown using Molecular Organic Chemical Vapour Deposition (MOCVD) have achieved efficiencies between 10% and 19% [5].

Experimental studies have been performed to characterise the (112) and (110) surfaces of CuInSe<sub>2</sub> single crystals [6]. As regards the experimental evidence on the CuGaSe<sub>2</sub> surfaces, Meeder and coworkers grew crystalline CuGaSe<sub>2</sub> samples and showed that their surfaces tend to be Cu-depleted and, if grown on soda-lime type of substrates, Na-rich [7]. Moreover, non-polar, non-stoichiometric (001) surfaces of CuGaSe<sub>2</sub> are relevant in the field of photovoltaic applications. For instance, surface-faceting is stronger on CuInSe<sub>2</sub> (001) surfaces as compared to CuGaSe<sub>2</sub> (001) surfaces, which implies that the CuGaSe<sub>2</sub> (001) surfaces are more stable than the CuGaSe<sub>2</sub> (112) surfaces. Non-stoichiometry is a stabilising factor in the CuGaSe<sub>2</sub> (001) surfaces when compared to the CuInSe<sub>2</sub> (001) surfaces [8]. In addition, non-stoichiometric (001) surfaces of CuGaSe<sub>2</sub> play an important role in the study of the grain boundaries of CuGaSe<sub>2</sub> [1]. However, thin film devices with absorber layers composed only of a CuGaSe<sub>2</sub> showed efficiencies of, at most, 9.5% [9]. These efficiencies of CuGaSe<sub>2</sub>-based solar cells can be slightly improved by substituting Ga atoms with In atoms in CuGaSe<sub>2</sub> –obtaining CuIn<sub>x</sub>Ga<sub>(1-x)</sub>Se<sub>2</sub>–, but</sub>further efficiency improvements can only be achieved if the surface and interface properties of the chalcopyrites forming the different layers are understood [8].

In this work, we have studied (001) surfaces of CuGaSe<sub>2</sub> that were prepared using a sputtering/annealing processing previously used for growing single-crystal surfaces such as CuInSe<sub>2</sub>(112), and (110) [10,11] and surfaces of polycrystalline CuInSe<sub>2</sub> [12]. The single crystalline (001) GuGaSe<sub>2</sub> surfaces that we have modelled here were grown by Denizou et al. using MOCVD [13,14]. The samples were subsequently Ar<sup>+</sup> sputtered and annealed, and their atomic surface structures and compositions were analysed using low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Denizou et al. observed clean, stable, unfacetted, non-stoichiometric  $(4 \times 1)$  reconstructions on the (001) surface of GuGaSe<sub>2</sub>, with a Se-rich, Cupoor stoichiometry [13]. According to Tasker's classification [15], the stoichiometric, unreconstructed (001) GuGaSe<sub>2</sub> surface is a polar surface. But the (001) surfaces of CuGaSe<sub>2</sub> that we have studied here have been reconstructed, and are non-stoichiometric and non-polar. We used ab initio thermodynamics to study the stability, under different environmental conditions, of several  $(4 \times 1)$  surface reconstructions. The atomic structure of these reconstructions is proposed on the basis of the experimental evidence and the computed relaxation of the surface layers. The role of Na in the surface's stability is also studied.

# 2. Methodology

# 2.1. Computational details

Density functional theory (DFT) calculations were performed using CRYSTAL [16] and the Becke, three-parameter, Lee-Yang-Parr



<sup>\*</sup> Corresponding author. E-mail address: l.liborio@imperial.ac.uk (L. Liborio).

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hybrid exchange functional (B3LYP). This functional has been shown to provide a reliable description of the electronic structure, geometry and energetics in a wide range of materials [17,18]. In particular, hybrid exchange functionals such as B3LYP provide a much better prediction of the band gap of semiconductors than the local density approximation (LDA) or generalised gradient approximation (GGA) DFT functionals, and are therefore likely to be more accurate in estimating the valence band offset of semiconductor heterojunctions [19].

Polarised triple valence Gaussian basis sets [16] for the copper (Cu), gallium (Ga), sodium (Na) and selenium (Se) atoms were used throughout, and these basis sets are listed in the supplementary material. For the Se atom's basis set, the most diffuse exponents of sp functions were optimised with respect to the ground state energy of CuGaSe<sub>2</sub> at the experimental geometry. The Coulomb and exchange integrals in CRYSTAL are truncated in direct space according to overlap criteria of the Gaussian basis. The algorithms have been described in detail elsewhere [20]. To secure converged energy values, in the current study the two Coulomb overlap criteria have been set to  $10^{-6}$  and the three exchange criteria to  $10^{-6}$ ,  $10^{-6}$  and  $10^{-12}$ . A Monkhorst–Pack shrinking factor of eight was used to sample the first Brillouin zone, and a Gilat net of eight points was used in the evaluation of the Fermi energy and density matrix [20].

All the surface structures were represented by periodically repeated symmetric slabs consisting of consecutive layers of Se atoms and CuGa atoms in the (001) direction. Test calculations with  $(1 \times 1)$  Se and CuGa terminated slabs, with a number of layers ranging from 5 up to 17, showed variations of the surface energy smaller than 0.015 J/m<sup>2</sup>. All the surface reconstructions studied in this work were simulated using symmetric slabs of 13 layers. These slabs have a centre of inversion: the simulated (001) surfaces are non-polar and non-stoichiometric. The lattice parameters and internal atomic positions of bulk CuGaSe<sub>2</sub> were optimised, and the relaxed CuGaSe<sub>2</sub> lattice parameters were used for building the surface slabs. In the optimisation of these slabs only the internal atomic positions were relaxed.

# 2.2. Surface energies

Total energy electronic structure calculations can be combined with thermodynamics in order to deduce the stable structures of complex surfaces over a range of environmental conditions. The equilibrium surface stoichiometry and free energy are actually a statistical average over all elementary adsorption and desorption processes from and to a particle reservoir. When the total number of adsorption processes equals the total number of desorption processes, the average surface composition and structure remains constant and the surface has achieved thermodynamic equilibrium with the environment. Our approach is based in the methodology developed by A. Zunger and coworkers for calculating the surface energies of chalcopyrites [21–23].

At thermodynamic equilibrium, the energy of different surface reconstructions in the ternary compound CuGaSe<sub>2</sub> is given by:

$$\gamma(T,p) = \frac{1}{2A} \left[ \left( G^{slab}(T,p,n_{Cu},n_{Ga},n_{Se}) - n_{Cu}\mu_{Cu}(T,p) - n_{Ga}\mu_{Ga}(T,p) - n_{Se}\mu_{Se}(T,p) \right] \right]$$
(1)

where  $G^{slab}(T,p,n_{Cu},n_{Ga},n_{Se})$  is the Gibbs free energy of the CuGaSe<sub>2</sub> slab, and  $n_i$  and  $\mu_i(T,p)s$  are the number of atoms and chemical potentials of each one of the slab's elemental components. Since it is assumed that CuGaSe<sub>2</sub> is in equilibrium with its elemental components:

$$G^{bulk}_{CuGaSe_2}(T,p) = \mu_{Cu}(T,p) + \mu_{Ga}(T,p) + 2\mu_{Se}(T,p)$$
(2)

where  $G_{CuGaSe_2}^{bulk}(T,p)$  is the Gibbs free energy of bulk CuGaSe<sub>2</sub>. Eqs. (2) and (1) can be combined to express the energy of a surface reconstruction in CuGaSe<sub>2</sub> as:

$$\begin{split} \gamma(T,p) &= \frac{1}{2A} \Big[ G^{slab}(T,p,n_{Cu},n_{Ga},n_{Se}) - \Big(\frac{n_{Se}}{2}\Big) G^{bulk}_{CuGaSe_2}(T,p) \\ &\quad + \Big( \Big(\frac{n_{Se}}{2}\Big) - n_{Cu} \Big) \mu_{Cu}(T,p) + \Big( \Big(\frac{n_{Se}}{2}\Big) - n_{Ga} \Big) \mu_{Ga}(T,p) \Big]. \end{split}$$

Defining  $\Delta \mu_i = \mu_i(T, p) - \mu_i^{\circ}$ , where  $\mu_i^{\circ}$  is the chemical potential at standard conditions (T=298 K, p=1 atm), the surface energy can be re-written as:

$$\begin{split} \gamma(T,p) &= \frac{1}{2A} \Big[ G^{slab}(T,p,n_{Cu},n_{Ga},n_{Se}) - \Big(\frac{n_{Se}}{2}\Big) G^{bulk}_{CuGaSe_2}(T,p) \\ &\quad + \Big( \Big(\frac{n_{Se}}{2}\Big) - n_{Cu} \Big) \mu_{Cu}^{\circ} + \Big( \Big(\frac{n_{Se}}{2}\Big) - n_{Ga} \Big) \mu_{Ga}^{\circ} \\ &\quad + \Big( \Big(\frac{n_{Se}}{2}\Big) - n_{Cu} \Big) \Delta \mu_{Cu} + \Big( \Big(\frac{n_{Se}}{2}\Big) - n_{Ga} \Big) \Delta \mu_{Ga} \Big]. \end{split}$$

As it is assumed that the solid bulk  $CuGaSe_2$  is in equilibrium, the upper bound of  $\mu_i$  is the chemical potential of the corresponding element in its standard state, as to avoid precipitation of the element, that is:

$$\Delta \mu_i \le 0. \tag{5}$$

We would like to know the region in the phase space where  $CuGaSe_2$  is stable. In this region, Eq. (2) must hold true and, considering Eq. (5), it can be re-written as:

$$\Delta G_{CuGaSe_2} = \Delta \mu_{Cu} + \Delta \mu_{Ga} + 2\Delta \mu_{Se}$$
(6)

where  $\Delta G_{CuGaSe_2}$  is the Gibbs free energy of formation of CuGaSe<sub>2</sub>. The chemical potentials are further restricted by other competing phases. In this work, the competing phases being considered are CuGa<sub>5</sub>Se<sub>8</sub>, Cu<sub>3</sub>Se<sub>2</sub> and GaSe. Therefore:

$$3\Delta\mu_{\rm Cu} + 2\Delta\mu_{\rm Se} \le \Delta G_{\rm Cu_3Se_2} \tag{7}$$

$$\Delta\mu_{Ga} + \Delta\mu_{Se} \le \Delta G_{GaSe} \tag{8}$$

$$\Delta \mu_{Cu} + 5\Delta \mu_{Ga} + 8\Delta \mu_{Se} \le \Delta G_{CuGa,Se_8} \tag{9}$$

with  $\Delta G_{Cu_3Se_2}$ ,  $\Delta G_{GaSe}$  and  $\Delta G_{CuGa_3Se_8}$  being the Gibbs formation energies of the competing phases. If the surface is doped with an extrinsic dopant such as Na, the Gibbs formation energy of Na-competing phases such as Na<sub>2</sub>Se needs to be considered as well. This phase adds an additional constraint to the system.

$$2\Delta\mu_{\rm Na} + \Delta\mu_{\rm Se} \le \Delta G_{\rm Na,Se} \tag{10}$$

The values of the chemical potentials of Cu, Ga and Se for which CuGaSe<sub>2</sub> is stable have been determined by combining Eqs. (6) and (7), and are represented by the white region in Fig. 3. Within this region, the limiting values of  $\Delta \mu_{Se}$  are given by:

$$\frac{\Delta G_{CuGaSe_2}}{2} \le \Delta \mu_{Se} \le 0. \tag{11}$$

These values for  $\Delta \mu_{\text{Se}}$  are then used in Eq. (10) to calculate the limiting values of  $\Delta \mu_{\text{Na}}$ , which is then used in the calculation of the surfaces energies of Na-doped surfaces.

Gibbs free energies are computationally very expensive to calculate from first principles and, therefore, they are usually approximated [24–26]. In this case, the approximations are applied when defining the variational limits of  $\Delta \mu_i$  (i = Cu, Ga, Se), which is done through the formation energies of CuGaSe<sub>2</sub> and its competing phases. In the following, the methodology is exemplified using the Gibbs



Fig. 1. Band structure and atom-projected density of states (DOS) of bulk CuGaSe<sub>2</sub>. The inset at the top-right part of the DOS shows an amplified picture of the band-gap region.

formation energy of  $CuGaSe_2$ , which is defined in Eq. (6). This equation can be written as follows:

$$\Delta G_{CuGaSe_2} = G_{CuGaSe_2} - G_{Ga} - G_{Cu} - 2G_{Se}$$
$$= E_{CuGaSe_2}^{DFT} - E_{Cu}^{DFT} - E_{Ga}^{DFT} - E_{Ga}^{DFT}$$
(12)

$$+ F_{CuGaSe_2}^{vib.} - F_{Cu}^{vib.} - F_{Ga}^{vib.}$$

$$+ p \left( V_{CuGaSe_2} - V_{Cu} - V_{Ga} \right)$$

$$- n_{Se} \mu_{Se}^{v}.$$

$$(13)$$

In this equation, the Gibbs free energy of the solid phases, G = E - TS + pV, is written as

$$G = E^{DFT} + F^{vib.} + pV.$$
(14)

 $E^{DFT}$  is the ab initio total energy of the material,  $F^{vib.} = E^{vib.} - TS^{vib.}$  is the *Helmholtz* vibrational energy [24], which depends on the phonons and is a function of temperature, and pV is the pressure-volume term.

The pV and F<sup>vib.</sup> terms are small for crystalline incompressible materials such as CuGaSe<sub>2</sub>, and Eq. (12) uses *differences* between these quantities to define the  $\Delta \mu_i$  variational limits. Consequently, the pV and F<sup>vib.</sup> contributions for these types of materials are of the order of 0.02 J/m<sup>2</sup> [24,26,27], and can be considered negligible. Therefore,  $\Delta G_{CuGaSe_2}$  can be written as:

$$\Delta G_{CuGaSe_2} = E_{CuGaSe_2}^{DFT} - E_{Cu}^{DFT} - E_{Ga}^{DFT} - n_{Se}\mu_{Se}^0$$
(15)

where  $E_{CuGaSe_2}^{DFT}$ ,  $E_{Cu}^{DFT}$  and  $E_{Ga}^{DFT}$  are the ab initio total energies of these materials in their solid standard states.  $E_{CuGaSe_2}^{DFT}$  is the total energy of bulk CuGaSe<sub>2</sub> in its tetragonal phase and  $\mu_{Se}^{0}$  is calculated in its diatomic molecular form using a standard methodology described elsewhere [28]. As regards Cu and Ga, the B3LYP approximation does not provide



Fig. 2. The (16 atom) conventional unit cell of CuGaSe<sub>2</sub> is shown.

accurate energies for metals and, therefore,  $E_{Cu}^{DFT}$  and  $E_{Ga}^{DFT}$  are calculated using the experimental standard formation energies,  $\Delta G^0$ , of GaSe and Cu<sub>3</sub>Se<sub>2</sub> as,

$$E_{Ga}^{DFT} = \left[ E_{GaSe}^{DFT} - n_{Se} \mu_{Se}^{o} - \Delta G_{GaSe}^{o} \right]$$
(16)

$$E_{Cu}^{DFT} = \frac{1}{3} \left[ E_{Cu_3 Se_2}^{DFT} - n_{Se} \mathring{\mu}_{Se} - \Delta G_{Cu_3 Se_2}^o \right].$$
(17)

Since the values of  $\Delta G^o_{CuGa_5Se_8}$  and  $\Delta G^o_{CuGaSe_2}$  eV are not available from experiments,  $E^{DFT}_{Ga}$  and  $E^{DFT}_{Cu}$  are used to estimate, the values of  $\Delta G^o_{CuGa_5Se_8} = -11.57$  eV and  $\Delta G^o_{CuGaSe_2} = -3.02$  eV.  $\Delta G^o_{GaSe} = -1.43$  eV was measured using combustion calorimetry [29], while  $\Delta G^o_{CuSe_2} = -1.67$  eV [30] and  $\Delta G^o_{Na_2Se} = -3.55$  eV [31] were estimated using differential thermal analysis.

Taking all these into consideration the expression for the surface energy -Eq. (4) – can be approximated as:

$$\begin{split} \gamma(T,p) &= \frac{1}{2A} \Big[ E_{slab}^{DFT} - \Big( \frac{n_{Se}}{2} \Big) E_{CuGaSe_2}^{DFT} + \Big( \Big( \frac{n_{Se}}{2} \Big) - n_{Cu} \Big) E_{Cu}^{DFT} \\ &+ \Big( \Big( \frac{n_{Se}}{2} \Big) - n_{Ga} \Big) E_{Ga}^{DFT} + \Big( \Big( \frac{n_{Se}}{2} \Big) - n_{Cu} \Big) \big) \Delta \mu_{Cu} \\ &+ \Big( \Big( \frac{n_{Se}}{2} \Big) - n_{Ga} \Big) \big) \Delta \mu_{Ga} \Big] \end{split} \tag{18}$$

which is the expression we will use for calculating the surface energies.



**Fig. 3.** Calculated phase diagram for the Cu–Ga–Se system indicating the stable phases in the vicinity of CuGaSe<sub>2</sub>.  $\Delta \mu_{Cu} = 0$  and  $\Delta \mu_{Ga} = 0$  indicate Cu–rich, Ga–rich regions, respectively. Since  $\Delta \mu_{Se}$  is defined through Eqs. (6) and (7), the  $\Delta \mu_{Cu} = \Delta \mu_{Ga} = 0$  also indicates a Se-poor region. The diagonal line which links the  $\Delta \mu_{Cu}$  and  $\Delta \mu_{Ga}$  axes represents a selenium rich region with  $\Delta \mu_{Se} = 0$ .

# 3. Results and discussion

# 3.1. CuGaSe<sub>2</sub> bulk

Fig. 2 shows the CuGaSe<sub>2</sub> crystalline unit cell, and Table 1 compares theoretical and experimental lattice parameters and band gaps. The first two lines show the theoretical lattice parameters calculated by us using the B3LYP [17,18] and PBE [32] functionals. The lattice constants predicted using the B3LYP are overestimated by 2% and are in somewhat worse agreement with experiment than those predicted from the PBE GGA functional. This can be understood from the 20% proportion of Fock exchange retained in the B3LYP functional. Increasing the proportion of exchange tends to decrease the lattice constant and open a larger band gap while compensating for electronic self interaction. On the other hand, the Heyd–Scuseria– Ernzerhof (HSE) [33] functional overestimates the values of the lattice parameters by a smaller amount, but gives a bandgap of 1.40 eV, which is significantly smaller than that observed.<sup>1</sup>

The points chosen for the BZ path for the band structure in Fig. 1 are the high symmetry points  $T(0, 0, \pi/a)$ ,  $\Gamma(0, 0, 0)$ ,  $N(\pi/a, \pi/a, 0)$  and  $P(\pi/a, \pi/a, \pi/2a)$ . Our B3LYP calculations give a direct band gap of 1.73 eV, which is the theoretical value that best compares to the two experimental values reported in Table 1. These values were measured at room temperature using electroluminescence techniques [35] and a combination of ultraviolet photoelectron –and inverse-photoelectron – spectroscopy [37].

The calculated atom-projected density of states of CuGaSe<sub>2</sub> is shown in Fig. 1. Our results indicate that the valence band maximum is mainly composed Cu 3d and Se 4p states, which is in agreement with the composition deduced from electroreflectance measurements [38] and with previous electronic structure calculations [39]. As regards the conduction band minimum, our results indicate that it is mainly formed by Ga 4s, Cu 4s and Se 4p states, again in agreement with previous electronic calculations [40]. Moreover, the Mulliken bond population of tetrahedrally coordinated Ga and Cu in CuGaSe<sub>2</sub> is 0.183|e| for the Cu-Se bond and 0.268|e| for the Ga-Se bond, indicating that Ga-Se bonds are more covalent in nature than Cu-Se bonds. These values can be compared to previous calculations of bond populations performed using Gaussian basis sets of a similar structure and quality. Previous CRYSTAL values of Mulliken populations for the (Mg, Al, Si) – O bond in MgO,  $Al_2O_3$  and SiO<sub>2</sub> oxides are of the order of 0.01, 0.148 and 0.290 [41]. This suggests a semi-ionic character for both the Cu-Se and Ga-Se, which is in agreement with previous theoretical results [42–44].

## 3.2. Bulk phase stability

Fig. 3 is the computed phase diagram as a function of the gallium and copper chemical potentials. It was calculated using the formalism described in Section 2.2 and highlights the stability region for CuGaSe<sub>2</sub>. This figure is a phase diagram projected in the ( $\Delta \mu_{Cu}$ ,  $\Delta \mu_{Ga}$ ) plane. Within this plane, the value of  $\Delta \mu_{Se}$  is constrained by Eqs. (6) and (7), and the diagonal line which links the  $\Delta \mu_{Cu}$  and

# Table 1

Comparison of theoretical and experimental results.

	a (Å)	c (Å)	$\eta = c/2a$	$E_{g}\left( eV ight)$	Ref.
Theory, B3LYP	5.739	11.311	0.985	1.73	Our calc.
Theory, PBE	5.692	11.302	0.993	0.38	Our calc.
Theory, PBE	5.685	11.220	0.987	0.03	[34]
Theory, HSE	5.637	11.120	0.986	1.40	[34]
Experiment	5.616	11.018	0.981	1.7	[35]
Experiment	5.614	11.022	0.982	1.65	[36,37]

 $\Delta \mu_{Ga}$  axes represents  $\Delta \mu_{Se} = 0$  eV. Points 1–2–3–4–5 indicate the corners of the stability region.

The CuGaSe<sub>2</sub> phase diagram shown in Fig. 3 can be compared to the one calculated by C. Persson and coworkers [21]. The main general difference between that phase diagram and ours is the number of CuGaSe<sub>2</sub>'s competing phases considered. Persson's diagram includes Ga<sub>2</sub>Se<sub>3</sub>(tetragonal), CuGa<sub>5</sub>Se<sub>8</sub>, GaSe, Cu<sub>3</sub>Se<sub>2</sub>, CuSe and Cu<sub>2</sub>Se as competing phases, while the phase diagram in Fig. 3 includes GaSe, CuGa<sub>5</sub>Se<sub>8</sub> and Cu<sub>3</sub>Se<sub>2</sub>. We did not include CuSe and Cu<sub>2</sub>Se because they do not contribute to define the border of the stability region for CuGaSe<sub>2</sub>. As regards Ga<sub>2</sub>Se<sub>3</sub>(tetragonal), the reason why it was not included is different.

The methodology used in [21] calculates the formation energies of the competing phases using ab initio calculations with the LDA functional. On the contrary, our methodology uses experimental formation energies, and we could not find an experimental value for  $Ga_2Se_3$ (tetragonal)'s formation energy.<sup>2</sup>

There are two other differences between our phase diagram and the one in Ref. [21]: the position of the GaSe equilibrium line and the value of CuGaSe<sub>2</sub> formation energy with respect to its components ( $\Delta G_{CuGaSe_2}$ ). The position of our GaSe equilibrium line was calculated using an experimental value for  $\Delta G_{GaSe}$ , as opposed to calculating the formation energies using ab initio calculations. As regards the difference in value for  $\Delta G_{CuGaSe_2}$ , we believe it is due to the value of  $\mu \hat{s}_{e}$ .<sup>3</sup>

# 3.3. Surface energies

Fig. 4(a) and (b) shows the relaxed, bulk-cut, Se-terminated and CuGa-terminated, fully-relaxed  $(1 \times 1)$  (001) surfaces of CuGaSe<sub>2</sub>. Fig. 4(a) shows that surface Se dimerise: This removes dangling bonds, lowering the surface energy. For the CuGa-terminated slabs, there is electrostatic repulsion between the Cu and Ga atoms and the surface 'rumples'. The Cu atoms are displaced deeper into the Se layer below by about 1.186 Å when compared to a Cu position in the bulk. Ga atoms are pushed out by approximately 0.582 Å and as a result, the Ga–Se bond lengthens to 2.730 Å.

Auger electron spectroscopy experiments suggest that the  $(4 \times 1)$  surface reconstructions observed with LEED are Cu-poor and Se-rich [14]. This suggests a model of the  $(4 \times 1)$  reconstruction in which Se and Cu defects are introduced in the surface layers of a Se-terminated slab. Passivation with Sodium (Na) is important to the performance of the chalcopyrite absorber: Na is known to accumulate at the surface and grain boundaries [45] and, therefore, we have explored the stability of Na<sub>Cu</sub> defects. Fig. 5 shows the top view of the

<sup>&</sup>lt;sup>1</sup> We do not have a satisfactory explanation for the discrepancy between the PBE results for the bang gap. The paper by Paier et al. [34] also presents PBE results for the CuGaS<sub>2</sub>. We have recently published a paper on the defects in CuGaS<sub>2</sub> [47]. The calculations in that paper were done using the B3LYP functional but, in order to document the performance of the PBE functional, we also performed PBE calculations on CuGaS<sub>2</sub>. We obtained a band gap of 0.79 eV that compares very well with the 0.7 eV obtained by Paier and coworkers. The problem, then, is apparently not due to the difference in the implementation of PBE in the codes used. Moreover, B3LYP gives us a reasonable value of the band gap of CuGaSe<sub>2</sub>, indicating that the discrepancy is unlikely to be due to inadequacies in the basis set or numerical conditions adopted in the culculations. We had an exchange of emails with Paier and coworkers, and we believe that the remaining difference in the approaches is perhaps the Fermi surface smearing used by Paier et al., which may have resulted in convergence to a near metallic state.

<sup>&</sup>lt;sup>2</sup> Ga<sub>2</sub>Se<sub>3</sub> as a bulk only exists as a Ga-defective material  $-Ga_{(2-x)}Se_3-$  with a zincblende structure in which a third of the Ga sites are vacant.  $Ga_{(2-x)}Se_3$  crystallizes into two forms:  $\alpha$  and  $\beta$ . In the  $\alpha$ -form, vacancies are disordered throughout the crystal, whereas in the  $\beta$ -form the vacancies form an ordered arrangement [61,62].

<sup>&</sup>lt;sup>3</sup> In our calculations, the elemental phase of Se is the diatomic molecular state at standard conditions, and we calculated the value of its chemical potential using a standard methodology [28]. We do not know which was the Se elemental phase in Persson's work but, assuming it was the diatomic Se molecule, the difference in value for  $\mu_{Se}$  can be due to the DFT functional being used. Compared to B3LYP, LDA and GGA are well known for overestimating the values of the total energies of molecules [63], which would result in an increase in the value of the chemical potential of Se and, consequently, a reduction in the value of  $\Delta G_{CuGaSe}$ .



Fig. 4. Top and lateral views of the relaxed: (a) Se-terminated and (b) CuGa-terminated (1×1) (001) surfaces of CuGaSe<sub>2</sub>.



Fig. 5. Unrelaxed Se-terminated (1×1) (001) surface. The black rectangle represents the (4×1) unit cell and the Se inside this cell is labelled 1-8.

unrelaxed Se-terminated (001) surface as a reference. The black rectangle indicates a  $(4 \times 1)$  surface unit cell, the atomic positions of Se in the top layer are numbered from 1 to 8. In Fig. 6 top and side views of the reconstructions studied in this work are displayed.

Reconstruction 6(a) is a (001) CuSe-terminated surface that is generated by the removal of the top layer of Ga atoms from the CuGa-terminated surface shown in Fig. 4(b). Reconstruction 6(d) is nearly stoichiometric (Cu<sub>0.917</sub>GaSe<sub>2</sub>): It is made by removing four Se atoms at locations 2, 4, 6 and 8, and then the Cu atom below Se 2 and 6. In reconstruction 6(c) the Cu atom below Se 2 and Se 6 is replaced by Na: The reconstructions 6(d) and (c) do not display dimerisation of surface Se. On the contrary, reconstruction 6(b), which is made by removing two Se atoms at positions 2 and 6 and the Cu atom below, has a Se-rich stoichiometry of Cu<sub>0.917</sub>GaSe<sub>2.167</sub> and presents dimerisation of the surface Se.

Fig. 7 shows the surface energies of the ideal Se-terminated, CuGaterminated and CuSe-terminated (1×1) surfaces, plus the (4×1) (b), (c) and (d) reconstructions. These surface energies are plotted as a function of the chemical potentials of Se, Cu and Ga, which are represented by the variables  $\Delta \mu_i$ . These variables have been constrained to vary along the border of the stability region set up in Fig. 3. In this figure, segments 1–5 and 1–2 represent the Cu and Ga rich regions, and segment 3–4 represents the Se rich region. Segment 2–3 ranges from intermediate conditions to the Se rich condition, and segment 4–5 encompasses both intermediate and extreme conditions.

The ideal  $(1 \times 1)$  CuGa-terminated surface is unstable under all environmental conditions and has the highest surface energy among the surfaces modelled. The  $(1 \times 1)$  Se-terminated surface is stable under most of the studied environmental conditions and at Se-rich conditions -along segment 3-4- it has the lowest surface energy of all reconstructions. The  $(1 \times 1)$  CuSe-termination (a) has the same energy as the  $(1 \times 1)$  CuGa-termination along the 5–1 segment, but otherwise is of lower energy than the CuGa-termination. Reconstruction  $(4 \times 1)(d)$  is nearly stoichiometric and, as a result, its energy is relatively insensitive to the environmental conditions. The atomic structure of reconstruction  $(4 \times 1)(c)$  is similar to reconstruction  $(4 \times 1)$ (d), except that a Na atom is replacing a Cu atom in the surface layer. The surface energy of reconstruction  $(4 \times 1)(c)$  is plotted along the border of the stability region for the two limiting values of  $\Delta \mu_{Na}$  as defined in Section 2.2. Na has a stabilising effect on the reconstructions in the upper limits of  $\Delta \mu_{Na}$ . As a result, in a Na-rich environment and under Cu-rich, Ga-rich and Se-poor conditions (point 1 Fig. 7), reconstruction  $(4 \times 1)(c)$  has the lowest surface energy.

We propose two complementary mechanisms for surface stabilisation. The first one is the ability of a surface reconstruction to coordinate Ga and Cu atoms at the surface, and the second one is the ability of the surface Se to eliminate dangling bonds. It is clear from Figs. 4 and 6 that Cu and Ga coordination is achieved with Seterminated surfaces. The surface Se then eliminates dangling bonds through dimerisation. It is for this reason that the unreconstructed Se-terminated surface is stable for most environmental conditions. Except from the Se-poor environmental conditions described by region 5–1in Fig. 3, it is the Cu and Ga coordination to Se which dominates the surface energy, and this helps explain the low surface energies of reconstructions  $(4 \times 1)(b)$  and Se-terminated  $(1 \times 1)$ , and the large surface energies of reconstructions  $(4 \times 1)(d)$ ,  $(4 \times 1)$ (c) and  $(1 \times 1)(a)$ .

The effects of surface Se dimerisation can be seen in the corresponding partial density of states (PDOS), and in the bond population of the Se forming the dimers. In bulk chalcopyrite-type CuGaSe<sub>2</sub>, Cu and Ga are tetrahedrally coordinated by four Se atoms. There are bond populations of 0.268|e| between Ga and Se and 0.183|e| between Cu and Se, but between Cu-Cu, Cu-Ga, Ga-Ga and Se-Se, the bond populations are of the order of at most 0.01|e|. For the  $(1 \times 1)$  Se-terminated surface indicated in Fig. 4(a), the bond population in the Se-dimers at the surface is 0.13|e|. As regards the  $(4 \times 1)$ reconstructions, only the Se dimers on surface (Fig. 6(b)) present a significant bond population of 0.128|e]: in all the other  $(4 \times 1)$  reconstructions, the bond population for the surface Se - Se contacts is negligible. Fig. 8 shows the PDOS of the  $(1 \times 1)$  and  $(4 \times 1)$  surface reconstructions described in Figs. 4(a) and 6(b), (c) and (d). The total DOS is projected onto contributions for Ga, Cu and Se bulk atoms, and onto pairs of surface Se atoms which have the closest interatomic distances in all the slab, and which are likely to be forming surface dimers. The clearest signature of surface Se dimerisation is the anti-bonding states of the surface Se dimers, which are indicated by their PDOS. Fig. 8(a) and (b) shows large peaks of surface Se PDOS above the Fermi energy. From a molecular orbital point of view, these peaks can be interpreted as empty antibonding orbitals of the surface Se dimers. These surface Se PDOS peaks disappear from the conduction band in Fig. 8(c) and (d), which indicates occupation of all the bonding and antibonding orbitals of the surface Se dimers, decreasing the covalent nature of the Se bonding at the surface. Except from the Se-poor environmental conditions described by region 5-1in Fig. 3, the surface energies of reconstructions (Fig. 8(a), (b), (c) and (d)), under most environmental conditions, is correlated with the bond population of its surface Se dimers: low surface energies are strongly related to high Se-Se bond populations.

It is well known that in chalcopyrites such as CuAlS<sub>2</sub> [46], CuGaS<sub>2</sub> [47], CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> [21] Cu vacancies have the lowest formation energies under most environmental conditions. When chalcopyrites are doped with Na, AES evidence shows that Na tends to accumulate at the surfaces and grain boundaries [48]. An example of this is CuInSe<sub>2</sub>: If available in large quantities, Na will replace Cu and form the more stable NaInSe<sub>2</sub> compound, which will precipitate to form a separate phase; when available in small quantities, Na will replace Cu and In atoms, forming Na<sub>Cu</sub> and Na<sub>In</sub> defects. The concentration of Na<sub>Cu</sub> defects is higher than the concentration of In<sub>Cu</sub> defects [49]. This results in the quenching of the In<sub>Cu</sub> and V<sub>Cu</sub> defects, which results in a decrease of the concentration of the  $(2V_{cu}^{-1} + In_{cu}^{-2})$  complex defect. The presence of small quantities of Na then contributes to the synthesis of Cu-poor chalcopyrites, avoiding the formation of the



**Fig. 6.** Studied surface reconstructions on the (001) surface of CuGaSe<sub>2</sub>. (a) is a (1×1) CuSe-terminated surface generated by removing Ga atoms from the (1×1) CuGa-terminated surface. (b) is made by removing the Se atoms 2 and 6, and the Cu atom below them, from the unreconstructed Se-terminated surface shown in Fig. 5 and has a Cu<sub>0.917</sub>GaSe<sub>2.167</sub> stoichiometry. In reconstruction (c) Se atoms 2 and 6 are removed and the Cu atom below them is replaced by Na. Finally, (d) has a Cu<sub>0.917</sub>GaSe<sub>2</sub> stoichiometry and it is made by removing four Se atoms at locations 2, 4, 6 and 8, and then the Cu atom below Se 2 and 6.



**Fig. 7.** Surface energies of the ideal Se-terminated, CuGa-terminated and CuSe-terminated  $(1 \times 1)$  surfaces, plus the  $(4 \times 1)(b)$ , (c) and (d) reconstructions. These energies are plotted as a function of the chemical potentials of Se, Cu and Ga, which are constrained to vary along the border of the stability region set up in Fig. 3.



**Fig. 8.** Projected densities of states (PDOS) of different surface reconstructions on the (001) surface of CuGaSe<sub>2</sub>. (a) shows the PDOS of the  $(1 \times 1)$  Se-terminated surface. (b) (c) and (d) show the PDOS of the  $(4 \times 1)$  reconstructions shown in Figs. 6(b), (c) and (d).

so called ordered defective compounds [50], increasing the p-type layer conductivity [51], and reducing the dependence on the compositional ratio of Cu/ln [52].

Moreover, Na enhances key features of polycrystalline Cu(In/Ga) Se<sub>2</sub> (CIGS) thin-film solar cells, such as the fill factor (FF) and the open circuit voltage [53,54]. Na is normally incorporated into CIGS films, during the deposition process, by thermal diffusion from a soda lime glass substrate. However, to improve the performance of nonalkali-substrate-based CIGS solar cells, various methods for Na incorporation have been reported, including co-evaporation of Na compounds during CIGS deposition [52] and deposition of a SiO<sub>x</sub>:Na layer prior to Mo deposition [55]. Among these methods of Na incorporation, evaporating NaF is one of the most effective ways: In this method, Na diffusion into CIGS differs from that of soda lime glass, and high-quality CIGS films could be obtained at low temperature [56]. Na also has the ability to retain Se at the surface. Experimental evidence [57–59] shows that, at Na-rich conditions, Na is likely to be forming Na<sub>2</sub>Se which, in turn, will form Na polyselenides such as Na<sub>2</sub>Se<sub>2</sub>. The formation of Na<sub>2</sub>Se<sub>2</sub> is an exothermic process and energy is needed to remove Se from the surface. The role of Na in chalcopyrites has been theoretically studied as well. Y. Yan and coworkers [60] used ab initio calculations to analyse the electronic structure of the CuInSe's grain boundaries, and they discussed the effect of Na in them. In particular, they defined a "segregation energy", that estimates how expensive it is for a Na atom to diffuse into a grain boundary. No thermodynamics was used in the definition of this energy: they only used ab initio total energies, which restricted the range of possible segregation energy values to only one.

Se-dimerisation helps to explain surface stability under most environmental conditions, except from the conditions under which the  $(4 \times 1)$  reconstructions were observed. LEED measurements show that  $(4 \times 1)$  reconstructions form on CuGaSe<sub>2</sub> (001) after several cycles of Ar<sup>+</sup> ion bombardment and subsequent annealing at UHV conditions. The observed surface reconstructions were clean, stable and unfacetted, with a Se-rich and Cu-poor stoichiometry [13]. Since we assume Se is present in the gas phase, the experimental UHV conditions can be represented in our phase diagram by low values of the  $\mu_{\text{Se}}$ . According to Eq. (7), region 5–1 in Fig. 3 has the lowest values of  $\mu_{Se}$  that can be achieved in a Cu, Ga and Se system. Under these conditions, reconstruction  $(4 \times 1)(b)$  has a lower surface energy than Seterminated  $(1 \times 1)$  surface and, under Na-rich conditions, the stable surface reconstruction is reconstruction  $(4 \times 1)(c)$ . Both these surfaces have Cu-poor and Se-rich stoichiometries of Cu<sub>0.97</sub>GaSe<sub>2.167</sub> and Cu<sub>0.97</sub>GaSe<sub>2</sub> respectively. The distance between the surface Se in reconstruction  $(4 \times 1)(c)$  lengthens by an average of 0.261 Å<sub>2</sub> when compared to that of reconstruction  $(4 \times 1)(b)$ , and Se dimerisation at the surface has disappeared. The limiting values of  $\Delta \mu_{Na}$  are calculated combining Eqs. (10) and (11). Region 5-1 of Fig. 3 is a Na-rich region and, in it, reconstruction  $(4 \times 1)(c)$  is predicted to be the stable one.

# 4. Conclusions

Ab initio thermodynamics has been used to study the stability of different surface reconstructions that were observed in CuGaSe<sub>2</sub> (001). It has been shown that, for most environmental conditions, the presence of Se at the surface, with its ability to dimerise and coordinate Cu and Ga ions at the surface, it is the main mechanism stabilising the surface. In particular, the atomic structure of the experimentally observed  $(4 \times 1)$  surface reconstructions can be described by Cu-poor Se-rich reconstructions  $(4 \times 1)(b)$  and (c), and it was established that the presence of Na stabilises the  $(4 \times 1)$  reconstruction.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.susc.2011.11.018.

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