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Chalcogen passivation of GaAs(1 0 0) surfaces: theoretical study

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Abstract

In this work, structural and electronic properties of Se- and S-passivated GaAs(1 0 0) surface reconstructions are investigated by density functional theory (DFT) based methods. We have performed total energy minimization of several model geometries of the reconstructed surfaces at different stoichiometry. The common feature is the appearance of a chalcogen layer on top of the Ga terminated surface, forming a Ga-chalcogenid like monolayer. In the case of selenium (Se), monomeric first layer formation is predicted, while in extrem chemically circumstances the sulphur (S) passivated surface can also reconstruct forming S-dimers. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

The GaAs(1 0 0) surface is one of the most studied polar semiconductor surfaces. It has attracted much interest, of both experimentalists and theoreticians because of its importance for the growth of multilayer device structures [1,2]. To improve the quality of organic thin layers grown upon these surfaces, chemical passivation is used, usually by depositing a chalcogenide on the GaAs(1 0 0) surface [3].

The clean GaAs surface has a high density of surface states. The purpose of the passivation is to remove these gap states and to make the surface inert against foreign atoms.

Group-VI elements are preferentially used for covalent crystals passivation. S, Se, or Te on GaAs(1 0 0) have been analysed by several authors. Pashley and Li [4,5] considered the Se/GaAs(1 0 0) surface and found, a well ordered (2 × 1) construction, using STM. Based on this evidence and on independent photoemission data [6], they proposed a structural model for this surface, satisfying the electron counting rule [7]. In their model Se located simultaneously below the surface replacing As, and also on the surface forming surface dimers. Gundel and Faschinger [8] have studied theoretically the cases of the Se and Te on GaAs(1 0 0), and have considered various possible structures. Based on LDA calculations, they concluded that the structures e, i (see Fig. 1) and an other Se rich (Fig. 2/6A of [8]) surface are the most stable ones under different chemical conditions.

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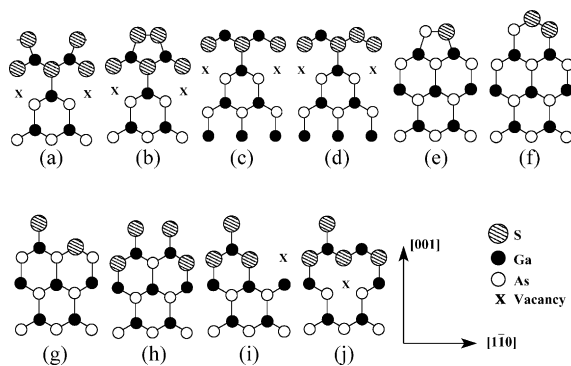


Fig. 1. Schematic ball and stick models of the structures considered in this work.

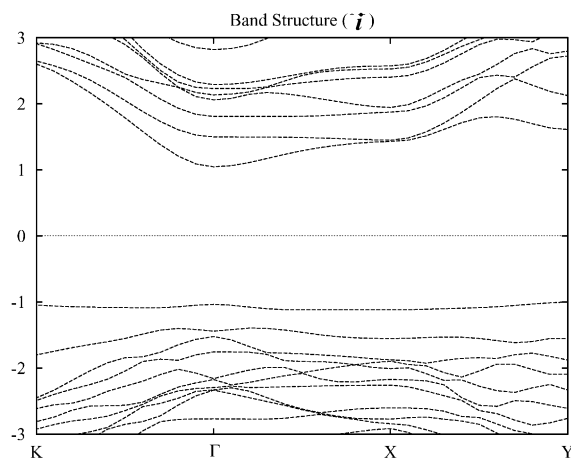


Fig. 2. Surface bands for structure Se/GaAs i.

In case of the S-passivated GaAs(1 0 0) the RHEED and LEED measurements suggest—depending on the temperature— 1×1 and 2×1 reconstruction for the Ga terminated surface [9–13]. Based on the photoelectron core-level spectroscopy and reflectance anisotropy measurements, the surface stoichiometry has not been completely clarified yet. While Moriarty et al. have considered mainly S–S surface dimer pairs [12], others observed not only Ga–S but Ga–Ga dimer pairs as well as S–As surface bonds depending on the initial substrate [14]. Moriarty’s study assumed a second S-sublayer, below the first atomic layer, because they detected two distinct S-bonding configurations by XPS measurements in the sulphur spectrum. Zahn et al. confirmed the existence of the chalcogenide-sublayer in case S- and Se-passivated GaAs [17]. Moreover, they

compared the XPS spectra of the Se- and S-passivated surfaces, and concluded that the two structure’s reconstruction have to be very similar to each other.

The sulphur monolayer on GaAs has already been investigated theoretically using first-principles pseudopotential calculations [15,16]. It was found that S adsorbs on the bridge site of either Ga- or As-terminated surface, but the GaS dimer coverage was predicted to be slightly metallic.

In this work we investigated theoretically the Se- and S-passivated GaAs(1 0 0) 2×1 surface reconstruction. For the Se/GaAs(1 0 0) 2×1 surface geometry we assume a single Se-atom instead of the Se-dimers postulated by Pashley and Li [4]. This is based on the STM-images, which seem to show a single Se-atom geometry (see details below). About the S/GaAs surface we assumed that it behaves similarly to the Se/GaAs, not only monolayer S adsorbs on the GaAs. Guided by some experimental results, and keeping in mind the electron counting rule we made calculations on the surface models depicted in Fig. 1. We present the corresponding surface formation energies as a function of different chemical potentials. We found that the surface structure depends the strongest on the sulphur chemical potential.

2. DFT-calculations

We use approximate methods based on the density functional theory. For the Se/GaAs the Fireball’96-code [18] was used, and the S/GaAs structures were calculated with the SCC-DFTB code (self-consistent-charge density functional tight binding) [19]. Both methods use localized orbitals as basis functions generated by solving the atomic problem within the DFT-LDA. The optimum structures have been determined by total energy minimization.

The surfaces were modeled by 9 monolayer thick slabs with periodic boundary conditions in two dimensions. The first 7 (6) monolayers were allowed to relax—in case of Se and (S) passivated GaAs, respectively—while the remaining atoms were fixed to preserve the bulk lattice spacing. In order to prevent the artificial charge transfer between the bottom of the slabs and the surface, we saturate the dangling bonds on the Ga terminated bottom with appropriately parametrized pseudo-hydrogen.

3. Results

3.1. Se/GaAs

Based on the experimental data for the Se/GaAs we made calculations the structures depicted in Fig. 1 (structures f, i and j) and in [4] (Pashley' structure *P*) [20]. Confirming the results of Gundel and Faschinger we conclude that the *i*-structure is the most stable one for a large range of the chemical potential (except for $\mu_{\text{As}} = \mu_{\text{As}}^{\text{bulk}}$ and $\mu_{\text{Se}} \cong \mu_{\text{Se}}^{\text{bulk}} - 1.8$ eV).

STM-simulations have been carried out [20] for the *i* (our preferred structure), and *P* for the Pashley model, to assess the validity of the obtained structural model. Analyzing the STM-currents and surface topography we find that the *i*-structure shows the largest (0.48 Å)

surface corrugation. This confirms that the Se-passivated surface contains only a single Se-atom in the top layer, in contrast with Se-dimers proposed by others [4]. The electronic band structure has a ~ 2 eV energy gap (see Fig. 2). Based on the local density of states (LDOS) associated with the surface layer atoms in Fig. 3 we can see that the topmost valence band is associated with the surface Se-atom, while the lowest conduction band is associated with bonds formed between the Se- and Ga-atoms of the 3rd and 4th layers. The detailed LDOS of the topmost Se-atoms with respect to the atomic orbitals reveals the p_x -character of the topmost valence band (x parallel to the surface).

3.2. S/GaAs

To investigate (2×1) structures (see Fig. 1), and the Pashley model (*P*) [4] we calculated the surface energy (Γ)/unit cell (as in, e.g. [8]). $\Gamma = E_{\text{tot}} - \sum_i \mu_i N_i$, where E_{tot} denotes the total energy of one supercell as obtained in the simulation, and μ_i and N_i the chemical potential and number of atoms of constituent i , respectively, within the supercell. Since it is hard to determine the chemical potential with the desired accuracy, we evaluated our results in a wide range (from the atomic sulphur till the eight molecules S-ring (bulk) form). Over this range we found four stable structures: the b, f, g and i see Fig. 4

In the first part, for the sulphur potential close to the atomic sulphur value gallium-sulfide terminated structures become stable under Ga rich circumstances: $\mu_{\text{As}} = \mu_{\text{As}}^{\text{bulk}} - \Delta H_f^0$. In these cases sulphur atoms occupy not only the top layer, but also the third layer positions. The sulphur atoms preferred integrating in the GaAs surface, replacing As-atoms. The first layers of structures are missing arsenic atoms and resemble a gallium-sulfide like layer. If the S chemical potential is close to the bulk value (the eight rings case), and the GaAs surface is rich in As, the favourable S/GaAs structures contain sulphur only in the top layer. In these structures S–As surface bonding also appears (f, g). These results are in good agreement with the experimental observations [14].

All the studied structures provide for a semiconductor surface. In case f, g and i, there are no remaining gap states, while in case b the number of gap states decreases substantially. Based on the LDOS

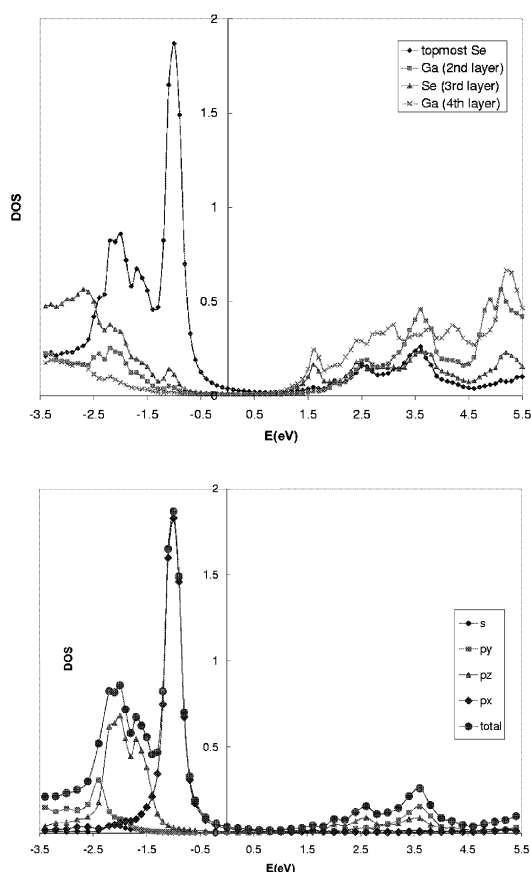


Fig. 3. LDOS for the atoms in the last four layers of the Se/GaAs *i*-structure (top). The projection on the different orbitals is shown for the topmost Se-atoms (bottom).

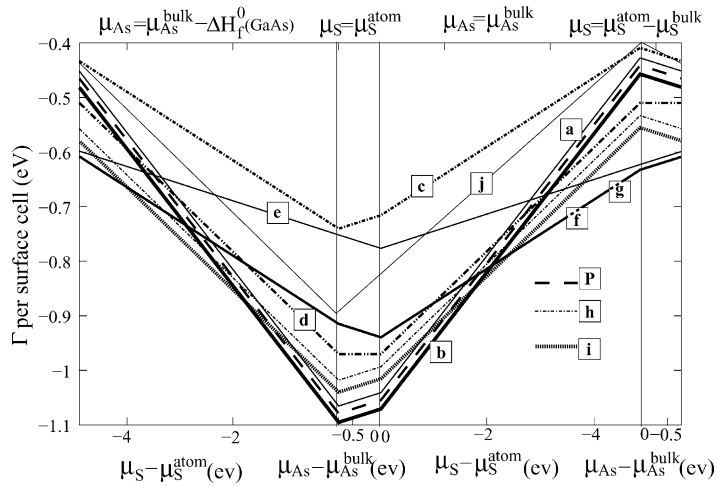


Fig. 4. Surface energy per surface cell of the S-adsorbed GaAs surface for the Fig. 1 and for the Pashley (*P*) [4] structures. Γ is given as a function of S and As chemical potential. It is allowed to change always either the μ_{As} or the μ_{S} value. Over the figure are the pinned values and below are given the changing chemical potentials.

calculation we can compare the Se- and S-passivated structures. The *i*-structure, the preferred one for Se passivation, is found also stable for a relatively large range of the S chemical potential on Ga rich GaAs. The top sulphur atoms occupied dangling bond perpendicular to the surface constitutes mainly the valence band edge states, and the third layer sulphur atoms' dangling bonds contribute $\sim 10\%$. The conduction band is associated with antibonding states formed between the S and Ga-atoms of the 3th and 4th crystal layers, similarly to the Se-passivated structure.

In our calculations the S–S dimer structure relaxed to (2×2) surface reconstruction, building an alternating dimer row. The topmost valence band is associated with the dangling bonds of the first and the third layer twofold coordinated sulphur atoms. The conduction band states are influenced by the Ga-atoms of the 2th crystal layers.

In As-rich material we found two possible surface reconstructions. LDOS calculations show that in the *f* structure the valence band edge states consist mainly of the topmost surface As dangling bond. At the *g*-structure the valence band edge surface states depend mainly on the top S-atoms dangling bond out of plane. The second top layer sulphur atom and the surface As-atoms contribute equally to the top valence band state also.

Our calculations concern different passivation circumstances. By the wet chemical passivation process

the sulphur is dissolved what can be described by strong approximations only, with a big margin of error. In the case of Se/GaAs we expect the *i* reconstruction based on the similarity between the simulated and the measured STM picture. For S/GaAs STM measurements are not available. We can make some additional consideration. First, the experimental results [17] predict almost the same surface reconstruction for the Se/GaAs and S/GaAs in Ga terminated case. Second, according to our calculation the LDOS of the two chalcogen passivated surface are very similar to each other for the *i*-structure. Finally the LEED measurements suggest a (2×1) surface reconstruction which can satisfy the *i*-structure but not the *b* structure. In summary, we can assume that the S/GaAs surface reconstructs to the *i*-structure in Ga terminated initial surface case.

4. Conclusion

We investigated Se- and S-passivated GaAs(1 0 0) surfaces. DFT based tight binding calculations and STM-image simulations suggest a gallium selenide like surface reconstruction, which is in agreement with the photoemission spectroscopy results. For S-passivated surfaces, for Ga rich GaAs case, structures with gallium-sulfide like overlayers were found.

The two energetically most favourable structures are the S–S dimer (2×2) surface reconstruction and the (2×1) reconstruction with one S-atom in the top layer. Based on the above considerations, we assume that for the most frequently used passivation circumstances the S-passivated surface reconstruction is similar to the Se/GaAs reconstruction. Both structures give rise to a semiconductor surface.

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