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Surface properties of chalcogen passivated GaAs(1 0 0)

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Abstract

Chalcogen atoms like sulphur or selenium are promising candidates for the passivation of GaAs(1 0 0) surfaces. The passivation can be obtained by evaporation of S or Se under ultra-high vacuum (UHV) conditions or by etching in chalcogen containing solutions. In both cases, an additional annealing of the samples leads to Ga-chalcogenide like surface layers showing a 2×1 low energy electron diffraction (LEED) pattern. We have analysed the Se/GaAs(1 0 0)- 2×1 geometry in detail by means of density functional theory (DFT) calculations. Comparing with photoemission data and scanning tunnelling microscopy (STM) currents we conclude that this geometry has a single Se atom in the last crystal layer bonded to two Ga atoms of the second layer, and another Se layer replacing the third As layer. While the theoretical calculations show that the band gap of Se-passivated GaAs(1 0 0) surfaces are free from surface states, the experimental data show a band bending that depends on the details of the passivation procedure used.

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1. Introduction

Chalcogen atoms have been successfully used for the passivation of GaAs(1 0 0) surfaces. A wet chemical etching of GaAs(1 0 0) in sulphide solutions results in an improvement of the performance of devices like bipolar transistors [1] or laser diodes [2–4]. The chalcogen passivation also improves the structural properties of a wide variety of materials grown on GaAs(1 0 0). Here, the epitaxial growth of iron films [5] or 3,4,9,10-perylene-tetracarboxylic dianhydride

(PTCDA) on chalcogen treated GaAs(1 0 0) surfaces should be mentioned [6,7]. The experimental results show that the chalcogen treatment chemically passivates the surfaces and reduces the band bending compared to non-passivated GaAs(1 0 0) [8].

During the passivation of GaAs(1 0 0) surfaces with chalcogen atoms an exchange reaction between the chalcogen atoms and the group V atoms at the surface results in the formation of a thin Ga-chalcogenide like layer at the surface showing a 2×1 reconstruction. Besides the experimental results presented up to now the detailed atomic structure is still under discussion. Pashley and co-workers have proposed a model (4C in Fig. 1) where the surface is terminated with a layer of chalcogen dimers, followed by a Ga layer and a second

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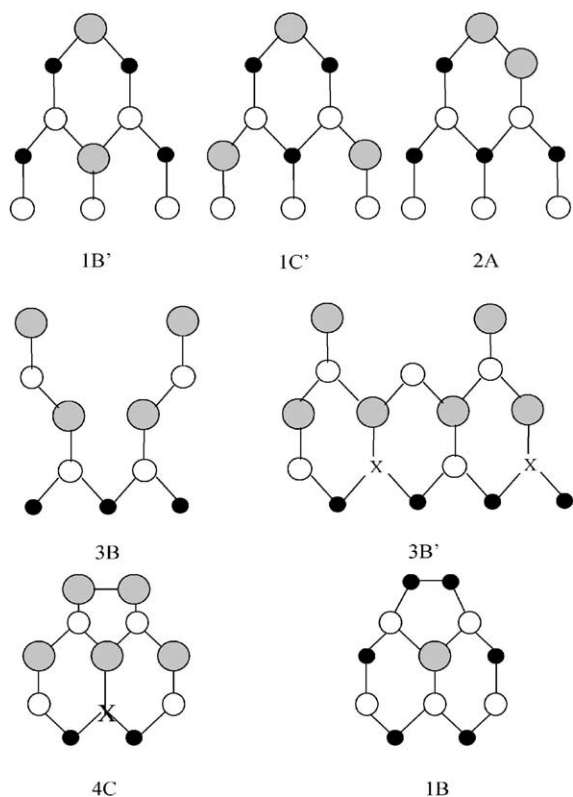


Fig. 1. Schematic ball-and-stick models of the structures considered in this work for the Se/GaAs(1 0 0) system. Grey circles correspond to Se atoms, white circles to Ga atoms and black circles to As atoms.

layer of chalcogen atoms [9,10]. The fourth atomic layer contains an equal amount of Ga atoms and vacancies and is followed by the GaAs bulk starting with an As layer. This structure model satisfies the electron counting rule [11]. Gundel and Faschinger [12] presented another promising structure model (3B) which has been further supported by DFT LDA calculations by Benito and co-workers [13]. In this structure model, the Se atoms do not form dimers on the surface and the second Ga layer is free of vacancies.

Other possible candidates for the ground state of the passivated system are structures 1B', 1C', and 2A, which also satisfy the experimentally observed 2×1 reconstruction and the electron counting rule. They have the same stoichiometry, with Se-atoms replacing As atoms at different sites. Structure 2A was already studied by Gundel and Faschinger [12]. Structures 1B' and 1C' have only one Se on top.

In this study, we present a combined experimental and theoretical study of the chemical, electronic and structural properties of selenium and sulphur modified GaAs(1 0 0) surfaces. A detailed discussion of the preparation of Se-passivated GaAs(1 0 0) surfaces and their characterisation by photoemission spectroscopy and theoretical calculated scanning tunnelling microscopy (STM) topographies will be presented elsewhere [13]. Here, we present the most important results of this study and compare passivated surfaces obtained by sulphur or selenium passivation using a treatment under ultra-high vacuum (UHV) conditions or wet chemical etching. The experimental results from soft X-ray photoemission spectroscopy (SXPS) and low energy electron diffraction (LEED) restrict the number of possible geometries to three. The most appropriate structure model is then determined by comparing theoretical calculated and experimentally determined corrugations in STM topographies.

2. Experimental

For the chalcogen passivation of GaAs(1 0 0) two different techniques were used: exposure to a flux of chalcogen atoms under UHV conditions and wet chemical etching in sulphur containing solutions. For the UHV treatment homoepitaxial n- and p-type GaAs(1 0 0) layers with a doping concentration of $N = 1 \times 10^{18} \text{ cm}^{-3}$ served as substrates in this study. After their growth by molecular beam epitaxy they were covered by a thick amorphous arsenic layer to protect the GaAs(1 0 0) surfaces against contamination and oxidation. These samples were transferred into an UHV system with a base pressure of $P < 2 \times 10^{-10}$ mbar. The arsenic layer was then removed by gentle annealing to 380 °C. This leads to an As-rich $c(4 \times 4)$ or $c(2 \times 4)$ surface reconstruction of the GaAs(1 0 0) surface as can be judged from the line-shape analysis of the measured photoemission spectra and additional LEED experiments. For the chalcogen passivation, the compounds SnS_2 and SnSe_2 were used as source materials. These compounds decompose at 340 and 550 °C according to $\text{SnSe}_2 \rightarrow \text{SnSe} + \text{Se}\uparrow$ and $\text{SnS}_2 \rightarrow \text{SnS} + \text{S}\uparrow$, respectively [14]. Sulphur and selenium were evaporated onto the substrates kept at 330 and 500 °C, respectively. For the wet chemical, sulphur passivation samples were first degreased and

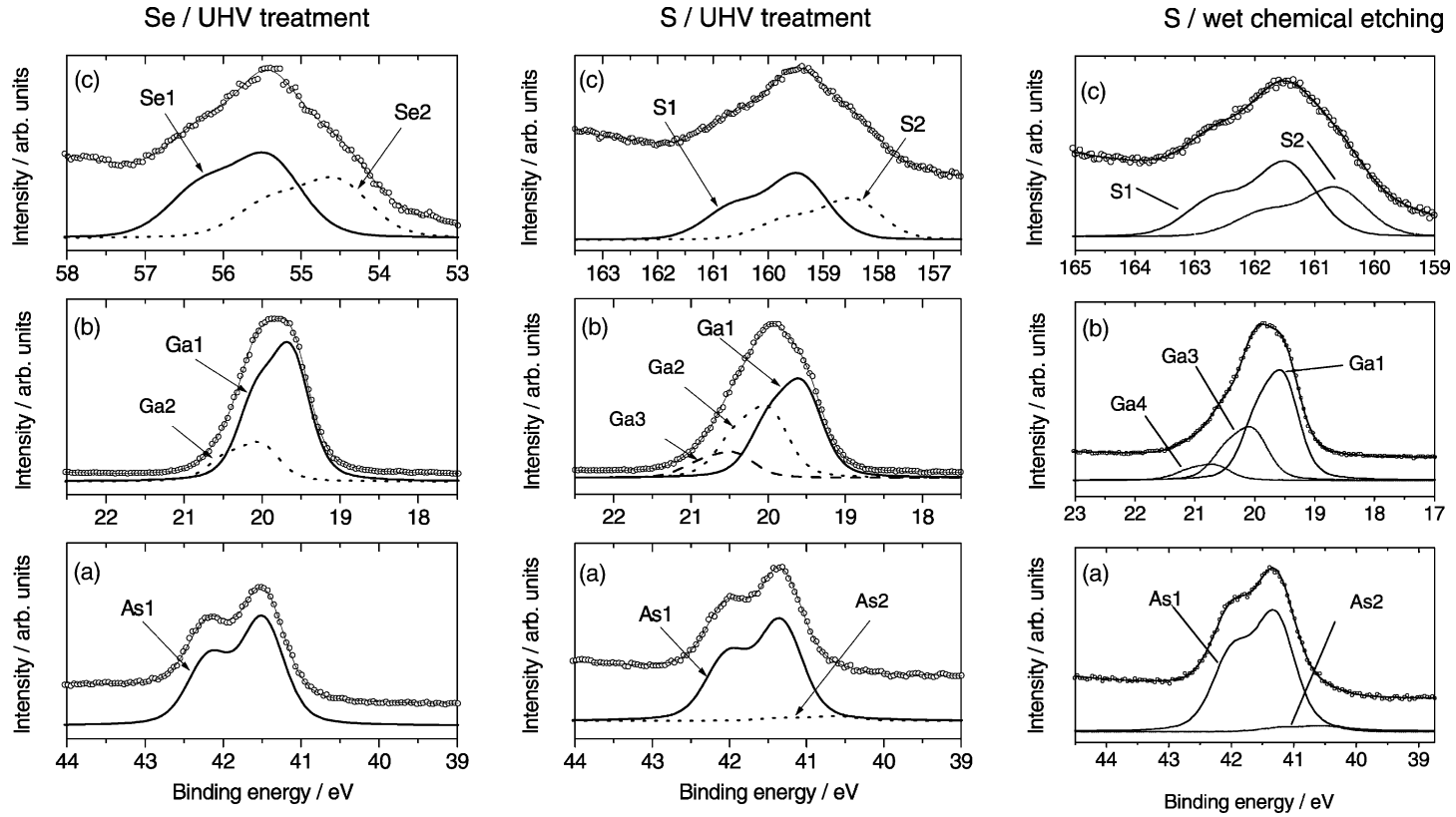


Fig. 2. Photoemission spectra of the chalcogen modified GaAs(1 0 0) surface prepared by different treatments: (a) the As 3d core level at 79 eV photon energy, (b) the Ga 3d core level at 60 eV photon energy and (c) Se 3d at 88 eV photon energy/S 2p at 195 eV photon energy. Binding energies are given with respect to the Fermi-level.

then etched in a 3:1 mixture of CCl_4 and S_2Cl_2 for 10 s. The etching is followed rinsing the samples successively in CCl_4 , acetone, ethanol and de-ionised water for 5 s each. After transferring the samples into a UHV system they are annealed at 430 °C. Both procedures lead to a well ordered (2×1) reconstructed surface as revealed by LEED [15].

The photoemission measurements were performed at the TGM 2 beamline of the synchrotron radiation source BESSY at Berlin. The UHV chamber at this beamline is equipped with a VG ADES 400 electron spectrometer providing a combined resolution of both light and photoelectrons of about 300 meV at 65 eV photon energy. The photoemission spectra were taken under surface sensitive conditions i.e. minimum escape depth of the detected photoelectrons.

3. Results and discussion

The photoelectron core level spectra were curve fitted using Voigt profiles and a non-linear least squares fitting routine. During curve fitting, the Lorentzian linewidth, spin-orbit splitting, and branching ratio were kept fixed at values providing satisfactory results over an entire series of spectra. The peak intensity, position, and Gaussian linewidth were variable. All binding energies are given for the $d_{5/2}$ or $p_{3/2}$ components of the spin orbit split core levels relative to the Fermi-level.

The As 3d, Ga 3d, Se 3d, and S 2p core level emission spectra for the GaAs(1 0 0) surfaces are shown in Fig. 2. For the Se-passivation under UHV conditions the As 3d consists only of one component As1 which is attributed to As in the four-fold co-ordinated environment of the GaAs bulk. The Ga 3d core level consists of two components: a bulk component Ga1 and a surface component Ga2 shifted by 0.37 eV towards higher binding energies. This surface component is attributed to Ga bonded to Se on the surface. The two Se 3d components Se1 and Se2 separated by 0.91 eV are attributed to surface and subsurface components, respectively. The shape of the Se 3d core level is similar to the Se 3d obtained for Ga_2Se_3 the only difference being a slightly larger energy difference between the Se1 and Se2 components of 1 eV for Ga_2Se_3 .

The S-passivated GaAs(1 0 0) surfaces obtained by either UHV treatment or wet chemical etching show

comparable core level emission spectra. As in the case of Se 3d, the S 2p core level consists of two components attributed to surface (S1) and subsurface (S2) sulphur. The Ga 3d and the As 3d are slightly different from the Se-passivated GaAs(1 0 0) showing two additional interface components Ga3 and As2. The similarity in the Se 3d and the S 2p leads to the conclusion that the S-passivation leads to the formation of a Ga_2S_3 like layer. The two interface components indicate that the As–S exchange reaction is less efficient than the As–Se exchange reaction, resulting in a less abrupt interface between Ga_2S_3 layer and GaAs bulk. This is supported by the fact, that a higher temperature is necessary for the S-passivation. All passivation processes result in surfaces showing a 2×1 reconstruction which survives considerable exposure to air revealing the chemical stability of the passivated surfaces. Since the As 3d core level shows only one component and the chalcogen atoms are found in two different chemical environments the number of possible structure model is reduced to structure 3B, 3B', and 4C.

The ionisation energy and the position of the Fermi-level with respect to the valence band maximum on the

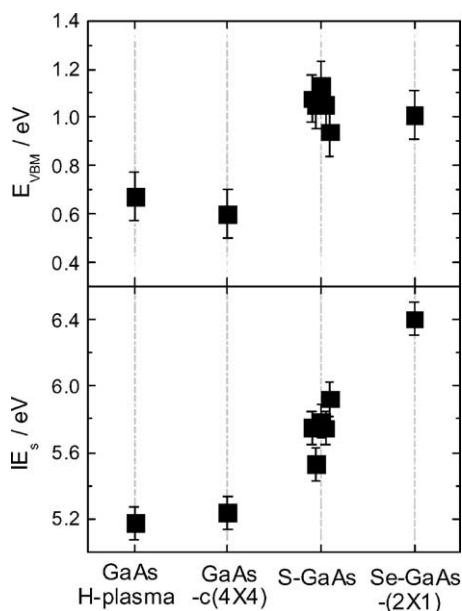


Fig. 3. Ionisation energy IE_s and position of the Fermi-level with respect to the valence band maximum E_{VBM} for differently treated GaAs(1 0 0) surfaces.

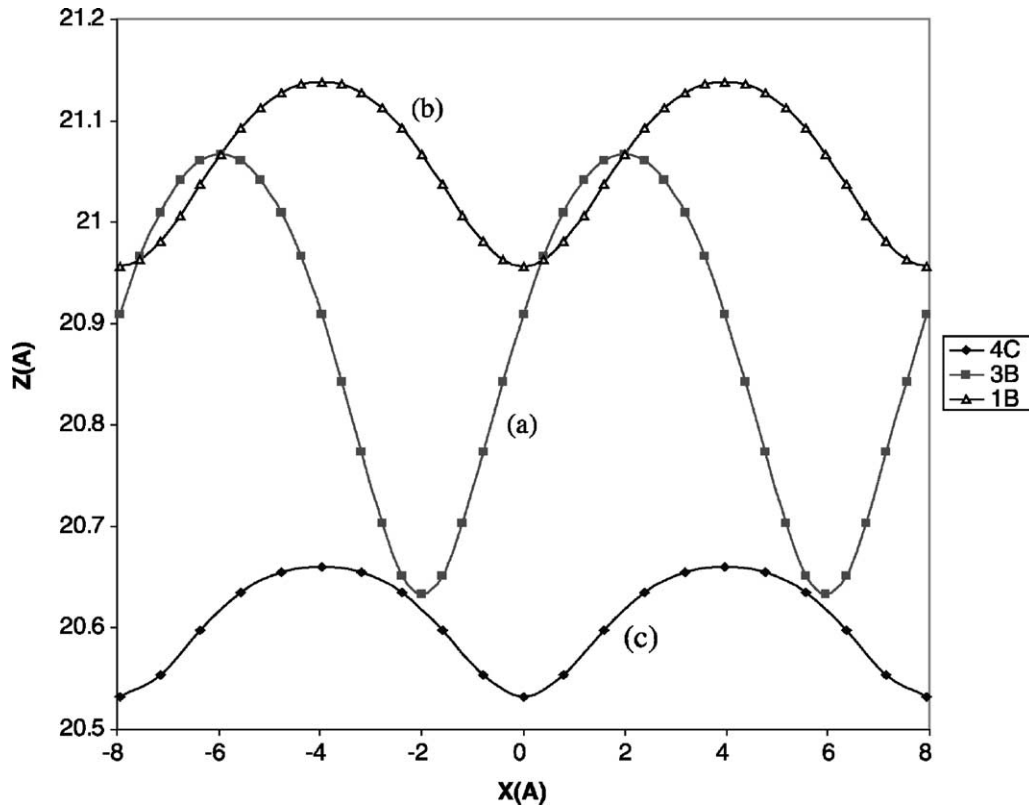


Fig. 4. Corrugation in surface topography along the Se dimers of the 4C (c) compared to 3B (a) and 1B (b) in the same direction. Units are given in Å.

chalcogen passivated surfaces compared to non-passivated surfaces are shown in Fig. 3. On samples cleaned by a H-plasma or by decapping of the As layer the Fermi-level is at about 0.65 and 0.6 eV above the valence band maximum, respectively. The chalcogen treatments shift the Fermi-level by about 0.4 eV towards the conduction band minimum. Compared to non-passivated samples the band bending is thus reduced to 0.4 eV for n-type GaAs. The ionisation energy, on the other hand, increases as a function of the chalcogen treatment. Since S and Se have a larger electronegativity than Ga, negative charge is transferred to the chalcogen atoms. This results in a surface dipole which increases the ionisation energy. The larger change in ionisation energy due to the Se treatment may be explained by the more efficient formation of a Ga-chalcogenide like layer.

The three structure models 3B, 3B', and 4C (see Fig. 1) supported by the photoemission spectroscopy

data will now be investigated in more detail by energy minimisation calculations using a first-principle local-orbital code (Fireball96) [16]. In our calculations, structure 3B' is by 4.0 eV energetically less favourable than the structure 3B due to creating the fourth-layer Ga vacancy. This leaves the structures 4C and 3B where the latter one is the most stable one. For these two structures and structure 1B the corrugation in the STM topography along the directions defined by the dimers in 4C and 1B is calculated. In structure 1B the surface is terminated by As dimers simulating the arrangement of As atoms on the clean substrate surface after As decapping.

The STM currents between a tungsten tip and the substrate are obtained using a LCAO method based on a local-orbital LDA calculation. The respective line scans for $V = 3.0$ eV and $I = 0.1$ nA are presented in Fig. 4. The corrugation for structure 3B is 0.5 Å and agrees well with the experimentally determined cor-

rugation of 0.7 Å obtained by Pashley and Li [9]. The corrugation of the structure 4C proposed by Pashley and Li is less than 0.2 Å and smaller than the theoretical corrugation for structure 1B. In conclusion, the theoretical STM results support the 3B model as the microscopic structure for the Se passivated surface with only a single Se atom in the topmost layer.

4. Conclusions

Chalcogen modifications of GaAs(1 0 0) in UHV and by wet chemical etching result in substrates covered by a well ordered Ga-chalcogenide like layer terminated by a chalcogen layer. Based on the comparison between the theoretical calculated STM topography and the experimental data the surfaces are found to be terminated by single chalcogen atoms. These surfaces are chemically stable and show a reduction in band bending compared to non-passivated surfaces. In contrast to the theoretical predictions, that the band gap of these surfaces is free of states, the sample prepared by the procedures described here still exhibit surface states. These surface states may be attributed to defects or dopant atoms at surface.

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