



# Schottky contacts on passivated GaAs(1 0 0) surfaces: barrier height and reactivity

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## Abstract

We present results on the experimental and theoretical investigations of metal contacts on chalcogen passivated GaAs(1 0 0) surfaces. Photoemission spectroscopy investigations show that depending on the metal used for the contact formation the chalcogen passivation reduces the interaction between metals and GaAs(1 0 0). For Sb no chemical reaction at all with the substrate surface is found, while In and Ag react with the topmost chalcogen layer. For Na and Mg, on the other hand, a strong interaction is found. The chalcogenide like layer on top of the GaAs is disrupted and the metals react with the GaAs bulk, resulting in the formation of Na–As and Mg–As compounds. Concerning the barrier heights a general trend is observed, in that the barrier heights are smaller and larger for chalcogen passivated n- and p-type doped substrates, respectively, compared to the barrier heights on non-passivated surfaces. This change in barrier height can qualitatively be explained by an interface dipole, induced by the chalcogen passivation.

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**Keywords:** Schottky contacts; GaAs; Metal–semiconductor contacts

## 1. Introduction

Most metal–semiconductor contacts are rectifying [1]. Schottky explained this behaviour by depletion layers on the semiconductor side of such interfaces [2]. The band bending in this space charge region is characterized by its barrier height, which is the energy distance between the Fermi-level and the edge of the respective majority-carrier band right at the interface.

In the first approaches to describe the band line-up in metal–semiconductor contacts only charge carrier transport over the barrier was considered and interface states were not taken into account. In this simple picture the vacuum levels of the metal and the semiconductor are aligned at the interface, i.e. no interface dipole exists. In this case the barrier height is found to be the difference between the work function of the metal and the electron affinity of the semiconductor. This is the famous Schottky–Mott rule [3,4]. For a given semiconductor the barrier heights of different metal contacts should scale linearly with the work function of the metal and the slope should be unity. Applying the same model to semiconductor heterostructures, the energy difference in the conduction

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band minima at the interface is given by the difference of the electron affinities of the semiconductors (Anderson rule) [5]. Already Schottky presented in his famous paper published 1940 data from Schweikert [6] which clearly displays that the Schottky–Mott rule does not hold. The barrier heights of metal–selenium contacts are found to scale with the work function of the metal, but the slope is found to be smaller than unity. Later on Bardeen proposed that interface states are responsible for the shortcomings of the Schottky–Mott rule [7].

Today, interface states are established as the primary mechanism determining the energy level alignment at clean, abrupt, and defect free semiconductor interfaces. In the energy range, where the metal conduction band overlaps the semiconductor band gap, the wave functions of the metal electrons decay exponentially into the semiconductor. Their barrier heights are then determined by the continuum of this induced density of gap states (IDGS) [8]. The IDGS derive from the bulk bands and, thus, their character changes across the band gap from more acceptor-like closer to the conduction band to predominantly donor-like nearer to the valence band. The energy level, where the character changes from acceptor to donor type, is called the charge neutrality levels (CNL). In this picture, the barrier height at metal semiconductor interfaces is a function of the charge transfer across the interface and scales with the difference of the metal and the semiconductor electronegativities. Secondary mechanisms due to interface reactions, diffusion, defects, and interface dipoles may result in deviations. Two mechanisms namely interface dipoles and reactivity, will be studied in this work by investigating barrier height formation of metal contacts on chalcogen passivated GaAs(1 0 0) surfaces.

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 sulfide solutions results in an improvement of the performance of devices like bipolar transistors [9] or laser diodes [10–12]. 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 gallium-chalcogenide like layer at the surface showing a  $2 \times 1$  reconstruction [13,14]. 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 [15]. These surfaces are chemically stable and show a reduction in band bending compared to non-passivated surfaces [15,16]. 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.

## 2. Experimental

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 ultra-high vacuum system with a base pressure of  $p < 2 \times 10^{-10}$  mbar. The arsenic layer was then removed by gentle annealing to about 380 °C. Depending on the exact sample temperature this leads to an As-rich  $c(4 \times 4)$  or  $2 \times 4$  surface reconstruction of the GaAs(1 0 0) surface (see Refs. [17,18]) as can be judged from the lineshape analysis of the measured photoemission spectra and additional LEED experiments. Here, the latter surface reconstruction appears for slightly higher sample temperatures. For the chalcogen passivation the compounds SnS<sub>2</sub> and SnSe<sub>2</sub> 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 [19]. Sulfur and selenium were evaporated onto the substrates kept at 330 and 500 °C, respectively. These modified GaAs(1 0 0) surfaces served as a starting point for the deposition of Sb, Ag, In, Mg, and Na. The latter material was evaporated from dispensers (SAES Getters). The thickness of the metal film was monitored by a quartz crystal microbalance. In the case of Na the time of exposure is taken. To investigate the chemical and electronic properties of the surfaces after the passivation and after successive metal exposures photoemission spectroscopy investigations were carried out at the BESSY I in Berlin. At each modification step photoemission spectra were recorded from the As 3d ( $h\nu = 79 \text{ eV}$ ), Ga 3d ( $h\nu = 60 \text{ eV}$ ), S 2p ( $h\nu = 195 \text{ eV}$ ),

Mg 2p ( $h\nu = 89$  eV), In 4d ( $h\nu = 60$  eV), Na 2p ( $h\nu = 70$  eV), and Sb 4d ( $h\nu = 70$  eV) core levels thus providing maximum surface sensitivity. The measured spectra were fitted using spin-orbit split Voigt profiles including a Shirley background.

### 3. Results and discussion

The barrier heights presented here are obtained from IV- and photoemission measurements. In the case of the IV measurements barrier heights of laterally homogenous Schottky contacts obtained by the extrapolation of the effective barrier height versus ideality factor curves to ideality factors of homogenous contacts where only image force lowering has to be considered. As an example for the determination of the barrier height using photoemission spectroscopy the respective data for Ag deposited on S-passivated GaAs(1 0 0) is shown in Fig. 1. Here, the Fermi-level position at the clean GaAs surface was determined by carefully measuring the distance between the Fermi-edge of the metal sample holder and the valence band maximum (VBM). This procedure can only be used for the clean surface, since the valence band emission will be reduced and the emission from the metal conduction band will appear after metal deposition, making an accurate determination of the semiconductor valence band maximum impossible. On the other

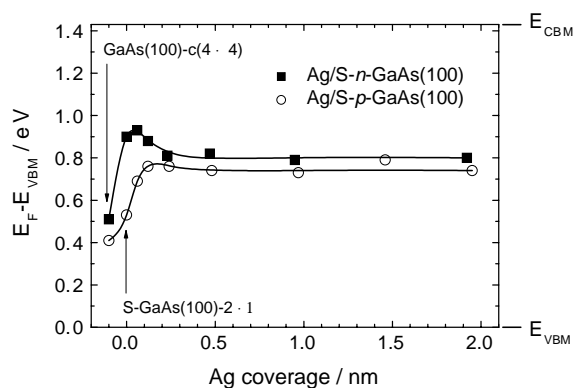


Fig. 1. Position of the Fermi-level relative to the valence band maximum  $E_{\text{VBM}}$  as a function of Ag coverage. The energy positions on the decapped GaAs(1 0 0)-c(4 × 4) and the S-passivated GaAs(1 0 0)-2 × 1 are shown as well.  $E_{\text{VBM}}$  and  $E_{\text{CBM}}$  indicate the energy position of the valence band maximum and conduction band minimum, respectively.

hand, the energy difference between the semiconductor valence band and the Ga 3d and As 3d core level emission from the GaAs bulk is unchanged. Therefore, changes in the Fermi-level position after successive metal coverages were followed by determining the change in the energy position in the Ga 3d and As 3d bulk components.

For the decapped samples the Fermi-level is found 0.5 and 0.4 eV above the valence band maximum on samples doped n- and p-type, respectively. Therefore, the GaAs(1 0 0) exhibit surface states of acceptor and donor type character. The S-passivation reduces the surface band bending on n-type doped samples, that is, the Fermi-level shifts by about 0.4 eV closer to its energy position in the bulk. On the surfaces of p-type doped samples, on the other hand, the band bending is even increased by 0.1 eV. For a coverage below one monolayer, which can be estimated by twice the covalent radius of Ag ( $r_{\text{cov}} = 0.134$  nm) to 0.27 nm, band bending is further increased on p-type doped surface, while only a small decrease is observed on n-type doped surfaces. This build-up of a depletion layer at low coverage, where isolated metal adatoms exist, is attributed to the formation of adatom-induced surface states of donor type [20]. In this coverage range metal-induced surface states appear, with the Fermi-level pinned at these surface states. These metal-induced surface states are of donor type and their energy position is found to scale linearly with the atomic ionisation energy of the metal atoms [21]. For coverages where the Ag films are metallic the Fermi-level is positioned at 0.8 and 0.74 eV above the valence band maximum on samples doped n- and p-type, respectively. Since the barrier height is defined as the energy difference between the majority-carrier band edge and the Fermi-level at the interface, the respective barrier heights for Ag contacts prepared on S-passivated n- and p-type doped GaAs(1 0 0) surfaces are 0.63 and 0.74 eV, respectively. It should be mentioned that these barrier heights fulfill the expected trend, that is, the sum of barrier heights on substrates with different type of doping should add up to the band gap of the semiconductor, which is 1.42 eV for GaAs.

Fig. 2 shows the trend in barrier heights of metal contacts on GaAs surfaces predicted by the IFIGS model [21] in comparison with experimental results. The barrier heights of Ni and Pd contacts are found to

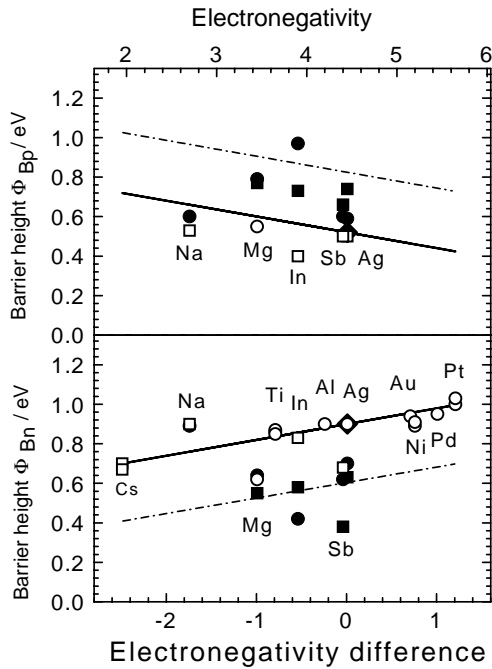


Fig. 2. Barrier heights of laterally homogenous GaAs Schottky contacts vs. the difference in Miedema electronegativity of the metal and the GaAs. IV results: (○) Au [38]; Al [39]; Ti [40–42]; Ni [43,44]; Pd [45]; Pt [46,47]; Mg/Ag [48]. Photoemission spectroscopy results: (□) Cs [49,50]; Sb [51]; In [52]; Na [53]; Se modified contacts: (●) Ag [24]; Mg [22]; Sb [22]; In [26]; Na [22]; S modified contacts: (■) Ag [25]; Mg [23]; Sb [28]; In [27]. The straight line and the dash-dotted line represent the prediction of the IFIGS theory without and with interface dipole, respectively. The symbol (◆) indicates the energy position of the CNL.

be below the IFIGS line due to the fact that both transition metals decompose GaAs at room temperature. In these cases non-abrupt interfaces are formed. In comparison to the barrier heights of metal contacts on bare GaAs surfaces, Fig. 2 shows the barrier heights for metal contacts prepared on S- or Se-passivated GaAs(1 0 0) surfaces. First, the chemical properties of these metal–chalcogen-passivated-GaAs interfaces will be discussed. New core level components can be observed for in the Ag 3d, Ga 3d, Se 3d, and S 2p core level spectra upon deposition of Mg. A detailed analysis of the binding energies of these new core level components reveals that an exchange between Mg and Ga atoms leads to the formation of magnesium chalcogenides and Ga clusters, the latter one segregating on the surface [22,23]. In addition, Mg reacts with the

GaAs bulk resulting in the formation of Mg–As compounds which also segregate to the surface. As a result the interface between the reacted surface layers and the GaAs bulk is shifted into the direction of the GaAs bulk as a function of Mg coverage. Similar observations have been made for the deposition of Na. In both cases a Fermi-edge is observed after depositing 0.23 nm Mg or evaporating Na for 870 s, indicating a metallization of the surface.

The deposition of In, Ag, and Sb, on the other hand, induces no new chemically shifted components in the As 3d and Ga 3d core level spectra. Only changes in the S 2p and Se 3d are observed, which indicates that interaction between the metals and the substrate surfaces is limited to the bonding of the metal atoms to the chalcogen surface atoms. For In and Ag the formation of islands is observed for coverages above 0.24 and 0.12 nm, respectively [24–27]. For both metals, the clustering is stronger on S than on Se modified GaAs surfaces, which implies a higher mobility of the atoms on the S modified GaAs surface. The growth modes of the metals have been determined from the attenuation of the Ga 3d and As 3d core level emissions as a function of the metal coverage. For the deposition of Ag and In on the chalcogen modified surfaces the growth modes agree with the respective growth modes on unmodified surfaces. A Fermi-edge is observed on Ag and In layers at 0.48 and 0.60 nm nominal thickness, respectively. Since the attenuation of the Ga 3d and As 3d is less than what is expected for a layer-by-layer growth of Sb, leading to the conclusion that islanding is observed for a nominal coverage above 0.17 nm [22,28]. This growth mode is in contrast to the layer-by-layer growth mode, which was observed for the Sb deposition on clean and unmodified GaAs(1 0 0) surfaces. Sb layer does not show any Fermi-edge up to the maximum thickness of 3.3 nm, which proves that it is semiconducting.

For the same metal–semiconductor contact the Schottky barrier heights for n- and p-doping of the semiconductor should add up to the band gap of the semiconductor. Comparing the Fermi-level positions for the different metals evaporated on chalcogen modified n- and p-type doped GaAs samples, it is found out that they follow this rule quite well. An exception are the Sb contacts, which is due to the fact that the Sb films are non-metallic. For Sb coverages



above 100 monolayers, which is much higher than what has been deposited in this investigation, Sb layers grown on n- and p-type doped GaAs(1 1 0) show a metallic behaviour [29]. The saturation value for the Fermi-level on Se and S modified n-(p-)GaAs(1 0 0) amounts to 0.81 (0.60) eV and 1.05 (0.66) eV, respectively. This is considerably higher than Fermi-level positions for Sb on unmodified n- and p-type doped GaAs(1 1 0), which amount to 0.75 and 0.5 eV, respectively [30].

The barrier heights of Schottky contacts on S- and Se-passivated GaAs(1 0 0) show a general trend. They are larger and smaller than the barrier heights on non-passivated p- and n-type doped GaAs(1 0 0) substrates, respectively. We have analysed theoretically this behaviour by using DFT-molecular dynamics simulations to determine the reactivity of the Se-passivated GaAs(1 0 0)- $2 \times 1$  reconstruction upon the deposition of In and Sb, and how the resulting interfaces pin the Fermi-level.

In our calculations, we use the Fireball'96 code [31,32] that has been shown to provide rather fast and accurate results of the geometries and electronic properties of semiconductor interfaces. Fig. 3 shows the Se-passivated GaAs(1 0 0)- $2 \times 1$  reconstruction, determined using a DFT-calculation [33]. This geometry has a single Se atom in the first crystal layer bonded to two Ga atoms of the second layer, and another Se layer replacing the third As layer. Fig. 4 shows the most stable geometries for the case of In-metallization of the passivated GaAs surface, by deposition of two extra In atoms per surface unit cell. Fig. 4a corresponds to a geometry for which the Se

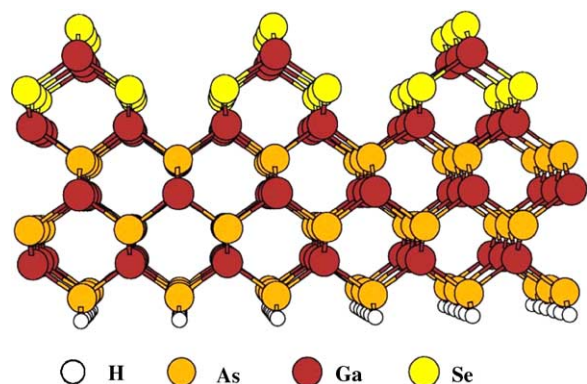


Fig. 3. Initial geometry of the Se-passivated GaAs(1 0 0) surface.

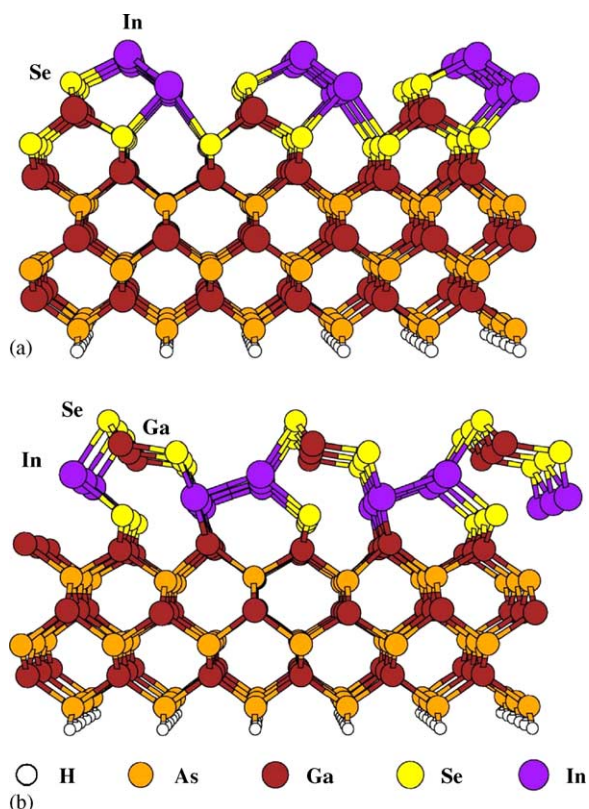


Fig. 4. Geometry of the (a) non-reacted In/Se-GaAs(1 0 0) and (b) reacted In/Se-GaAs(1 0 0) interface.

atoms of the initial structure are still bonded to the Ga atoms in the third GaAs layer. On top of this, we found a layer formed by two In atoms and one Se atom per surface unit cell. These In atoms form characteristic zig-zag chains along the  $[1, -1, 0]$  direction. The case of Fig. 4b corresponds to a geometry where the interchange between In and Se atoms appears in the third GaAs layer, while the surface is still terminated by Se and Ga atoms. For the case shown in Fig. 4a the atoms have a more or less tetrahedral coordination and the “bonds” shown represent directions of electronic charge accumulation. For the other case, the In atoms have a more complicated coordination and it is not straightforward to determine and visualize the maxima in charge distribution. A more detailed discussion is beyond the scope of these contribution. The chemisorption energies of these two cases are 4.63 and 4.95 eV, respectively, where these energies are calculated subtracting from the total energy the sum of the

energies of the passivated semiconductor surface and the two isolated metal atoms. Our calculations suggest that the geometry of Fig. 4b is slightly the most stable one, showing that In may disrupt the passivated surface. The energy difference is not very significant, however, suggesting that the surface preparation may affect to its stability.

The Sb-case is not shown here: it is sufficient to mention that our calculations do not show any intermixing between the Sb atoms and the Se-passivated surface. Moreover, the most stable geometry for this case is similar to the one found for In in Fig. 4a.

These results are very interesting and seem to be in agreement with the experimental evidence discussed above: In may show a small reactivity with the Se-passivated GaAs surface, while Sb shows none.

In order to elucidate how that reactivity affects the Schottky barrier formation of the system, we have also analysed the density of states and the Fermi-energy of the different cases shown above.

Here, we summarize our main results and will publish elsewhere details about the corresponding interface density of states. The main conclusion coming out of our calculations is the following:

- (a) On n-type doped substrates, unreacted interfaces show an important shift of the Fermi-level toward the conduction band. In particular, for Sb this Fermi-level appears to be practically at the semiconductor conduction band edge.
- (b) Reacted interfaces yield an interface Fermi-level that is close to the one found for clean GaAs surfaces.

Regarding the experimental data discussed above notice that Sb is not reactive, which is in agreement with our calculations. In is only slightly reactive, which can be understood in terms of the small differences between the energies of the cases shown in Fig. 4a and b. The experimental shift in the Fermi-level found for In and Sb confirms that in our experiments both cases are practically unreactive. We should mention that for a very reactive metal the Schottky barrier would be practically the same for the passivated and the clean interfaces: this is confirmed by Na, a case where the metal reactivity suggests a situation similar to the one found in Fig. 4a; theoretically, we have also found that Ga is very reactive showing a strong intermixing with the passivated layer.

Regarding the Fermi-level shift induced by the Se or S passivation, we should say that our Fireball-calculations are not very accurate due to the poor description of the GaAs conduction band. This trend can be explained in a model assuming that the chalcogen induced surface dipole still exists at the metal–semiconductor interface and contributes to the charge transfer across the interface. The electronegativity of the passivating atoms is larger than the electronegativities of the substrate atoms. This results in charge of positive sign on the semiconductor side of the interface, which is compensated by equal charge of opposite sign in the metal-induced gap states. Therefore, the Fermi-level moves closer to the conduction band minimum, i.e., the barrier heights on n- and p-type substrates are decreased and increased, respectively.

The chalcogen induced surface dipole can be calculated as follows. The charge transfer in covalent adsorbate substrate bonds on semiconductor surfaces leads to surface dipoles, which change the ionisation energy. According to Pauling's concept [34], the ionic character  $\Delta q_1$  of covalent single bonds in diatomic molecules may be described by the difference  $X_A - X_B$  of the electronegativities of the two atoms involved. A revised version of Pauling's original correlation is [35]

$$\Delta q_1 = 0.16|X_A - X_B| + 0.035|X_A - X_B|^2. \quad (1)$$

The dipole moment of such molecules may then be written as

$$\mu_0 = \Delta q_1 e_0 \sum r_{\text{cov}}, \quad (2)$$

where  $e_0$  is the electronic charge and  $\sum r_{\text{cov}}$  the sum of the covalent radii of the atoms involved. Using the surface-molecule approach, which considers nearest-neighbour interaction between adatoms and surface atoms of the substrate only, Pauling's concept is easily applied to adatoms on semiconductor surfaces.

Adatom-induced surface dipoles may be described as an electric double layer. The voltage drop across this layer causes the change of the ionisation energy. The maximal variation of the ionisation energy may be estimated for maximal normal component of the dipole moment or, in other words, assuming the adsorbate substrate bonds to be perpendicular to the surface. Considering the mutual interaction between adatom-induced surface dipoles, the change

in ionisation energy is given by [36]

$$\Delta I = -\frac{e_0}{\varepsilon_0} \frac{\mu_0 N_{\text{ad}}}{1 + 9\alpha_{\text{ad}} N_{\text{ad}}^{3/2}}, \quad (3)$$

with  $\varepsilon_0$  and  $\alpha_{\text{ad}}$  being the permittivity of vacuum and the polarization of adatoms, respectively. Due to adatoms being electronegative or electropositive compared to the substrate surface atoms the ionisation energy will increase or decrease, respectively. With the Pauling's electronegativities of  $X_{\text{Ga}} = 1.81$  and  $X_{\text{S}} = 2.58$  the charge transfer between Ga and S amounts to  $\Delta q = 0.144$ . The distance between the S and Ga in the first surface layer perpendicular to the surface amounts to 0.11 nm [37]. With these two values the dipole moment normal to the surface amounts to  $2.54 \times 10^{-30}$  C m. With the density of surface dipoles being equal to the density of atoms on a GaAs(1 0 0) of  $6.26 \times 10^{14}$  cm $^{-2}$  (see Ref. [21]) and the polarizability of  $2.9 \times 10^{-24}$  cm $^{-3}$  the change in ionisation energy amounts to 1.28 eV. The same calculation can be done for the Se covered surface using  $2.9 \times 10^{-24}$  cm $^{-3}$  and 2.55 for the polarizability and electronegativity of Se, respectively. Here, the ionisation energy is expected to vary by 1.12 eV. Both chalcogen atoms are negatively charged due to their higher electronegativity compared to Ga and the ionisation energy is expected to increase. The change in barrier height is then estimated from (3) by

$$\Delta\phi_{\text{Bi}} = \frac{\Delta I}{\varepsilon_{\text{I}}} \quad (4)$$

where  $\varepsilon_{\text{I}}$  is the dielectric interface constant of the semiconductor. With a dielectric interface constant of 4 for GaAs (see [21]) the S and Se induced change in barrier height amounts to 0.32 and 0.28 eV, respectively. This change is indicated by the dashed lines in Fig. 2, which are shifted by 0.3 eV with respect to the IFIGS theory line. As can be seen, this simple model explains the general trend in barrier heights quite well.

#### 4. Summary

The influence of chalcogen passivation on the chemical and electronic properties of metal/GaAs interfaces has been investigated by combined experimental and theoretical techniques. Photoemission spectroscopy measurements reveal, that Sb forms an

abrupt, non-reacted interface on chalcogen passivated GaAs(1 0 0) surfaces Ag and In are found to react with the top chalcogen layer, while Na and Mg disrupt the chalcogenide like passivation layer. For the latter metals, i.e. Na and Mg, a reaction with the GaAs bulk and the formation of Na–As and Mg–As compounds is observed. These findings are in excellent agreement with the DFT-molecular dynamics simulations, which predict a non-reactive interface for Sb and an interface reaction for In limited to the top layers of the Se-passivated surface. For interfaces which lack any interface reaction the theoretical calculations predict a shift of the Fermi-level towards the conduction band, or, in other words, a decrease in barrier height. This is indeed observed for metal contacts prepared on chalcogen passivated GaAs(1 0 0) which are n-type doped. For reacted interfaces the Fermi-level should be close to the one found for metal contacts on clean GaAs surfaces.

The decrease and increase of barrier heights on n-type and p-type doped GaAs(1 0 0) substrates, respectively, can be attributed to an interface dipole. This interface stems from the chalcogen induced surface dipoles, which still exist at the interfaces and modify the charge transfer into the interface states. In a simple molecule picture the change in barrier height due to this charge transfer can be estimated to 0.32 and 0.28 eV for the S- and Se-passivated GaAs(1 0 0), respectively. These values are in good agreement with the experimental data.

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