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# Chemical trends in Schottky barriers: Charge transfer into adsorbate-induced gap states and defects

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The chemical trends reported for barrier heights in metal-GaAs contacts are explained by a charge transfer between the metal and adsorbate-induced gap states, which are identified as the virtual gap states of the complex band structure of GaAs, as well as fabrication-induced defects of donor type. Following the concept of the ionicity of chemical bonds, the charge transfer is described by the difference in the electronegativities of overlayer and substrate atoms. The density of fabrication-induced defects varies considerably.

As early as 1938, Schottky explained the rectifying behavior of metal-semiconductor contacts by a depletion layer on the semiconductor side of the interface.[1] The electron flow across the junction is thus determined by the energy distance from the Fermi level to the bottom of the conduction band when the semiconductor is doped *n*-type. Several models have been proposed for explaining the chemical trends observed with the barrier heights in such Schottky contacts.

The first proposal of this kind dates back to Mott,[2] who suggested that the barrier height of a metal-semiconductor contact equals the difference of the metal work function and the semiconductor electron affinity. The first systematic investigation[3] indeed revealed the barrier heights of metal-selenium contacts to be linearly related to the work functions of the metals involved but to be considerably smaller than expected from the Mott-Schottky rule just mentioned. To resolve this discrepancy, Bardeen[4] proposed interface states to determine the position of the Fermi level within the band gap at the interface. Such interface states result in the formation of a double layer at the interface, which was later on included in the analysis of the charge balance at such junctions.[5,6] The Mott-Schottky rule is then obtained with no interface states present at all while very large densities of interface states are pinning the Fermi level at their charge-neutrality level and the barrier heights become independent of the metals used. In the past, two basically different models have been proposed to explain the physical nature of such interface states.

Heine[7] argued that the wave functions of the metal electrons are tailing into the semiconductor for energies where the conduction band of the metal overlaps the band gap of the semiconductor. By this a dipole layer forms as it does at the metal-vacuum interface. The properties of those tails of the metal-electron wave functions are thus determined by the virtual gap states (VGS's) of the complex band structure of the semiconductor. The character of these states is predominantly acceptorlike and donorlike closer to the conduction and the valence band, respectively. At their branch point or, in other words, their charge-neutrality level, their decay length is smallest but increases towards both band edges. These tails of the metal wave functions into the semiconductor have also been called adsorbate-induced surface states[8] or metal-induced gap states (MIGS's).[9]

Later on, Wieder,[10] Spicer *et al.*,[11] and also Williams *et al.*[12] suggested that at semiconductor interfaces the Fermi level gets pinned by energy levels of native defects such as vacancies,[11,13] or antisite defects,[14] which are created in the semiconductor during the formation of the interface. For a review the reader is referred to Refs. 15 and 16.

Quite recently, Mönch[17] has analyzed the chemical trends of barrier heights reported for metal- and silicide-silicon contacts. The formation of dipole layers at the interface was attributed to the differences in electronegativity between silicon and the metals or silicides. The large body of experimental data and their chemical trends could be explained when adsorbate- or metal-induced gap states, which are identified as the VGS's of the complex band structure of the semiconductor, and fabrication-induced defects of donor-type were considered. This new VGS-plus-defects model of the barrier heights in Schottky contacts will be applied to metal-GaAs junctions in the present paper.

In the past, the analysis of the barrier heights in metal-semiconductor contacts was often based on the charge-neutrality condition

$$Q_{SS}+Q_{SC}=0 , \qquad (1)$$

i.e., the surface band bending adjusts so as to achieve a balance between the space charge $Q_{SC}$ and the excess charge $Q_{SS}$ in surface states. Equation (1) is valid at clean semiconductor surfaces. At interfaces, where two different materials are in contact, the charge-neutrality condition (1) needs to be modified since a charge transfer may additionally occur across the interface due to chemical bonding. This phenomenon is most easily demonstrated by considering the adsorption of atoms, which are much more electropositive or electronegative than the semiconductor substrate used.

The adsorption of cesium,[18–20] of chlorine,[21] and of sulfur[22] on cleaved GaAs(110) surfaces, for example, is known to cause adsorbate-induced surface dipoles and surface states, which are observed via changes of the ionization energy and the buildup of surface band bending, respectively, as a function of adsorbate coverage. The adsorbate-induced dipoles may be described by an electric double layer made up by adequately charged adatoms and adsorbate-induced surface states in the semiconductor. At an interface the charge-neutrality condition (1) of the clean surface has now to be replaced by

$$Q_{\mathrm{ad}}+Q_{\mathrm{SS}}+Q_{\mathrm{SC}}=0\ , \tag{2}$$

where $Q_{\mathrm{ad}}$ is the total charge per cm$^2$ carried by the adatoms.

The adsorption of cesium decreases the ionization energy of the GaAs substrate while it is increased by the adsorption of chlorine or sulfur. The adsorbed atoms of cesium and chlorine or sulfur are thus charged positively and negatively, respectively. As a consequence, the adsorbate-induced surface states are carrying a negative charge with cesium and a positive one with chlorine or sulfur adsorbed. This opposite sign of the charge transfer between adsorbate and substrate results from the fact that cesium and chlorine or sulfur are much more electropositive and electronegative, respectively, than gallium arsenide. The magnitude and the sign of the charge transfer may be estimated from the differences in the electronegativities of the adsorbates and the substrate by following Pauling's concept of the partial ionic character of covalent bonds.[23] The physical origin of the adsorbate-induced surface states, which are forming the adsorbate-induced surface dipoles together with the partly charged adatoms, shall be discussed in the following.

In a one-dimensional semiconductor, the sign of the appropriate Fourier coefficient of the periodic potential in conjunction with the position of the matching plane determines whether or not a virtual gap state of the complex band structure of the chain will form a real surface state. The energy and by this the character of this surface state are given by the same Fourier coefficient of the potential and the depth of the potential well at the surface state are given by the same Fourier coefficient of the potential and the depth of the potential well at the surface.[24–26] At adsorbate-covered surfaces, those virtual gap states will then happen to become adsorbate-induced difference in electronegativities.[7]

The charge transfer between adatoms and adsorbate-induced surface states of the substrate also mainly determines the position of the Fermi level at the surface, i.e., the surface band bending. The density of virtual gap states and thus of adsorbate-induced surface states measures some $10^{14}$ states per eV and cm$^2$ (Ref. 6) and thus the space charge $Q_{\mathrm{SC}}$ only plays a minor role in determining the surface band bending via the charge-neutrality condition (2).

The VGS model of adsorbate-induced surface states is strongly supported by experimental and theoretical data. In Fig. 1 the positions of the Fermi level below the conduction-band bottom as measured with cesium, sulfur, and chlorine adsorbed on cleaved GaAs(110) surfaces are plotted versus the difference $\Delta X = X_{\mathrm{ad}} - X_{\mathrm{sub}}$ between the electronegativities of the adsorbates and the GaAs substrate. Here $\Delta X$ stands for the charge transfer between adatoms and adsorbate-induced surface states. The electronegativities given by Miedema[27] are used; they are linearly related to the Pauling scale by

$$X_{\mathrm{Mied}} = 1.79 X_{\mathrm{Paul}} - 0.8\ . \tag{3}$$

The electronegativities given by Miedema are preferred since they were derived from chemical trends in the properties of metallic alloys and compounds. The conclusions reached remain unchanged when Pauling's scale is used instead of Miedema's. The linear interpolation between the three experimental data points ($r = 0.99$) results in a charge-neutrality level of the adsorbate-induced surface states which agrees to within 40 meV with the energy predicted for the branch point of the VGS of GaAs by Tersoff.[28] An earlier estimate by Tejedor and Flores[29] deviates from this value by only 50 meV. The same model shall now be adopted for metal-semiconductor contacts.

The barrier heights reported for metal-GaAs contacts[30–33] are also plotted in Fig. 1. The selection of the data is based on the following considerations. First, all the barrier heights displayed were evaluated from current-voltage characteristics of Schottky diodes and have been corrected for image-force lowering. This means that, for example, the large body of results obtained with photoemission spectroscopy is not included since the metal coverage, at which the Fermi level gets pinned, generally depends on the growth conditions of the metal film as, for example, the substrate temperature and the evaporation rate. Second, with the exception of the Ru data point,[32] results communicated by Waldrop[30,31] for (100)- and by Newman *et al.*[33] for (110)-oriented GaAs substrates were considered only. Each of the two groups prepared all their samples under the same experimental conditions although the techniques used were different for the two substrate orientations.

In Fig. 1 the data points for the Schottky diodes fabricated with rare-earth metals (RE), titanium, lead, silver,

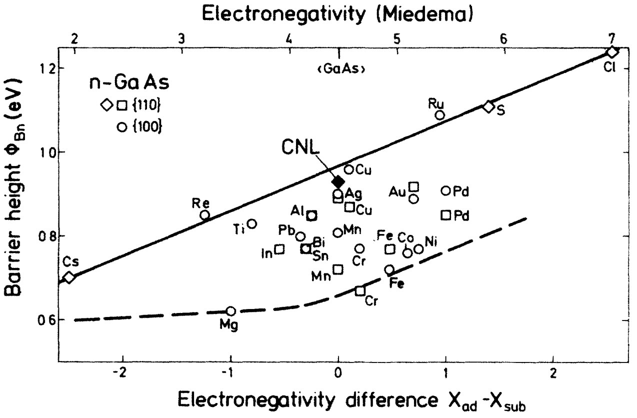

FIG. 1. Barrier heights $\Phi_{Bn}$ reported for metal-GaAs contacts and for adsorbates on GaAs cleaved surfaces plotted vs the electronegativity differences between the adatoms and the substrate with $X_{\mathrm{GaAs}} = 4.45$. The electronegativities were taken from Miedema (Ref. 27), and the charge-neutrality level CNL of the virtual gap states of the complex band structure of GaAs was given by Tersoff (Ref. 28).

copper, and ruthenium are all following the chemical trend predicted from the VGS model of adsorbate- (Ref. 8) or, what is the same, metal-induced gap states.[9,34] Remarkably, the other metals give barrier heights which are lower than predicted by that model. This conclusion will not be altered when the pinning positions of the Fermi level as deduced from the energy-distribution curves of photoemitted electrons are included. The scatter of the data points entered in Fig. 1 will be attributed to the presence of fabrication-induced defects of donor type.

In defect-free metal-semiconductor contacts the variation of the barrier height as a function of the transfer of charge across the interface or, what is equivalent, of the electronegativity of the metal is determined by the density of states $D_{\mathrm{VGS}}$ of the VGS of the semiconductor and the effective width $\delta_{\mathrm{eff}}$ of the dipole layer at the interface.[5,6] With the charge-neutrality level $E_0$ of the VGS lying well within the bulk band gap of a direct semiconductor, both the density of states $D_{\mathrm{VGS}}$ as well as the effective width $\delta_{\mathrm{eff}}$, which is determined by the decay length of the VGS,[7] are almost constant when the electron energy deviates by less than approximately one quarter of the gap energy from the charge-neutrality level of the VGS.[6] For a specific semiconductor, the barrier heights then vary linearly as a function of the metal electronegativity.[5,6,35]

With fabrication-induced defects present at a metal-semiconductor contact the condition of interface charge-neutrality now reads

$$Q_{\mathrm{ad}}+Q_{\mathrm{SS}}+Q_{\mathrm{def}}+Q_{\mathrm{SC}}=0 , \qquad (4)$$

since charge $Q_{\mathrm{def}}$ in defects has to be considered in addition to the space charge and charged adatoms as well as adatom-induced interface states. Let us assume interface defects of donor type which exhibit an energy level in the upper half of the band gap. For very large transfer of negative charge into the adatom-induced gap states, the VGS model of adatom-induced interface states predicts low barrier heights, i.e., the Fermi level is found close to the conduction-band bottom and the interface defects assumed are neutral. With increasing electronegativity of the metal or, in other words, with decreasing negative charge in metal-induced gap states, the Fermi level moves towards the charge-neutrality level of the VGS and by this approaches the energy level of the fabrication-induced donors, which then become positively charged. The Fermi level gets pinned close to the defect level, i.e., the barrier height remains constant, until all the defects are charged and, eventually, the adatom-induced gap states will again accommodate charge. The $\Phi_{Bn}$-versus-$\Delta X$ curve then runs parallel to that line observed with no fabrication-induced defects being present. The dashed line in Fig. 1 gives the relationship $\Phi_{Bn}(\Delta X)$ for the largest density of defects being compatible with the experimental data. The "pinned" part of the curve, which is determined by an assumed position of a defect level at 0.65 eV below the conduction-band bottom, is very ill defined since it is based on one data point only. In the framework of the model presented here, the densities of fabrication-induced defects are lowest with the rare-earth metals, Ti, Pb, Ag, Cu, and Ru, but largest with Fe, Co, and Ni.

The density of states of the adsorbate-induced gap states may be estimated from the difference in the position of the Fermi level at the interface of Schottky diodes prepared with substrates doped *n*- and *p*-type. Waldrop[30] has measured the respective barrier heights $\Phi_{Bn}$ and $\Phi_{Bp}$ for 14 different metals and has found them to add up to the band-gap energy minus $\delta\Phi_B=0.04\pm0.03$ eV on the average. Since the barrier heights amount to $E_g/2+0.1$ eV on the average depletion layers are present with substrates doped *p*- as well as *n*-type. According to the charge-neutrality condition (2), the density of adsorbate-induced gap (AIGS) states is then given by $D_{\mathrm{VGS}}=(Q_{\mathrm{SC}}^{n}-Q_{\mathrm{SC}}^{p})/\delta\Phi_B$ since due to their energy position in the upper half of the band gap the fabrication-induced defects will always be charged independent of the type of substrate doping. Here, $Q_{\mathrm{sc}}$ is the space-charge density in the depletion layer. With the assumption that the GaAs samples used only contained shallow impurities, the density of states of the AIGS is estimated as $5\times10^{13}$ states per cm$^2$ and eV. Theoretical models predicted $3\times10^{14}$ states per cm$^2$ and eV.[6,34,36] The deviation is partly attributed to the large margins of experimental error with $\Phi_{Bp}$, which is mostly due to the nonideality of the Schottky contacts on *p*-type GaAs, and to the unknown density of deep impurities in the substrates. This means that the value estimated for the density of AIGS represents a lower limit only.

The data plotted in Fig. 1 clearly show that the chemical trends observed in the barrier heights of metal-GaAs contacts may be understood by a chemically driven charge transfer across the interface into adsorbate-induced gap states, which are identified as the virtual gap states of the complex band structure of the semiconductor, and into fabrication-induced defects of donor type with energy levels in the upper half of the band gap. The same model was also successfully used to describe the chemical trends of the barrier heights reported for metal- and silicide-silicon contacts.[17] The charge transfer across the metal-semiconductor interface is modeled by the difference of the electronegativities of the metal and the semiconductor. Neither for GaAs nor for Si Schottky contacts can the energy position of the fabrication-induced donor-type defects be determined from the data available hitherto.

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