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To cite this version:
P. Langlade, P. Masri. CONTRIBUTION OF THE DEFECTS TO THE ELECTRONIC PROPERTIES OF THE METAL SEMICONDUCTOR INTERFACE. Journal de Physique Colloques, 1984, 45 (C5), pp.C5-441-C5-447. <10.1051/jphyscol:1984566>. <jpa-00224185>

HAL Id: jpa-00224185
https://hal.archives-ouvertes.fr/jpa-00224185
Submitted on 1 Jan 1984

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CONTRIBUTION OF THE DEFECTS TO THE ELECTRONIC PROPERTIES OF THE METAL SEMICONDUCTOR INTERFACE

P. Langlade+ and P. Masri

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Résumé
Le contact métal-semiconducteur joue un rôle essentiel dans les propriétés des circuits électroniques à semiconducteur. Des progrès récents dans ce domaine montrent que les propriétés électriques sont contrôlées par des états d'interface, apparaissant dès les premiers stades de la métallisation. Dans ce contexte, nous avons étudié l'influence des lacunes de surface sur les propriétés de l'interface de façon self consistante dans le modèle moléculaire après avoir caractérisé en détail la surface idéale. Nous montrons que le barycentre des états associés aux lacunes III et V a tendance à se déplacer du bas de la bande interdite vers le haut en fonction de l'ionicité du composé. Ce résultat est comparé à la relation existant entre l'ancrage du niveau de Fermi par l'absorption métallique et l'ionicité du composé.

Abstract
The metal-semiconductor contact plays an essential role in the properties of semiconductor devices. Recent progress in this field show that the electronic properties are controlled by the interface states, which appear during the first stages of metallization. In this context, we have studied the influence of the (110) surface vacancies on the properties of the interface in a self consistent way within the molecular model framework after the characterization of the ideal (110) surface. We show that the barycenter of the levels associated with the V and III vacancies has a tendency to move towards the upper part of the forbidden gap as ionicity of the compound increases. This result can be compared to the existing relation between the pinning of the Fermi level by a metallic adsorption and the compound's ionicity.

Introduction
The origin of the Schottky barrier at the metal/III-V semiconductor interface is of a great importance because its comprehension is bonded to technological applications, the Schottky diode being one of the most elementary of electronic devices. During the last few years, a large effort has been devoted to the research of the metal-semiconductor interface and different models have been proposed (1). The most studied system is those of the metal on the (110) face of the III-V's because there are no electronic states in the band gap and therefore it is easy to follow the electronic role of the metal on the surface properties. It is now well established that the barrier is controled by interface states, appearing at the first stages of metallization which are resulting from defects at or near the surface of the semiconductor; the "unified model" (2) has been developped to explain the Fermi level pinning by cation and anion vacancies.

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The aim of this work is to bring a contribution on this main point. In a first
time, we have studied the ideal vacancies at a well characterized (110) zinc-
blende surface and their influence on the Schottky barrier.

For thus, we have choosen:
- a parameter which introduces the perturbation inherent to the surface,
as say the electrostatic potential.
- a model which qualitatively describes the physical properties of the
bulk of the III-V compounds versus one parameter, the ionicity, as say the
molecular model.
- to characterize the ideal surface by mean of a self consistent
calculation.
- to study the effect of ponctual defect like vacancies on the electronic
structure.

Electronic structure of the ideal surface

Description of the bulk - Molecular model

Prior to introduce the vacancies at the surface, we must have a characterization
of the ideal surface. For thus, we need a parameter which shows the perturbation
created by the surface it-self: we have chosen the electrostatic energy
because it is a function of the ionicity of the bond and allows us to a
comparison between a family of compounds. Then, the bulk properties have to be
described in relation with this parameter: we have done it with the molecular
model in which the crystal is a collection of molecule (Atcm III-Atcm V),
developped for the first time by Coulson and al. (3) and modified by the
theoricians' group of Lille (4,5).

In the tight binding approximation, the hamiltonian is specified by:
- intra-atomic terms $\alpha_{AB} = \langle \Phi_A | H | \Phi_B \rangle$
- off-diagonal terms $\beta = \langle \Phi_A | H | \Phi_B \rangle$

where $\Phi_A, \Phi_B$ are the atomic orbital of the A,B atom.

The resulting molecular orbitals are:
$\Phi_a = M (\Phi_A + \lambda \Phi_B)$
$\Phi_a,l = M (\lambda \Phi_A - \Phi_B)$

$\lambda$ is a parameter which takes the bond polarity in to account. Since the
atoms have a different electro negativity, there is a net charge on every atom:

$n_A^o = \frac{8}{1 + \lambda^2} - N^2$

$n_A^o = \text{charge in the bulk - charge of the free atom (N). The neutrality of the}
crystal brings to: $n_B^o = - n_A^o$.

We can then define the ionicity of the bond as:

$f_i = \frac{1 - \lambda^2}{1 + \lambda^2}$
The resolution of the Schroedinger equation in a self consistent manner brings to the results of table I (6).

<table>
<thead>
<tr>
<th></th>
<th>( \lambda )</th>
<th>( n^0 )</th>
<th>( f_i )</th>
<th>( f_i ) Phillips</th>
<th>( \alpha A ) eV</th>
<th>( \alpha B ) eV</th>
<th>( \beta = \alpha - \beta ) A B eV</th>
<th>( E_{a1} ) eV</th>
<th>( E_1 ) eV</th>
<th>( E_g = E_{a1} - E_1 ) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb</td>
<td>0.576</td>
<td>1.01</td>
<td>0.50</td>
<td>0.26</td>
<td>-6.3</td>
<td>-4.21</td>
<td>2.08</td>
<td>-2.72</td>
<td>-6.89</td>
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<tr>
<td>GaAs</td>
<td>0.534</td>
<td>1.23</td>
<td>0.56</td>
<td>0.31</td>
<td>-6.73</td>
<td>-3.83</td>
<td>2.9</td>
<td>-2.61</td>
<td>-7.83</td>
<td>5.22</td>
</tr>
<tr>
<td>InAs</td>
<td>0.511</td>
<td>1.34</td>
<td>0.59</td>
<td>0.36</td>
<td>-5.85</td>
<td>-3.22</td>
<td>2.64</td>
<td>-2.89</td>
<td>-7.39</td>
<td>4.5</td>
</tr>
<tr>
<td>GaP</td>
<td>0.497</td>
<td>1.42</td>
<td>0.60</td>
<td>0.37</td>
<td>-7.38</td>
<td>-3.77</td>
<td>3.6</td>
<td>-2.95</td>
<td>-8.92</td>
<td>5.97</td>
</tr>
<tr>
<td>InP</td>
<td>0.465</td>
<td>1.58</td>
<td>0.65</td>
<td>0.42</td>
<td>-5.79</td>
<td>-2.46</td>
<td>3.32</td>
<td>-2.73</td>
<td>-7.89</td>
<td>5.17</td>
</tr>
</tbody>
</table>

Table I - The different parameters of the molecular model.

There is a charge transfer from the atom III to the atom V in all the cases in good agreement with several published results (7) and a linear relation exists with the ionicity (Fig. 1).

![Figure 1 - Relation between the net charges and the ionicity](image)

Therefore, the widths of the "band gap" in this model follow the real order even if they are to great.

Structure at the surface

The creation of the surface gives rise to the disparition of a part of the energetic interactions and the electronic structure of the first layers is modified: the net charges are not the same as in the bulk and the resulting potential strengths too. Like it is evident these two quantities are independent, the use of self consistence is necessary. Then we have to fit the molecular model to the case of the surface who there is only two dimensions. The principle of calculation is :

\( a \) - to cut the crystal in parallel plans oriented (110), identified by the index \( j \);

\( b \) - the net charge of the atoms in \( j \) plan is noted \( n_{Aj} \) and \( n_{Bj} = n_{Bj}^0 \), except for the plans perturbed by the surface.

\( c \) - the variations of population on a bond are proportional to the variation of the intra-atomic terms :

\[ \Delta n_{Aj} = c \Delta (\alpha_{Aj} - \alpha_{Bj}) \]

\( d \) - the intra-atomic terms are expressed in function of the net charges :

\[ \alpha_{Aj} = \alpha_{A}^0 + J_{A} n_{Aj} + \sum_{\theta=A,B} \gamma_{Aj,\theta} k n_{\theta k} \]
where the coefficients \( \gamma_{AJ,ek} \) are lattice sums, of the form \( \frac{1}{\alpha_{AJ} - \alpha_{Bk}} \) for the electrostatic interactions.

e - from the expression of the variations \( n_{AJ}', n_{Bk}', \alpha_{AJ}', \alpha_{Bk}' \), we have a set of linear equations, whose dimension is limited by the depth of the perturbation.

The calculations are then self consistent and have been developed in réf. 6.

In the Table II, are reported the charges transfers at the surface and in the perturbated plans and the associated energy levels.

<table>
<thead>
<tr>
<th></th>
<th>( n^o_A )</th>
<th>( n^s_A )</th>
<th>( n^s_B )</th>
<th>( n_{Al} )</th>
<th>( n_{Bl} )</th>
<th>( \alpha_{AS} - \alpha_{A_{vol}} )</th>
<th>( \alpha_{BS} - \alpha_{B_{vol}} )</th>
<th>( \alpha_{A1} - \alpha_{A_{vol}} )</th>
<th>( \alpha_{B1} - \alpha_{B_{vol}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb</td>
<td>1.01</td>
<td>0.918</td>
<td>-0.882</td>
<td>-0.299</td>
<td>0.416</td>
<td>2.62</td>
<td>- 0.99</td>
<td>- 0.9</td>
<td>2.07</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.23</td>
<td>0.578</td>
<td>-0.581</td>
<td>-0.096</td>
<td>0.098</td>
<td>1.01</td>
<td>- 1.07</td>
<td>- 0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>InAs</td>
<td>1.34</td>
<td>0.524</td>
<td>-0.5</td>
<td>-0.074</td>
<td>0.055</td>
<td>0.963</td>
<td>- 0.788</td>
<td>- 0.659</td>
<td>0.463</td>
</tr>
<tr>
<td>GaP</td>
<td>1.42</td>
<td>0.485</td>
<td>-0.475</td>
<td>-0.059</td>
<td>0.051</td>
<td>0.9367</td>
<td>- 0.68</td>
<td>- 0.061</td>
<td>0.52</td>
</tr>
<tr>
<td>InP</td>
<td>1.58</td>
<td>0.424</td>
<td>-0.406</td>
<td>-0.044</td>
<td>0.028</td>
<td>1.04</td>
<td>- 0.32</td>
<td>- 0.49</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table II

Some trends are arising from the results:

a - the perturbation created by the surface runs on two plans and has an oscillatory nature

b - the answer of the system is a charge transfer in all the cases:

+ an excess of electrons on the more electronegative atom at the surface (a lack of electrons on the electropositive one)
+ a lack of electrons on the more electronegative atom on the first internal plan.

c - these transfer lead to a more ionic surface than the bulk

d - a true relation exist between the magnitude of the transfer and the ionicity: the more important are the transfers, the weaker the ionicity.

The intra-atomic terms of the electronegative atoms at the surface are always weaker than those of the electropositive one, except for GaSb for which the instability is great.

From a general point of view, our results are in good agreement with experimental observations and theoretical calculations. The interesting point is the relation of the perturbation with the compound ionicity. It is known (8) that the "covalent reconstruction" produces atom displacements up to three plans in the bulk, little variations of the bond length, while the "ionic one" is only characterized by a surface relaxation and more important changes in the bond length.

Owing to the fact that there is a change in the Ga 3d and As 3d core level binding energies, Eastman and ai. (9) deduce that the GaAs surface is more ionic than the bulk. Therefore, calculations of Pandey (9) support this hypothesis; they find that the charge transfer from Ga to As at the surface is of order of 0.3 electron, this effect being reduced by surface relaxation. We have neglected this point because the aim of relaxation is to minimize the surface energy and then it is clear that it would reduce the charge transfer at the surface and bring the energy levels closer to the bands without modify the tendency in...
function of the ionicity.

Charge transfers and energy levels associated to the vacancie

In the molecular model, a vacancie is created by taking out an atom from the lattice and neglecting the induced distortion and the coupling between the nearest neighbors dangling bonds. The formalism of the calculation is:

- a - to create a vacancie at the (110) surface of the III-V compounds
- b - to distribute the keeping electronic charge on the dangling bonds, taking the neutrality of the bond and the situation at the ideal surface (more ionic than the bulk) into account.
- c - to calculate in a self consistent way the effect on the electronic structure of the neighbors.

We have supposed that the vacancie is created in its bulk charge stage as say the V vacancie corresponds to the disappearing of $5 + n_A^0$ electrons and a III one to those of $3 + n_B^0$. Then, $3 + n_A$s in the case V and $5 + n_B$s in the case III, electrons have to be distributed in the dangling bonds.

The evaluation of the intra-atomic terms is made in the same manner as for the surface: they are linear functions of the net charges on the atoms produced by the vacancie. But the defect has a very low symmetry and the resulting potential is localized around the vacancie. Therefore, for the coulomb-type interactions, which are the proportionality coefficients of the linear relations, it is not possible to use a method based on the periodicity like the k representation in a plan. We have chosen to directly evaluate the interactions between perturbed atoms with sums of the form $\frac{1}{r}$. The intra-atomic terms are expressed as:

$$\alpha \gamma_{i,j} = \alpha \gamma_1 + \sum_{\gamma} \delta_{\gamma,i,j} n_{\gamma,i,j} + \sum_{\Theta=A,B} \sum_{k} \sum_{l} \frac{1}{r_{\gamma,i,j} - r_{\Theta,k,l}} \alpha \delta_{\Theta}$$

where $\gamma$ is the index of the atom natur: $A$ - $B$

i is the index of the plan to which the $\gamma$ atom belongs

j is the index locating the position of the $\gamma$ atom of the i plan with respect to the vacancie.

As for the surface, the charge changes on a bond are a linear function of the intra-atomic terms of the two atoms indebted in the bond. This lead to a set of linear equations.

The results are summarized in Table III for the net charges on the atom with respect to their charge level in the case of the ideal surface and in Table IV for the electronic levels associated to the dangling bonds.

The remarkable trends are:

- a - the perturbation converges quickly and is nearly localized on the nearest neighbors of the vacancie.

- b - the answer of the system is a charge transfer, which is function of the situation before the introduction of the defect: for a V vacancie, for example, an excess of electrons is distributed. The nearest neighbors III have before the defect a lack of electrons for those of the surface plan and an excess for those of the first in-plan. After the defect, the atoms at the surface have recovered the distributed excess and those of the first in-plan have lost a part of their charge.
c - the magnitude of the transfer decreases with the increasing ionicity.

d - these charge transfers bring the neighbor of the vacancy in a state near to that of the bulk; they have a tendency to cancel the perturbation created on the surface.

e - the energetic levels of the dangling bonds at the surface and in the first in-plan are at the same position. Therefore, all the compounds have the same behaviour, except for GaSb which has the lowest ionicity and is at the lower limit of validation of our partially ionic model.

f - the most important effect is that the barycenter of the $\alpha_{B_1^-}(V)$ and $\alpha_{As^-}(III)$ energy levels has a tendency to move towards the upper part of the forbidden gap as ionicity of the compound increases. This result can be compared to the existing relation between the pinning of the Fermi level by a metallic adsorption and the compound's ionicity (2).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
 & $n_{As}^B$ & $n_{B_1}^S$ & $n_{As}^-1$ & $n_{B_2}^S$ & $n_{B_1}^-1$ & $n_{Al}^-1$ & $n_{Al}^-2$ & $n_{As}^-2$ & $n_{Al}^-1$ \\
\hline
GaSb & 0.908 & 1.337 & 0.783 & 0.004 & -0.299 & -0.21 & -0.095 & 0.151 & 0.215 \\
GaAs & 0.578 & 0.373 & 0.089 & 0.015 & -0.139 & -0.012 & -0.002 & 0.049 & 0.034 \\
InAs & 0.524 & 0.295 & 0.046 & 0.008 & -0.087 & -0.002 & 0 & 0.024 & 0.019 \\
Gap & 0.485 & 0.278 & 0.046 & 0.008 & -0.087 & -0.002 & 0 & 0.024 & 0.019 \\
InP & 0.424 & 0.221 & 0.029 & 0.004 & -0.052 & 0 & 0 & 0.011 & 0.012 \\
\hline
\end{tabular}
\caption{Tableau III-a : Charge nette sur les atomes dans la lacune V}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
 & $n_{B}^B$ & $n_{As}^-1$ & $n_{B_1}^S$ & $n_{As}^-2$ & $n_{B_1}^-1$ & $n_{Al}^-1$ & $n_{Al}^-2$ & $n_{B_2}^-1$ & $n_{Al}^-2$ \\
\hline
GaSb & -0.882 & -1.085 & -0.622 & 0.483 & 0.226 & 0.155 & 0.069 & -0.132 & -0.186 \\
GaAs & -0.581 & -0.374 & -0.09 & -0.015 & 0.139 & 0.012 & 0.002 & -0.049 & -0.034 \\
InAs & -0.5 & -0.284 & -0.056 & -0.01 & 0.097 & 0.005 & 0 & -0.028 & -0.021 \\
Gap & -0.475 & -0.272 & -0.045 & -0.008 & 0.085 & 0.002 & 0 & -0.024 & -0.019 \\
InP & -0.406 & -0.217 & -0.029 & -0.005 & 0.057 & 0 & 0 & -0.013 & -0.012 \\
\hline
\end{tabular}
\caption{Tableau III-b : charge nette sur les atomes dans la lacune III.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
 & $\delta_{B_1^-}-\delta_{B_1}^-$ & $\delta_{As^-}-\delta_{As}^-1$ & $\delta_{B_2^-}-\delta_{B_2}^-1$ & $\delta_{B_1^-1}-\delta_{B_1}^-$ & $\delta_{Al^-1}-\delta_{Al}^-1$ & $\delta_{B_1^-2}-\delta_{B_1}^-$ & $\delta_{Al^-2}-\delta_{Al}^-2$ & $\delta_{B_2^-2}-\delta_{B_2}^-2$ & $\delta_{B_2^-1}-\delta_{B_2}^-1$ \\
\hline
GaAs & 1.63 & 2.13 & 0.29 & -0.64 & 0.94 & 0.97 & 0.71 & -0.74 \\
InAs & 0.43 & 0.98 & -0.1 & -0.92 & -0.28 & 0.31 & 0.12 & -0.88 \\
Gap & 0.5 & 0.94 & -0.1 & -0.95 & -0.28 & 0.32 & -0.11 & -0.96 \\
InP & 0.08 & 0.55 & -0.18 & -0.86 & -0.3 & 0.12 & -0.04 & -0.84 \\
\hline
\end{tabular}
\caption{Tableau IV-a : États associés aux atomes perturbés par une lacune V}
\end{table}
For Spicer and al., the position of the pinning for GaSb, GaAs and InP, changes from the lower part of the gap to the upper part for InP, around the middle for GaAs.

This result is in good agreement with the theoretical calculations in a more refined model of A. Dow and Smith (10); they show that: the levels of the vacancy are not perturbated when the vacancy is moving from the bulk up to 2 plans to the surface. With the increasing of ionicity, the anion-levels have a tendency to come closer to the conduction band while the cation one levels come closer to the valence band.

It seems clear that the vacancies could form deep levels in the band gap for the partially covalent semiconductors and then, the control of the barrier Schottky by these levels could be explained; it would be not the case for the ionic compounds, the levels associated to the vacancies being too closer to the bands; these compounds would follow the Schottky theory.

Conclusion

In conclusion, we have developed a rough but physical model which well describes the important properties of the crystal in function of a parameter like ionicity.

It allows us to perform an ideal surface characterization and to follow the influence of the ponnctual defect like vacancy. It seems that the explanation of the Fermi level pinning by vacancy induced states is one of the most possible. An effort to fit the model to other defects has to be done for a better comparison.

References

1 For a review, see: BRILLSON L.J., Surface Science Reports, Vol 2., no 2 (1982).

Tableau IV-b : Etats associés aux atomes perturbés par une lacune III

<table>
<thead>
<tr>
<th>en eV</th>
<th>$\alpha_{8,1}^2$ As</th>
<th>$\beta_{8,1}^2$ As</th>
<th>$\alpha_{8,2}^2$ As</th>
<th>$\beta_{8,2}^2$ As</th>
<th>$\alpha_{11}^2$ Al</th>
<th>$\beta_{11}^2$ Al</th>
<th>$\alpha_{12}^2$ Al</th>
<th>$\beta_{12}^2$ Al</th>
<th>$\alpha_{21}^2$ Al</th>
<th>$\beta_{21}^2$ Al</th>
<th>$\alpha_{22}^2$ Al</th>
<th>$\beta_{22}^2$ Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb</td>
<td>-9.14</td>
<td>-11.12</td>
<td>-2.91</td>
<td>-3.56</td>
<td>-2.81</td>
<td>-5.33</td>
<td>-5.32</td>
<td>-0.73</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>GaAs</td>
<td>-1.33</td>
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<td>-0.15</td>
<td>0.8</td>
<td>0.09</td>
<td>-0.78</td>
<td>-0.52</td>
<td>0.89</td>
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</tr>
<tr>
<td>InAs</td>
<td>-0.71</td>
<td>-0.94</td>
<td>0.08</td>
<td>0.97</td>
<td>0.27</td>
<td>-0.33</td>
<td>-0.09</td>
<td>0.84</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>GaP</td>
<td>-0.66</td>
<td>-0.93</td>
<td>0.1</td>
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<td>0.28</td>
<td>-0.32</td>
<td>-0.09</td>
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<tr>
<td>InP</td>
<td>-0.43</td>
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<td>0.17</td>
<td>0.92</td>
<td>0.3</td>
<td>-0.12</td>
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