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To cite this version:

M. Lannoo. The role of dangling bonds in the properties of surfaces and interfaces of semiconductors. Revue de Physique Appliquee, 1990, 25 (9), pp.887-894. 10.1051/rphysap:01990002509088700 . jpa-00246252
The role of dangling bonds in the properties of surfaces and interfaces of semiconductors

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(Received on December 21, 1989, accepted on February 8, 1990)

Résumé. — On montre que les liaisons pendantes peuvent être utilisées pour fournir une description unifiée des propriétés physiques des semiconducteurs tétraédriques dans une grande variété de situations, en particulier à leurs surfaces et interfaces. Une présentation est d’abord donnée de leurs manifestations directes : centre Pb à l’interface Si-SiO₂, liaison pendante dans le silicium amorphe, lacunes et surfaces des semiconducteurs. On démontre ensuite que les mêmes états de liaisons pendantes peuvent être utilisés comme un outil puissant pour corréler les propriétés physiques dans des cas où ils ne semblent pas pouvoir jouer de rôle direct : blocage des niveaux d’impuretés, hétérojonctions, barrières Schottky et leur formation à basse température.

Abstract. — It is shown that dangling bonds can be used to provide a unified description of the physical properties of tetrahedral semiconductors in a large variety of different situations and, in particular, at their surfaces and interfaces. A discussion is first given of their direct manifestations : Pb center at the Si-SiO₂ interface, dangling bond in a-Si, vacancies and semiconductor surfaces. It is then demonstrated that the same dangling bond states can be used as a powerful tool to correlate the physical properties in cases where they do not play an apparently direct role : pinning of impurity levels, heterojunctions, Schottky barriers and their formation at low temperature.

1. Introduction.

The aim of the present paper is to provide a general picture of the physical properties of the surfaces and interfaces of tetrahedral semiconductors. This picture is based on the use of dangling bonds which serve as a tool to provide a unifying description of apparently widely different situations. We first review well documented cases where dangling bonds are known to exist and use them to establish the general common features characterizing the dangling bond states. We then use this information to analyze situations where these dangling bond states do not occur any more, i.e. where there is rebonding with other atoms. This happens for instance for bulk impurities and at interfaces (heterojunctions or Schottky barriers). We show that the use of the dangling bond concept allows to correlate all these physical situations in a quantitative manner.

Section II provides a simple qualitative introduction to the notion of dangling bonds in tetrahedral semiconductors. Attention is then paid to their direct manifestations, allowing to get a fairly complete and general information about their basic features. These informations are then used in section 4 to discuss the pinning of transition metal impurity levels and its connexion with band discontinuities at interfaces (heterojunctions and Schottky barriers).

This paper represents a short and simplified overview of these related situations. More detailed informations and references can be found in reference [1].

2. The notion of dangling bonds.

We consider here the tetrahedral semiconductors, i.e. the elements of column IV, the III-V and II-VI compounds. These systems crystallize in the zincblende structure where each atom has four nearest neighbors in a tetrahedral coordination. The average number of valence electrons per atom is four and the bonding configuration corresponds to the situation which is schematically pictured in figure 1a, i.e. with...
two electrons per bond. This corresponds to the strong covalent character exhibited by these materials.

In this chemical bond picture the simplest way to introduce dangling bonds is to create a vacancy. This is shown in figure 1b for a purely covalent material like Si. The removal of the central atom involves the rupture of four covalent bonds, i.e. the creation of four dangling bonds schematically pictured on this figure. The neutral vacancy corresponds to four non-bonded electrons, i.e. to one electron per dangling bond. However to be really useful this naïve view must correspond closely to the most important features of the electronic structure. This can be achieved through the use of the molecular [2] or bond orbital [3] description of these materials. This one is based on the tight binding approximation in which the wave function is written as a linear combination of the free atom states. Use is made of a minimal basis set consisting of the « s » and « p » valence states of each atom, which are furthermore assumed to be orthonormal.

The problem then reduces to the diagonalization of a $4N \times 4N$ Hamiltonian matrix, if $N$ is the number of atoms in the crystal. In perfect crystals this can be simplified through the use of Bloch's theorem, leading to $8 \times 8$ matrices for each wave vector $k$. However, as regards physical understanding, it is much better to proceed differently and try to isolate the dominant terms in the Hamiltonian matrix. This can be achieved through a basis change, by building four equivalent sp3 hybrids out of the s and p states of each atom. The main virtue of these hybrids is that they have a strong positive lobe pointing in the direction of one given nearest neighbor, as shown in figure 2. In this basis the dominant elements of the Hamiltonian matrix are those connecting pairs of sp3 hybrids involved in the same bond. The neglect of all other matrix elements, as a zeroth order level, leads to the molecular model in which all pairs of sp3 hybrids can be treated independently. This is equivalent to a set of identical diatomic molecules, each of them giving rise to one bonding and one antibonding state as shown in figure 3a. The degeneracy of these levels is equal to the number of bonds and, as there are two electrons per bond, the ground state of the system corresponds to two electrons per bonding state. This justifies the qualitative description of figure la completely.

It is interesting to examine the nature of dangling bonds in the molecular description. The removal of one atom creates a situation where the four sp3 hybrids pointing towards the vacancy have no more partner to form bonding and antibonding states. They are the dangling orbitals whose energy, in a pure covalent system like Si, is the sp3 energy, i.e. the center of gravity of the bonding and antibonding levels. For the neutral vacancy there are four electrons to distribute over the four dangling bond

\begin{center}
\includegraphics[width=0.5\textwidth]{figure1.png}
\end{center}

Fig. 1. — Schematic representation of : a) the bonds in the zinc-blende materials ; b) the dangling bonds near a vacancy.

\begin{center}
\includegraphics[width=0.5\textwidth]{figure2.png}
\end{center}

Fig. 2. — Representation of the sp3 hybrids in tetrahedrally bonded materials.

\begin{center}
\includegraphics[width=0.5\textwidth]{figure3.png}
\end{center}

Fig. 3. — Broadening of the molecular levels into bands.
states i.e., statistically one electron per dangling bond. Again this confirms the simple chemical picture.

Let us now discuss the effect of including all interactions that have been neglected in the molecular model. These interactions connect the neighboring bonding, antibonding and dangling bond states together. The main result is a broadening of the highly degenerate set of bonding and antibonding states respectively into a filled valence band and an empty conduction band, as shown in figure 3. On the other hand each individual dangling bond first interacts with its backbonds, resulting in a shift of its energy level and a delocalization of its wave function with respect to the original sp³ state. This is shown in figure 3b for pure covalent systems like Si, the resulting energy level still falling within the forbidden gap. Finally the vacancy case can be understood as a system of four such dangling bonds in interaction. As discussed later this splits the fourfold degenerate dangling bond level into a lower non degenerate component of Al symmetry and a triply degenerate one of T² symmetry.

3. Direct manifestations of dangling bonds.

The cases that will be investigated here are: the isolated dangling bond (P₆ center at the Si-SiO₂ interface and the dangling bond in a-Si), the vacancy and the case of surfaces.

3.1. THE ISOLATED DANGLING BOND. — Experimentally this isolated dangling bond situation is best realized for the P₆ center, i.e. the tricoordinated silicon atom at the Si-SiO₂ interface [4 to 8] but it can also occur in amorphous silicon [9,10] as well as grain boundaries or dislocations. It has been identified mainly through electron spin resonance (e.s.r.) [4] deep level transient spectroscopy (D.L.T.S.) [6,11], capacitance measurements versus frequency [4] and optical experiments [9,12]. The picture which emerges is the following: i) the isolated dangling bond can exist in three charge states: positive $D^+$, neutral $D_0$ and negative $D^-$. These respectively correspond to zero, one and two electrons in the dangling bond state; ii) the effective Coulomb term $U_{\text{eff}}$, i.e. the difference in energy between the acceptor and donor levels ranges from 0.2 to 0.3 eV in a-Si [9] to about 0.6 eV at the Si-SiO₂ interface [6].

The E.S.R. measurements give informations on the paramagnetic state $D_0$ through the g tensor and the hyperfine interaction. Analysis of the results indicates that the effective « s » electron population on the trivalent atom is 7.6% and the « p » one 59.4% which corresponds to a localization of the dangling bond state on this atom amounting to 67% and a « s » to « p » ratio of 13% instead of 25% in a pure sp³ hybrid. This last feature shows a tendency towards a planar sp² hybridization.

Several calculations have been devoted to the isolated dangling bond. However only two of them have dealt with the tricoordinated silicon atom embedded in an infinite system other than a Bethe lattice. The first one is a self consistent local density calculation [13] which concludes that the purely electronic value of the Coulomb term (i.e. in the absence of atomic relaxation) is $U = 0.5$ eV. The second one is a tight-binding Green's function treatment in which the dangling bond levels are calculated by imposing local neutrality on the tricoordinated silicon [14]. In this way the donor and acceptor levels are respectively $E(0, + ) = 0.05$ eV and $E(0, - ) = 0.7$ eV. Their difference corresponds to $U = 0.65$ eV in good correspondence with the local density result. Both values correspond to a dangling bond in a bulk system and can be understood simply in the following way: the purely intraatomic Coulomb term is about 12 eV for a Si atom; it is first reduced by a factor of 2 since the dangling bond state is only localized at 70% on the trivalent atom; finally dielectric screening reduces it by a further factor of $\epsilon_0 \sim 10$. The final result $6/\epsilon_0$ gives the desired order of magnitude 0.6 eV. At the Si-SiO₂ interface however the situation becomes different because screening is less efficient. A very simple argument leads to replace $\epsilon_0$ by $(\epsilon_0 + 1)/2$ so that the electronic Coulomb term for the P₆ center should be twice the previous value, i.e. $U(P₆) \sim 1.2$ eV.

An extremely important issue is the importance of the electron-lattice interaction. There is no reason for the tricoordinated atom to keep its tetrahedral position. A very simple tight binding model [15] shows that this atom does indeed experience an axial force that depends on the population of the dangling bond state. This is confirmed by more sophisticated calculations [13] but could also have been predicted on the basis of quite general arguments developed for molecules and known as V.S.E.P.R. (valence shell electron pair repulsion theory [16]). In V.S.E.P.R. the molecular geometry directly depends upon the configuration of electron pairs in the valence shell of a given central atom. These pairs are considered as bonding if the two electrons are involved in a covalent bond and non bonding if this is not the case. The general principle that governs the molecular geometry is that this one should maximize the distance between pairs to minimize their mutual repulsion. Considering the pairs as equivalent naturally leads to the following geometries: linear (2 pairs), equilateral triangle (3 pairs), tetrahedron (4 pairs), trigonal bypyramid (5 pairs) and octahedron (6 pairs).

These principles can directly be applied to the tricoordinated silicon atom. If the dangling bond
state is empty \((D^+)\) there are three pairs of bonding electrons and V.S.E.P.R. theory tells us that the natural configuration is planar (interbond angle: 120°). If the dangling bond state is filled with two electrons \((D^-)\), then the arrangement should be tetrahedral (interbond angle: 109°). In fact this last conclusion should be slightly modified since V.S.E.P.R. theory states that non bonding pairs tend to occupy more space than the others, which would reduce slightly the interbond angle from its value of 109°. Finally the situation for \(D^\circ\) is obviously intermediate. These empirical rules are in complete agreement with recent calculations which predict a relaxation towards a planar configuration for \(D^\circ\) and \(D^-\).

The fact that there is a charge state dependent relaxation of the tricoordinated atom modifies the difference in energy between the acceptor and donor levels, i.e. the effective Coulomb parameter. This can be understood on the basis of the following simple argument: i) when the tricoordinated atom is lowered (i.e. tends towards a planar configuration) then the dangling bond level is raised since it tends towards a pure « p » level as in graphite; ii) when it is raised (i.e. the interbond angle tends towards 90°) then the dangling bond level is lowered since it tends towards a pure « s » state as in a-As. This reduces the effective Coulomb term, equal to the difference between the electronic contribution and the relaxation one, of order 0.6 eV for the Pb center and slightly negative in a-Si.

3.2 VACANCY DEFECTS. — As discussed by Watkins [17] some time ago vacancies are usually characterized by relatively large distortions. The origin of these can be understood on the basis of a fairly simple model based on the fact that the vacancy corresponds to four interacting dangling bonds. In view of the tetrahedral symmetry the fourfold degenerate dangling bond state (in the absence of interaction) splits into two levels: a lower non degenerate one of \(A_1\) symmetry and an upper triply degenerate one of \(T_2\) symmetry. In silicon the center of gravity of the \(A_1\) and \(T_2\) levels is at about \(E_v + 0.25\) eV [18 to 20] i.e. the isolated dangling bond level discussed above and the \(A_1\) and \(T_2\) splitting is of order 1.8 eV. This \(A_1\) and \(T_2\) splitting is characteristic of all vacancies in zinc-blende compounds. Their properties can vary drastically with the electron population \(N_e\) of the \(A_1\) and \(T_2\) levels. In particular, filling the \(T_2\) degenerate state will give rise to symmetry-lowering Jahn-Teller distortions. The resulting symmetry of the defect is found to be tetragonal, trigonal or mixed. In each case the \(T_2\) level is split which ensures the gain in energy. This simple picture is fully confirmed by experimental observations, mainly by e.p.r. on \(V_{Si}^-\) and \(V_{Ge}^-\). A very interesting conclusion is that \(V_{Si}^{0+}, V_{Si}^- V_{Ge}^-\) form a negative \(U\) system, i.e. that the distortion contribution overweights the electronic one. This was shown theoretically [21] as well as experimentally [22].

3.3 SURFACE PROPERTIES. — Let us first consider the situation at ideal surfaces. The Si(111) surface consists of an array of relatively weakly interacting dangling bonds. Theory predicts a narrow surface band of width \(~\sim 1\) eV whose center of gravity lies just above the top of the valence band. This corresponds to the isolated dangling bond energies. These have been determined [23] from a tight binding treatment and by imposing local neutrality on the tricoordinated atoms. They are reported in table I. For instance it is seen that the As dangling bond level is lower by \(~\sim 0.73\) eV than the Ga one. On GaAs(110) this gives rise to two surface bands separated by \(~\sim 1.25\) eV. The difference between these two numbers is due to the interaction between the nearest neighbors’ Ga and As dangling bonds which increases the splitting and thus the gap between the As and Ga derived subbands.

It is known that the surfaces of zinc blende materials are subject to extensive atomic reorganization. For instance, the Si(111) surface should at least experience a relaxation, essentially consisting of a contraction of the first interlayer spacing. This is easily explained from our discussion of section 1 since the neutral surface has one electron per dangling bond, in which case we have seen that there must be an inwards displacement of each tricoordinated atom. However, superposed to this effect

Table I. — Calculated values of the anion and cation dangling bond energies together with the predicted and experimental values of the ionization potentials (all values in eV).

<table>
<thead>
<tr>
<th></th>
<th>(E_{db})</th>
<th>(E_{db})</th>
<th>(I_p)</th>
<th>(I_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>anion</td>
<td>cation</td>
<td>theor.</td>
<td>exp.</td>
</tr>
<tr>
<td>Si</td>
<td>0.11</td>
<td>0.11</td>
<td>5.60</td>
<td>5.53</td>
</tr>
<tr>
<td>Ge</td>
<td>-0.10</td>
<td>-0.10</td>
<td>5.23</td>
<td>4.80</td>
</tr>
<tr>
<td>C</td>
<td>1.48</td>
<td>1.48</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AlAs</td>
<td>0.47</td>
<td>1.37</td>
<td>5.79</td>
<td>—</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.08</td>
<td>0.59</td>
<td>5.06</td>
<td>4.91</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.10</td>
<td>0.83</td>
<td>5.55</td>
<td>5.56</td>
</tr>
<tr>
<td>GaP</td>
<td>0.28</td>
<td>1.34</td>
<td>5.92</td>
<td>6.01</td>
</tr>
<tr>
<td>InP</td>
<td>0.48</td>
<td>1.08</td>
<td>6.07</td>
<td>5.85</td>
</tr>
<tr>
<td>InSb</td>
<td>0.27</td>
<td>0.41</td>
<td>5.47</td>
<td>5.42</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0</td>
<td>0.53</td>
<td>4.95</td>
<td>4.90</td>
</tr>
<tr>
<td>CdTe</td>
<td>6.69</td>
<td>6.76</td>
<td>5.37</td>
<td>5.72</td>
</tr>
</tbody>
</table>
there is a reconstruction of the surface. Such a reconstruction is usually such that it satisfies the following requirements: i) minimization of the number of broken bonds per surface atom, ii) preservation of the bondlength between nearest neighbors, iii) tendency for filled dangling bonds to achieve a planar local configuration.

The metastable Si(111) 2 x 1 surface is obtained by cleavage. The most successful description of its atomic structure is provided by the π bonding chain model [24] which not only satisfies the criteria given above but also leads to an increase in energy through π bonding between nearest neighbors' dangling bonds, while the unreconstructed surface is characterized by second nearest neighbors' parallel dangling bonds. The other clear-cut case is Si(100) (2 x 1). Here the unrelaxed surface has two dangling bonds per atom. This is highly unstable and the system experiences extensive rebonding between pairs of dangling bonds which were pointing towards the same neighbor. This gives the dimer model with one dangling bond per surface atom. However there is further gain in energy occurring in the asymmetric dimer model [25], again because of the competition between covalent bonding and the population dependent tendency towards planar configuration.

The final case we consider here is GaAs(110) with alternate Ga and As dangling bonds along chains. There are two electrons per pair of dangling bonds but these populate the As dangling bond state which is lower in energy. The Ga atom has an empty dangling bond and thus relaxes towards a planar configuration. The opposite is true for the As atom, with a filled dangling bond, which is slightly raised. Both types of displacements can be achieved by a rotation which practically preserves bondlengths. The final result is that both surface bands are expelled from the gap, as shown experimentally and theoretically [26].

Finally an interesting point is that one can use tight binding to determine the absolute position of the top of the valence bands, i.e. the ionization potentials for the different semiconductors [27]. These are compared in table I to the experimental values, showing very good agreement.

4. Indirect manifestations.

Here we consider various cases for which the dangling bonds have no more physical existence and show that they can be extremely useful as reference or pinning levels.

4.1 Pinning of impurity levels. — This general phenomenon can be understood simply in a tight binding picture. We consider atomic states of a substitutional impurity which have T2 symmetry in the Td point group. This problem can be treated very accurately via a renormalized defect molecule model [28] which is equivalent to coupling the T2 impurity states with the T3 dangling bond states of the vacancy. This results in a 2 x 2 matrix whose solutions are a triply degenerate bonding state t2 and a triply degenerate antibonding state t2*. This simple treatment can be made selfconsistent by allowing the impurity atomic state to vary linearly by an amount U . n with the excess electron population n on this atom. Considering the limit of infinite U and the fact that U . n must remain finite then one gets the condition n ~ 0, i.e. a local charge neutrality condition. This means that the impurity level must be adjusted in such a way that one gets neutrality on this atom. In other words the impurity levels are pinned with respect to the vacancy states at a distance in energy which only depends on the population of the t2 and t2* states. An important consequence is that the distance in energy between the levels of different impurities belonging to the same family will be the same in different isovalent compounds [29, 30]. This simple view is strikingly confirmed by the experimental evidence for transition metals [31], as shown in figure 4 for the III-V compounds.

Finally an interesting point is that one can use tight binding to determine the absolute position of the top of the valence bands, i.e. the ionization potentials for the different semiconductors [27]. These are compared in table I to the experimental values, showing very good agreement.

4.2 Interface discontinuities. — The knowledge of semiconductor interfaces has been greatly improved recently. A central quantity for metal-semiconductor interfaces as well as semiconductor heterojunctions is the band discontinuity. This is...
fixed by the Schottky barrier height in the first case and the band offset in the second case. Full calculations of these quantities have been performed recently but it is of fundamental interest to get a simpler description of the underlying physics. The most successful attempt was provided by the concept of charge neutrality level \([32, 33]\). For the semiconductor this level \(E_B\) plays the same role as the Fermi level for a metal. Thus the Schottky barrier height is simply obtained by aligning the metal Fermi level \(E_F\) and the semiconductor neutrality level \(E_B\). In a similar way the heterojunction band offset is obtained by aligning \(E_B\) on both sides. Tersoff has proposed a prescription \([33]\) for calculating \(E_B\) that leads to fairly good agreement with experiment.

This simplified theory in itself does not tell enough about what happens microscopically. This can be done with the use of dangling bonds. At both types of interfaces these are strongly coupled either to metal atoms or to other dangling bonds and one could believe that the concept of dangling bond is no more interesting. This is not so however since they play at least the role of a reference level. The argument at the metal semiconductor interface is that the interaction between the surface dangling bonds and the metallic continuum leads to a half filled resonance centered on the average dangling bond energy. If the resonance has a symmetrical shape the direct conclusion is that the Fermi level is at the average dangling bond energy \(E_{db}\). One is thus led to identify \(E_{db}\) with the neutrality level \(E_B\). This is confirmed for heterojunctions where one can show \([23]\) that the condition of local neutrality on each side of the interface corresponds to the alignment of \(E_{db}\) on each side. Finally numerical calculations of \(E_{db}\) still give more credit to this identification.

An interesting question in this field has been the empirical correlation which has been shown to exist between transition metal impurity levels, Schottky barrier heights and heterojunction band offsets \([31]\). The basic reason can be found in the discussions given before, the transition metal levels being pinned to the vacancy dangling bond states which are themselves intimately related to the average dangling bond energy \([29, 30]\). This shows that, although indirectly, the dangling bond energy level plays an important role as a reference level in all these systems.

4.3 FORMATION OF THE SCHOTTKY BARRIER AT LOW TEMPERATURES. — Recently the formation of Schottky barriers has been studied experimentally at different temperatures \([34, 35]\). Figure 5 shows that the evolution of the surface Fermi level \(E_{FS}\) versus coverage is very different between 300 K and 80 K and between \(n\) and \(p\) type materials. This difference has been attributed to the fact that, at room temperature, surface diffusion can occur, leading to the formation of islands of adatoms. In the low temperature case this phenomenon would not occur leading, at low coverage, to a distribution of individual adatom-semiconductor bonds.

This idea can be checked theoretically by using a molecular model in which one adatom is coupled for instance to one dangling bond. This was done independently in references \([36]\) and \([37]\). As shown in Fig. 6, the theoretical curve of the surface Fermi level \(E_{FS}\) versus coverage: (a) for Cs (b) for Ag.
in detail in reference [36] the corresponding tight binding parameters can be determined from well-defined rules and the calculations can be made selfconsistent, which represents an essential step of the treatment. The theoretical results are given in figure 6 for Cs and Ag and it is clear that they explain the main experimental features except for a dip which is not seen experimentally (possible explanations for this are given in [36]). The main conclusions of this study are that the plateau on p type materials corresponds to the position of the adatom-Ga bonding state which only acts as a donor and the final pinning position is given by the average dangling bond energy confirming the discussion of the previous section. Figure 7 shows the predicted donor ionization energies versus the free adatom levels. This curve follows closely the experimental results of reference [34].

All these elements again confirm the fact that the dangling bond states are basic energy references in the understanding of chemisorption on semiconductor surfaces.

5. Conclusion.

We have analyzed a number of situations where dangling bond states are created and shown that they all present common basic features such as: the dangling bond state energy, the electron-lattice interaction, the Coulomb parameter and the dangling bond localization on the tricoordinated atom. We have also shown that cases where rebonding occurs can also be usefully analyzed by using the characteristics of the dangling bonds. The main successes of this approach are the relation between transition metal impurity levels, heterojunction band offsets and Schottky barrier heights. Finally the same kind of arguments allows an understanding of the formation of the Schottky barrier at low temperature.

References


