METAL-SEMICONDUCTOR INTERFACE FORMATION

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The more and more detailled study of an increasing number of me-
tal-semiconductor (MS) interfaces tends to demonstrate the pre-
vailing part played by the different local bonds associated with
the compositional change at the interface. In the case of the
abrupt interfaces both geometrical properties an electronical
equilibrium are settled at a coverage below one monolayer. A few
cases are discussed here which show the variety of physical phe-
nomena involved in the barrier height fixation in contradiction
with all attempts to a unified model.

INTRODUCTION

The historical evolution of the MS (metal-semiconductor) inter-
face concept has followed the progress in the diverse experimen-
tal methods and theorical approaches. It appears as the refine-
ment of an initially simple model, associated with a better per-
ception of the different structural parameters. At first the
electronic properties of the MS contact have been thought to be
governed either by the metal M (Schottky (I)) or the semiconduc-
tor S (Bardeen (2)). Then after swinging between the two (3-6),
the physical properties of the system appear progressively as
governed by the atomic interaction at the interface between the
atoms of both metal and semiconductor, the local bonds which are
formed being dominant. The multiplicity of the systems studied
has led to a gradation of the reactions at the interface in
which the limit cases are :

- a cohabitation metal-semiconductor without any visible mo-
dification of the substrate properties and with a geometric
extension of the transitional zone limited to the first ato-
mic planes in contact.

- a form of intermixture more or less spread along the

growing direction with a transition zone between semiconductor and metal which might, according to the cases, go from a two-dimensional buffer layer, a few $\overset{o}{A}$ thick, to a three dimensional alloy several hundred $\overset{o}{A}$ thick.
This first view of the MS interface sets the problem of the adequacy between the system under study and the experimental approach. With regard to our work and discussions in this article we are chiefly interested by interfaces with no or little intermixture in their phase of formation : it makes the use of surface physics methods specially suited to study the early stages of the formation under vacuum of such interfaces. Although the studies on these systems started a few decades ago, a good appreciation of interfacial physics has been reached only within the last few years. Nowadays it looks like a game between the semiconductor and metal characteristics and likewise between the interactions of both. In order to separate more easily the determinant part of each component, the study of the less reactive systems is the best adapted to a comprehensive approach of the MS interfaces. During the interface formation this study is deployed round the three following aspects :
  - the evolution of the semiconductor surface intrinsic properties
  - the development of the interfacial structures
  - the formation of the metal layer.
The success of this approach is subordinated to the possibility to carry out the following operations :
  - the preparation of the semiconductor substrate surface, clean, well characterized (reproductiveness) both geometrically (orientation, defects, surface restructuration) and electronicaly (electronic states). As a matter of fact, for many years, in spite of the lack of many present experimental skills (7) the influence of the surface quality had been already observed. Until now our experimental work has been concerned with the Si (III) face, both 2xI and 7x7 reconstructed

and GaAs (IIO) surfaces cleaved under ultra-high vacuum. THe experimental methods were : LEED (low energy electron diffraction), AES (Auger electron spectroscopy), ELS (electron loss spectroscopy) and PYS (photoemission yield spectroscopy) - the deposition of an accurately calibrated amount θ of pure metal on the clean surface. The coexistence of preparation and measurements in the same ultra-high vacuum system requires the use of the MBE technic (molecular beam epitaxy) where the effusion cells can provide a deposition rate as low as $IO^{-4}ML/s$. The smallest coverage able to provoke a measurable modification of the surface is used as a start. If I monolayer (ML) is I deposited atom per semiconductor surface atom, less than O.I ML on Si (III) give observable changes in the interfacial characteristics while $IO^{-3}ML$ already modifies the surface properties of GaAs (IIO).

The development of the MS interface which comes with the substrate evolution and with the metallic deposition may be easily described through two sets of phenomena well established in surface physics. The first concerns geometrical properties where the following effects can appear

- surface substrate _relaxation_ induced by the deposited atoms
- two-dimensional _structuration_ of the deposition ($\theta < I$ ML) the ordering of which depends as much on the substrate surface as the metallic species
- _epitaxy_ of the metal on the semiconductor ($\theta > I$ ML).

The second concerns the change in the electron state densities which may reveal

- the _evolution_ (concervation, displacement or removal) of the electron surface states of the clean substrate surface. This evolution is the double mark of both deposition reactivity and the part played by the semiconductor in the Fermi level pinning and consequently of the Schottky barrier.
- the _creation_ of new states at the interface related to the MS interactions and also to the first MM interactions

when the deposition becomes sufficient or if some metallic aggregates are formed

Where the MS interface is established

The major point which appears in the MS interfaces formed on Si (III) and GaAs (IIO) by Ag, Cu, Au, Ga, In or Al with or without annealing, is the extreme sensitivity of the electronical properties of the system to the number of deposited atoms. It governs the fixation of the Fermi level position with respect to the bulk bands of the semiconductor (barrier height) at metal coverages lower or much lower than one monolayer for all the studied cases. The MS contact no longer appeared as a metal-semiconductor surface and a two-dimensional layer of foreign atoms which on the whole determines the future contact physics : once this two-dimensional layer completed, further metal deposition do not modify its character. The adsorbed atoms may be considered as any impurities on the surface and in some cases (GaAs) the metal effect in the first deposition stage is similar to the interaction with a gas such as oxygen. Let us note also that this intermediate area between semiconductor and metal is often a two-dimensional structured network where the metal atom arrangement is peculiar to this zone and does not correspond to the one projected from the bulk.

The MS interfacial geometry

θ ml	Ag.Si(111) 2x1	Ag.Si(111) 7x7	Ag.Si(111) 7x7	Ga.Si(111) 2x1	In.Si(111) 2x1	Al.Si(111) 2x1
0.05			annealed			
0.3					$\sqrt{3} \times \sqrt{3}$-R30°	$\sqrt{3} \times \sqrt{3}$-R30°
0.7	$\sqrt{7} \times \sqrt{7}$-R19°			$\sqrt{3} \times \sqrt{3}$-R30°	2x2	
1			$\sqrt{3} \times \sqrt{3}$-R30°			
2	epitaxy 1x1			1x1	epitaxy	
4		epitaxy 1x1				epitaxy

Table I - LEED structures of some M-Si (III) systems.

Certain surfaces such as Si (III) have a geometry which promote the building of structured interfacial planes (table n°I). The variety of the encountered structures in the M-Si (III) compositions is remarkable and points out the natural tendency of the (III) face's three-fold symmetry to accept different parallel structures provoked by the metal arrangement in the surface network. The ad-atom position varies from one metal to another either along the surface plane or within the last atomic layer. For instance let us quote tw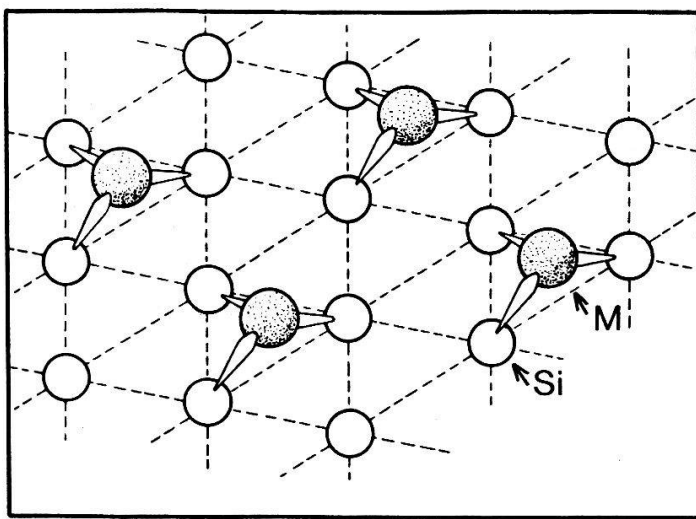o characteristics examples. First the metal atom can take and adsoption site governed by the dangling bond geometry of the semiconductor surface (Fig.I). This is the case of Ga, In, Al on Si (III) (8) where I/3 ML brings out a $\sqrt{3} \times \sqrt{3}$-R 30° structure which is interpreteted as the binding of the metal atom to three Si surface atoms the dangling bond of which is replaced by a covalent bond. In the second case it may be possible that the metal atom ignores these preferential sites and adsorbs in some intersticial positions (Fig.2) where the nature of the bonds is less pronounced and where a two-dimen-

Fig1 Metal(like Ga,In,Al)bound on Si(111) The dangling bonds are used.The deposition is $\sqrt{3} \times \sqrt{3}$-R30°structured.

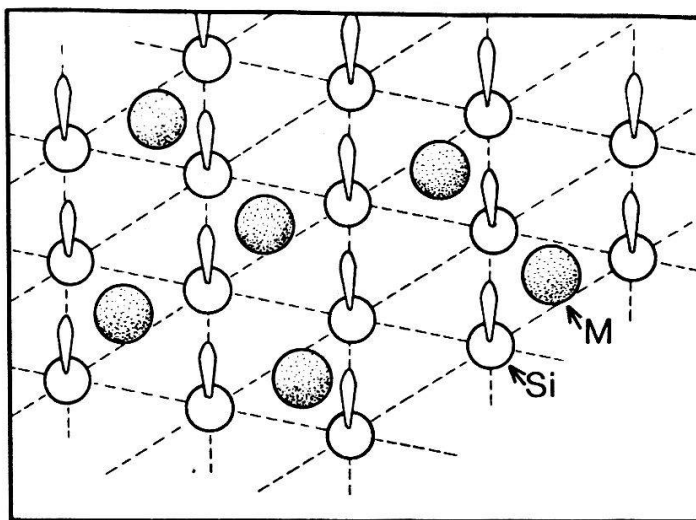Fig.2 Metal (like Ag) in intersticial position on Si(111).The dangling bounds are conserved.

sional coordination is allowed. This is the case for instance
of Ag on Si (III) 2×I (9) where a new $\sqrt{7}\times\sqrt{7}$ - R I9° structure
(Fig.2) has been observed. In these two kinds of adsorption the
substrate surface geometry is only very slightly modified as
shown by the different LEED analyses. Another class of geometri-
cal interface interaction appears with the (IIO) face of GaAs.
In this case the additional structures induced by the first me-
tal plane are uncommon, but the electronical structure analyses
show, as we shall see later, that the surface atoms of the subs-
trate undergo a restructuration perpendicular to the surface
which tends to bring the surface geometry toward its unrecons-
tructed (unrelaxed) structure. The lack of well defined adsorp-
tion sites along the (IIO) face explains the absence of metal in-
duced superstructures. Let us note however that Ag exhibits a
peculiar behavior where an atom alignment occurs at low coverage
in the [$\bar{1}$IO] direction, which initiates the metal epitaxy in an
unexpected direction of growth (IO). The first transition layer
being achieved, the other atoms of metal arriving see a two-di-
mensional system with both M and S atoms. It may be possible
that the new arrivals find an adsorption position in this system
which keeps the initial coordination but with an increased num-
ber of atoms per elementary cell : this is the case of Ga on Si
(III). On the contrary the new ad-atoms can break the existing
coordination and produce some transitory structures as in In
on Si (III). The surface atom mobility along the forming MS sys-
tem is often sufficient to provoke atom clustering which gives
a voluminal metal. Typical examples of epitaxy are found at room
temperature with Ag and In on Si (III) 2×I as well as Ag on GaAs
(IIO) where the surface substrate cristalline direction induces
an epitaxial direction of the growing metallic layer. At covera-
ge higher than IO ML the layer thickness is often inhomogeneous
with islands more or less spread along the surface. The shape of
these islands can be changed by thermal processing as in the
case of Ag on Si (III) 7×7 (II).

MS interfacial electronic structures

From the clean semiconductor surface with its geometrical defects (steps, etc..) and with its intrinsic electronical state density (valence, dangling bonds, defect of the real surface), the adsorbed metal atom can be thought of as a perturbation center from which the effect on the surface's electronic equilibrium can be interpreted either in term of defect (of which the nature might be specified) or in that of surface reactivity. Alltogether microscopic interactions give some structural evolution macroscopically marked by some Fermi level E_F pinning position in the semiconductor gap and perceptible in the Schottky barrier measur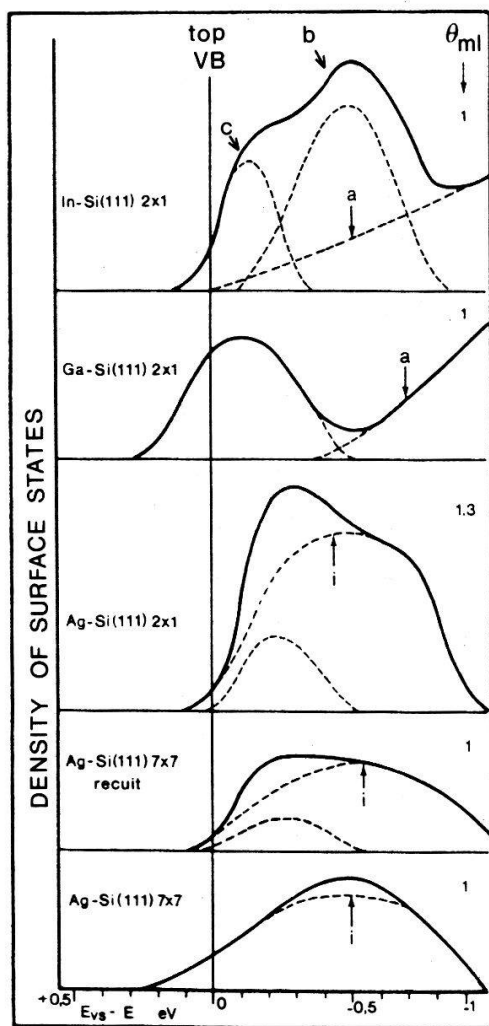ement. As a first exemple let us note the Ag-Si (III) 2xI (9) case where the Si dangling bonds (i in Fig.3) appear as maintened, E_F being determined by the substrate's intrinsic surface states, is not modified by the very weak density of states induced by the metal. Only a work function shift towards the metal one, induces an overall shift of the energy levels without any band bending modification. This behavior shows the determinant effect of the semiconductor surface on the Schottky barrier determination. Such a behavior is specific to the Ag-Si (III) 2xI system but it cannot be generalized to any system on Si. For example on Si (III) 7x7 the effect of Ag is more important and with Ga and In the deposited atoms control the electronic properties of the interface. For the latest systems in accordance

Fig.3 Density of electronical surface states M-Si i-Si(111)2x1-7x7 clean a,b,c-metal induced.

with the adsorption model given above (Fig.I) the dangling bond states of the semiconductor disappear and are rapidly replaced by bonding electron states (a, b, c in Fig.3) near the valence band edge. They spread into the gap and stabilize the Fermi level in a position, which appears almost independent of the initial surface s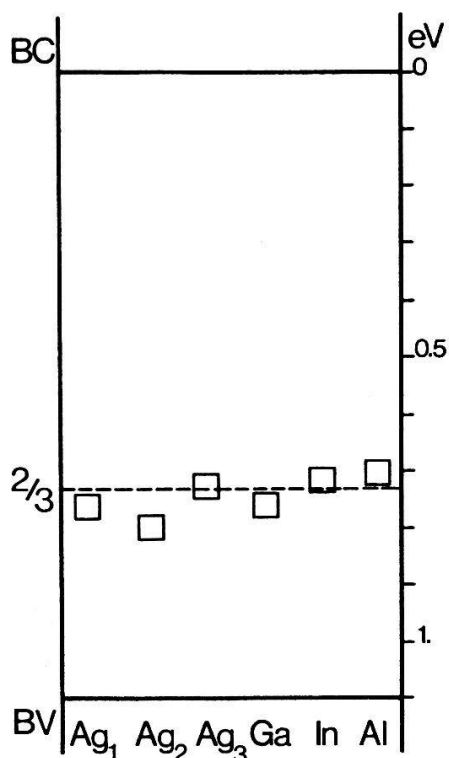tructure and of the metal species, close to $\frac{2}{3}$ Eg below the conduction band edge (fig.4). The shape of the interface state distribution gives to this two-dimensional region a character which is more covalent than metallic, the MS bonds on the silicon sites showing a strong spatial localization. With such systems the metal plays a determinant role for the electrical characteristics of the MS contact. Another class of interactions at the interface is found with the deposition of some metals (here Ag, Ga, In, Al) on cleaved GaAs (IIO). The analysis of the density of states near the threshold shows a great sensitivity of the electronical equibrium to the metal coverage. More precisely a few 10^{-2}ML of metal are

Fig.4 Fermi level M-Si
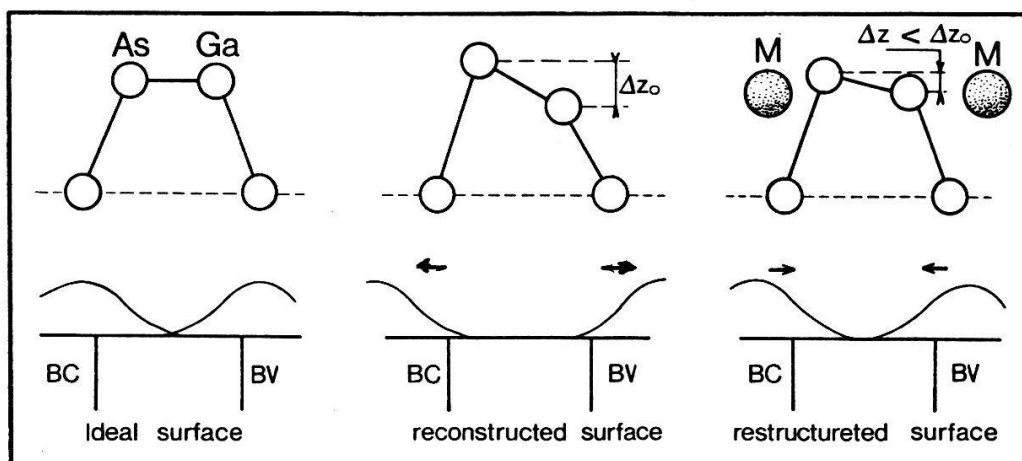$Ag_1=Ag-Si(111), Ag_2=Ag-Si(111)7x7, Ag_3=Ag-Si(111)$ annealed.

Fig.5 Metal-GaAs(110)restructureted surface model

sufficient to stabilize the Fermi level in the gap at a position which is that of the future Schottky barrier, and which is almost independant of the deposited metal. One explanation for such sensitivity is the effect of substrate restructuration induced by the deposited atoms (Fig.5)which as been mentioned
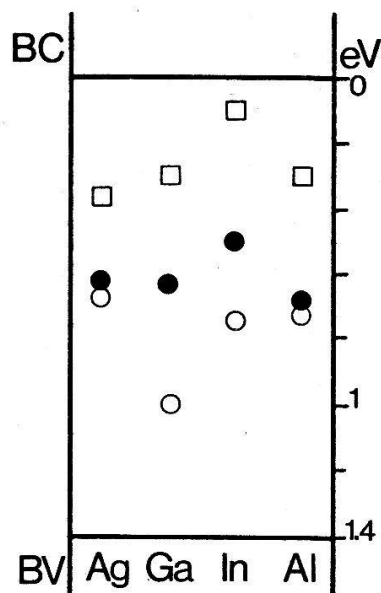
earlier. A return of As and Ga atoms from the semiconductor toward their ideal extrapolated bulk positions should bring back into the gap the electronic states initially removed by the substrate relaxation after cleavage. These intrinsic states lead to the Fermi level pinning at a position which is a fonction of the quantity of displaced states, then in relation with the restructuration importance. The other contributions come from the MS interaction states and are proportional to the number of deposited atoms below I ML and play a part in the I ML coverage range. Fig.6 gives the Fermi level position, in the gap, for the four M-GaAs (IIO) interfaces studied in our experi-

Fig.6 Fermi level M-Ga As(110)-●n.type,Op.type (1ML),□metal work func-tion(0=4eV under vaccum level)

ments. The Al has a different behaviour and seems to be more reactive than the other three metals : the formation of an interfacial compound is possible in this case.

CONCLUSION

The few results and observations which have been given here on MS systems with small intermixing show the double aspect of the interfacial physics which is at the origin of several generations of more or less unified explanatory models. It is the diversity of the physical processes which determines the MS contact characteristics in apparent contrast with certain behaviour constant (such as the barrier height) which would rather favorise a unified model. Nowadays in the present state of our

knowledge, if we want to put the accent on one of the most
characteristic features of the MS interfaces, we should hold
our attention on the extreme sensitivity of the electronic
structure of the local bonds in the interfacial region. As a
consequence the future MS contact parameters are defined in the
early coverage stage, in the one monolayer range.

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