Silicon surfaces: metallic character, oxidation and adhesion

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Several years of extensive research [1-14] have considerably clarified the properties of the noble metal-semiconductor interface. Among others, one important result is that the first noble metal monolayer plays a crucial role in determining the properties of the whole interface. In particular, the fact that this monolayer presents some long range order or not has a great importance. There are at least two cases where basic properties of the interface are drastically changed by this ordering.

The first example is the growth mode of noble metal atoms. When deposited on a Si(111) 7 x 7 surface maintained at room temperature, the first Ag or Au monolayer does not exhibit long range order. No clear low energy electron diffraction pattern is visible. This means that there is no crystalline order on distances larger than \( \sim 200 \) Å. Such a layer may be called « amorphous » and Ag or Au atoms subsequently deposited on it grow in a layer by layer fashion. (Frank Van der Merwe mechanism [1, 7].) However, if the first noble metal monolayer has been annealed to obtain an ordered structure, clearly visible by low energy electron diffraction, the subsequently deposited metal atoms agglomerate and form 3D crystallites (Stranski Krastanov mechanism [1, 7]).

The second example is the absorption of oxygen on the interface. Recent studies have provided intriguing results and two opposite phenomena have been reported [10, 11]. In the case of metal deposition on a Si substrate maintained at room temperature, the presence of a few metal monolayers enhances considerably the oxidation of silicon atoms [10]. \( \text{SiO}_2 \) tetrahedra corresponding to the complete oxidation state of Si atoms, are grown at room temperature by exposing the surface to an oxygen dose of \( 10^4-10^5 \) Langmuirs. Such behaviour has been evidenced for monolayers of gold [10], silver and copper [8] on the (111) Si surface.

In contrast with the preceding results, ordered metal layers, usually obtained by annealing a room temperature metal deposit or by depositing the metal on a hot substrate have been found to prevent any oxygen adsorption on the surface. This has been established for the \( \sqrt{3} \times \sqrt{3} \text{R(30)} \) structures of gold and silver [11] on the Si(111) surface. After the oxidizing procedure (\( 10^4-10^5 \) Langmuirs), no oxygen signal has been detected on the surface, giving a sticking coefficient which is zero when measured with the sensitivity of conventional surface techniques. The case of the oxidation of the clean Si(111) 7 x 7 surface stays between these two extremes. It is well known that \( \text{SiO}_2 \) tetrahedra do not grow at room temperature with oxygen dose of \( 10^5 \) Langmuirs. Nevertheless an oxygen monolayer the precise structure of which is not clearly elucidated,
covers the Si surface. Qualitatively and quantitatively this is an intermediate case between the two extreme
cases already mentioned.

The purpose of this letter is to present a qualitative
discussion of these phenomena in view of recent ultra violet photoemission spectroscopy (UPS) results [12, 13]. We first emphasize the correlation which seems to exist between the metallic character of the surface and the case of the oxygen adsorption and we shall then discuss the different noble metal growth modes. Although these phenomena seem very different at first sight, they may however originate from the same physical property of the surface.

The concept of energy is the more intuitive one when dealing with these chemisorption phenomena. As stated by Berthelot in 1867, the direction of the chemical change is determined by the exothermicity of the reaction. The standard free energy change corresponding to Si and Ag oxidation being negative, one or several oxides should form spontaneously at the surface under oxygen exposure. For adsorption processes, there is in general a close correlation between the initial heat of chemisorption, related to the energy of the metal oxygen bond and the heat of formation \( \Delta H \) of the corresponding stable oxide [15]. This suggests that Si atoms \( \Delta H(\text{SiO}_2) = -205.4 \text{ kcal mol}^{-1} \) will have a much stronger tendency to oxidize than Au one \( \Delta H \sim 0 \) and Ag ones \( \Delta H(\text{Ag}_2\text{O}) = -7.3 \text{ kcal mol}^{-1} \) in agreement with the experimental findings: gold or silver oxide has never been detected after oxidation in the previously described experiments.

From these thermodynamic considerations and from the known properties of the Si-Au junction [9] we can understand at least qualitatively the enhancement of the oxidation of Si atoms observed in the case of the room temperature grown Si-Au interface. Two factors may contribute to this enhancement. The first one is the metastability of the Au-Si amorphous alloys which form at the beginning of the interface growth [9]. Si atoms which have diffused into the first metal layers are weakly bonded when compared to the crystalline Si covalent bonding. Moreover, the amorphous alloy does not correspond to an equilibrium configuration of the interface as it will be seen later. The large free energy of formation of SiO\(_2\) can then provide the driving force for the atomic rearrangement and for the SiO\(_4\) tetrahedra growth. The second factor is the metallic character of the surface. Both Si atoms which are in a metallic state [16] and Au ones contribute to the electronic density at the Fermi level. These electrons may enhance the oxidation reaction as it has recently been reported for near noble metal silicides [17]. Although the Si-Ag interface is far less reactive than the Si-Au one, some limited penetration of silver atoms into the 1st and 2nd Si planes can also provoke a weakening of the covalent bonding and a similar enhancement of the oxidation of Si atoms.

The case of the passivation of the Si surface by Ag or Au \( \sqrt{3} \times \sqrt{3} \) \( R(30) \) structures [11] is however more intriguing. To understand this behaviour, we shall try in the following discussion to assess the relative importance of the geometrical and electronic factors.

Let us first mention that we shall speak indistinctively of the \( \sqrt{3} \) ordered structures of gold and silver. They are both obtained for a metal coverage of about one monolayer [18] and they present the same passivation property for oxidation. The geometrical arrangement of atoms is probably very similar in both cases.

Several models have already been proposed for the \( \sqrt{3} \) structures and the problem is still debated.

For our discussion it is convenient to classify them into two categories, whether noble metal atoms are placed on top of the Si surface plane or embedded into it. In the first class, Ag or Au atoms have been successively placed directly on top of the Si surface atoms [19] or in the form of trimers with several possible orientations [2, 4]. Whatever its precise arrangement, the presence of a gold monolayer on top of the Si substrate may provide an explanation for the non adsorption of oxygen: this one adsorbs on a gold (111) surface only at temperatures higher than 300 \( ^\circ \text{C} \) [20] as expected from the very low heat of adsorption. However, this conclusion is not so nearly persuasive as it seems for several reasons: i) the \( \sqrt{3} \) metallic monolayer is much less dense than the (111) Au plane with 45% less Au atoms. ii) A similar explanation of the passivation is less probable to hold for the Ag \( \sqrt{3} \) structure since oxygen is known to adsorb on pure silver surfaces [21]. iii) Finally, the most important argument is that recent experiments using ion backscattering [5], LEED analysis [6], and surface EXAFS [7], have suggested that the noble metal atoms of the \( \sqrt{3} \) structure are embedded into the silicon surface, probably in the hollow site [7] as shown in figure 1. The exact amount of embedment is not known and this is the last important unknown parameter to determine the \( \sqrt{3} \) geometrical structure.

Fig. 1. — Si(111) surface layer with Ag adsorption sites as deduced from SEXAFS [Ref. [7]].
This has important consequences on the oxygen adsorption since the surface layer is either pure silicon (in the case of a strong intermixing, metal atoms between the 1st and 2nd Si surface planes) or a mixture of Si and Au or Ag atoms (in the case of a slight embedment). In both cases, these Si atoms are not «screened» from the oxygen gas by Au atoms and we believe that geometrical arguments alone cannot explain the absence of any oxygen adsorbed atoms. The change in the reactivity of Si atoms is probably associated to a change in the electronic properties. The modifications of the valence band spectra of the noble metal covered Si(111) surface upon annealing have recently been investigated by UPS [12, 13]. They have already been discussed and we shall only emphasize here the points which seem relevant to the oxygen adsorption. The overall picture is that upon annealing, the valence band exhibits very little change. The d band peaks of gold and silver are only better defined and slightly displaced to lower binding energies. In fact the most important modification lies at the Fermi level as shown in figure 2. We notice that the $\sqrt{3}$ ordered surface has a more pronounced semiconductor character, in contrast to the Si(111) 7 x 7 surface and the Si-Au interface grown at room temperature, which are both slightly metallic. We suggest here that this point is relevant to the oxygen adsorption. The chemical bonding depends on the possibility of a charge transfer between the surface atoms and the adsorbed specie and this one seems difficult to realize in the case of the $\sqrt{3}$ structure. It is worth emphasizing that the emission of the dangling bonds at 0.8 eV below the Fermi level is no longer present for the gold covered surfaces. These dangling bonds electrons which confer a weak metallic character to the Si(111) 7 x 7 clean surface allows the formation of an oxygen monolayer on it. For the $\sqrt{3}$ surface they probably participate in very stable [22] Si-metal bonds together with the valence electrons of Ag or Au atoms. This is reflected spectroscopically by the more pronounced semiconductor character of the surface and the apparition of new interface states [12, 13]. Chemically, the surface has a very low reactivity. Within this framework, it is worth noticing that the existence of a long range order and the less metallic character of the surface are two consequences of the very stable atomic configuration which is obtained after annealing. The long range order alone is not responsible for the passivation of the surface.

From a theoretical point of view, these differences in the metallic character illustrates a general rule for covalent materials: a natural tendency is to eliminate all dangling hybrids from the gap by displacing them deep into the conduction and valence band. This is true for surfaces [23] and amorphous semiconductors [24]. When foreign atoms are present on the surface they will tend to bond in a way as to eliminate carriers.

The importance of electrons at the Fermi level has already been acknowledged in catalysis. We have suggested here that this point is relevant to the case of oxygen adsorption on semiconducting or weakly metallic surfaces. It is a prime factor which gives only tendencies. Going beyond this simple picture by invoking more elaborated theories such as density of unpaired electrons or resonances between levels of the adsorbate and of the substrate seems to us speculative. It would require a knowledge of the electronic properties of the silicon-noble metal interface which is not available at the present time. A review of the existing literature supports our conclusions concerning the correlation between the metallic character and Si oxidation.

A first example is the case of the different clean silicon (111) surfaces. It is known [25] that the 2 x 1 reconstructed surface has a less pronounced metallic character than the 7 x 7 reconstructed one. It has been reported that the kinetic of oxygen adsorption is an order of magnitude slower in the case of the 2 x 1 surface [26].

A second example is the room temperature oxidation of silicide surfaces. It has been found in this case that the density of state at the Fermi level $N(E_F)$ depends strongly on the stoichiometry and is strongly correlated to the oxidation behaviour [17]: the lower $N(E_F)$, the more difficult the oxidation of the surface. This is the case for Ni, Pd, Pt, Cr and V silicide compounds and a similar phenomena has been recently reported for cobalt silicide [27].

![Fig. 2. — Valence band emission near the Fermi level for the following different surfaces (from Ref. [12]): Si(111) 7 x 7 clean surfaces, Si + Au ($\Theta = 1.6$) 1.6 gold monolayers have been deposited at room temperature giving an amorphous metallic alloy, Si + Au $\Theta = 1$ (3 x 3 R 30°): a room temperature deposition of 1 monolayer has been annealed at 500 °C to obtain the $\sqrt{3}$ ordered structure. All spectra have been recorded at normal emission with an incident photon energy of 21 eV.](image-url)
A third example is the high temperature oxidation of bulk silicides. In this case, the linear coefficient of oxidation depends on the nature of the silicide [28]. For silicide with a metallic character it is two orders of magnitude larger than it is for pure silicon. For silicide with a marked semiconductor nature, the linear coefficient has value intermediate between those of pure Si and those for metallic silicides.

Our last example concerns the laser induced enhanced oxidation rate of crystalline Si [29]. An explanation of these effects is probably internal photoemission of electrons into the conduction band of the already grown SiO₂ and these electrons can then combine with oxygen dissolved into the SiO₂.

All these examples give the consistent picture that the oxidation of Si atoms is enhanced whenever they are in a metallic environment. The detailed mechanism of this enhancement is still obscure and cannot be deduced from these experiments. As previously suggested for the oxidation of the room temperature grown Si-noble metal interface, two factors are probably important: A) the stability of the material (in the previous examples low $N(E_F)$ are usually associated with more stable structure), B) the presence of transferable electrons at $E_F$ which may ease the breaking of the oxygen molecule and/or the creation of atomic oxygen excited states.

Finally, we want now to briefly present another surface phenomena where the ability of surface atoms to make bonds with adsorbed species plays a crucial role. As already mentioned, under ultra high vacuum conditions, silver grows in a layer by layer mode when deposited on a Si(111) 7 x 7 substrate at room temperature, but forms crystallites when the first monolayer has been annealed to obtain a $\sqrt{3}$ structure. These different growth modes can be easily distinguished by monitoring the Auger growth kinetics (Fig. 3). The layer by layer growth corresponds to the monotonous increase of the metal signal while the formation of crystallites which start at a coverage of - 1 monolayer appears as a plateau in the growth curve. They occupy indeed a weak portion of the surface and makes a negligible contribution to the Auger signal. Several other techniques [9, 30] have confirmed the presence of crystallites.

We must mention that there is still some controversy on the state of Ag atoms when deposited on a substrate at room temperature. It has been suggested [30] that there may exist very small crystallites which are impossible to detect in Auger kinetics and may form an almost continuous 2D layer. This does not change the nature of our conclusion since it is clear that, in this case, the presence of the $\sqrt{3}$ structure dramatically increases the size of these clusters. The important point is that once the $\sqrt{3}$ structure has been formed on the surface, the subsequently deposited Ag atoms agglomerate even when deposited at room temperature. This means that the enhanced mobility of Ag atoms on the $\sqrt{3}$ surface which allows them to form crystallites depends on the state of the surface and not on the temperature. Although a supplementary 6 x 6 structure is observed before agglomeration, the same phenomena is also observed in the Si-Au case.

Differently stated we can say that the adhesion of Ag and Au atoms is good on the Si 7 x 7 surface covered with one amorphous monolayer and becomes poor on the ordered Ag and Au, $\sqrt{3}$ stabilized structure. The same qualitative argument which has been used to explain the absence of oxygen adsorption is probably relevant to the metal agglomeration. On the insulating surface the adsorbed species become mobile and tend to form metal-metal bonding in 3D crystallites rather than bonds with atoms of the surface.

The extreme example of emptying the electronic states near the Fermi level is the one of silicon dioxide where the top of the valence band is about 4.5 eV below the Fermi level. In agreement with our suggestions, the noble and near noble metals are well known « to ball up » when deposited on SiO₂ [29]. Refractory metals does not exhibit the same behaviour. However, this must be ascribed to the fact that their oxide heat of formation is very large and the presence of two species (Si and the refractory metal) with very strong tendencies to oxidize, changes the nature of the problem.

In summary, we have seen that the existence of long range ordered noble metal structure on the silicon surface completely changes its properties:

i) the adsorption of oxygen becomes negligible,

ii) if one deposits more noble metal atoms on it, they agglomerate and 3D crystallites grow.

Fig. 3. — Peak to peak intensity of the silver Auger (MNN) transition as a function of silver coverage. At room temperature the growth mode is a layer by layer one — at 400 °C, crystallites start to form at a coverage of ~ 1 monolayer. The important point is that Ag atoms deposited on a $\sqrt{3}$ structure form crystallites even at room temperature, i.e. the Auger growth kinetic is like the one observed at 400 °C.
We have suggested that these peculiar changes are related to the same physical property which is a kind of paradox: by depositing metal atoms on the Si surface in an equilibrium configuration which gives rise to an ordered structure, the surface acquires a less metallic character. This decrease of $N(E_F)$ has been inferred from UPS data and reflects the participation of the dangling bonds electrons of the Si surface in very stable Si-Au, Si-Ag bonds. The importance of $l_Y(E_F)$, although already acknowledged in catalysis is however a new concept for weakly metallic and semiconducting surfaces. A review of the existing literature has given some support to our suggestions.

Several important consequences may be emphasized:

i) One may expect a drastic reduction of the oxygen sticking coefficient once several monolayers of SiO$_2$ have already been formed. This may be relevant to the peculiarities of the growth kinetics in the very first stages of SiO$_2$ growth and to the saturation of SiO$_2$ growth for oxidation under low oxygen pressure [32].

ii) We have presented here some results which constitute a counter-example to the rule of selective chemisorption which is the basis of surface titration in chemical analysis. The components of the superficial silicon-noble metal alloys cannot be treated with regard to chemisorption as individual, chemically distinguishable atoms. It is clear that the adsorption on the Si-noble metal interfaces, ordered or disordered, is not predictable from adsorption on each component taken separately. This reflects in fact the importance of local electronic properties.

References

[15] See for example, Chemistry of the Metal Gas Interface, Roberts and McKee.
[18] The coverage is referenced to the number of Si Surface atoms. One monolayer thus corresponds to 7.86 $\times$ 10$^{14}$ atoms/cm$^2$.
[22] The Si-Au and Si-Ag $\sqrt{3}$ structure are very stable up to respectively 800 °C and 600 °C. From desorption experiments, the energy of the Si-Ag bond has been estimated to 3 eV.