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Electronic properties of metal-rich Au–Si compounds and interfaces

O Bisi†, C Calandra†, L Braicovich‡, I Abbati‡, G Rossi§, I Lindau§ and W E Spicer§

† Istituto di Fisica, Università di Modena, 41100 Modena, Italy

‡ Istituto di Fisica, Politecnico di Milano, Milano, Italy

§ Stanford Electronics Laboratories, Stanford University, Stanford, Ca 94305, USA

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Abstract. A theoretical analysis of the electron density of states in the δ -phase Au_3Si compound is given and the main aspects of the hybridisation between Si p and gold d orbitals are discussed. Differences in the electronic behaviour of Au–Si compounds with respect to those produced by nearly noble metals are pointed out. The theoretical results are compared with new photoemission data, which have been taken with synchrotron radiation using photon energy at the Cooper minimum, in order to distinguish the orbital contribution to the main structures. The general features of the experimental results agree with the theoretical model. A description of the main aspects of the chemical bond at the interface between Si and noble metals is provided.

1. Introduction

The occurrence of solid state reactions at the interface between gold films and silicon has been the subject of several experimental investigations (Braicovich *et al* 1979, Cros *et al* 1980, Okuno *et al* 1980, Perfetti *et al* 1980). It is generally accepted that diffusion of Si into gold takes place, giving rise to a thin alloyed layer or to some metastable compounds. While the metallurgical characterisation of the interface is often difficult, under certain circumstances, particularly when the substrate deposition and/or the annealing temperatures are greater than 100 °C, the orthorhombic δ -gold silicide Au_3Si phase has been detected at the interface and within a thin layer at the surface of the film (Magee and Peng 1978). Other studies have reported silicide compositions such as Au_5Si or $\text{Au}_{31}\text{Si}_8$ with somewhat different structures. A common feature of all these phases is that they lie close to the deep eutectic point of the Au–Si phase diagram: a fact which agrees with the experimental findings for other Schottky interfaces (Ottaviani *et al* 1980).

The electronic properties of these interface phases have been studied with many spectroscopic techniques as energy loss spectroscopy, Auger electron spectroscopy and photoemission spectroscopy. These experimental works have shown several interesting features of both valence and core electron spectra, providing a direct evidence of the modifications occurring in the electronic structure after deposition or as a consequence of different thermal treatments.

In spite of that a theoretical understanding of the main features of the electronic structures of the interface compounds is still lacking, mainly because of the difficulties of performing self-consistent theoretical calculations of the bulk band structures for the experimentally reported phases.

In a previous paper in this journal (Bisi and Calandra 1981, hereafter referred to as I), two of the authors have shown that it is possible to understand the basic features of the chemical bond in nearly noble silicides and to provide an explanation of the trend of the experimental data, by using a semi-empirical extended Hückel approach to calculate the bulk band structure. These theoretical results give an insight into the electronic properties of the interface phases too, and can be useful in the interpretation of the valence band spectra.

To clarify these aspects of the Au–Si system, we have undertaken a similar theoretical investigation for the Au₃Si compound. The first part of the present paper will be devoted to the presentation of the results of such a theoretical study and to a comparison with the outcomes of previous calculations for nearly noble silicides. It will be seen that the presence of a closed d shell gives rise to significant differences in the distribution of the valence electrons, so that the conclusion obtained in paper I does not apply to the gold silicide case.

The second part of the paper will be devoted to the presentation of experimental results on Si–Au interfaces, which can be used for a significant comparison with the theoretical model. By exploiting the energy dependence of the partial ionisation cross section, we were able to distinguish the relative contributions of sp and d states in the photoelectron energy distribution curves (EDCs) from Si–Au interfaces and to assign the major structures to definite orbitals. A comparison with the theoretical densities of states (DOS) shows the adequacy of the theory in describing the basic chemical features of the interface phases. We are confident that this treatment is meaningful, although the measurements have been carried out in situations lacking of range order and not structurally characterised, since the preparation of stoichiometric bulk silicides was beyond the technical capabilities of the apparatus. In fact we have taken measurements for Au deposited onto Si (111) at increasing coverage and we have focused the attention only on the general features of the spectra, which do not depend upon the coverage.

2. Theoretical results

Among the metastable phases found close to the deep eutectic of the Au–Si phase diagram, the δ -phase Au₃Si is the simplest, being an orthorhombic structure, whose cell consists of eight nearly cubic subcells (Andersen *et al* 1971, Marchal *et al* 1980) obtained by slight distortions of the cubic cell of figure 1.

As previously mentioned, a self-consistent calculation of the bulk band structure assuming the orthorhombic structure is computationally heavy, in view of the large number of atoms in the unit cell. On the other hand the small distortions which take place on passing from the cubic to the orthorhombic structure are not likely to alter the main features of the electronic properties of Au₃Si significantly. We have therefore performed the calculation assuming a cubic cell as in figure 1.

The method of calculation has been discussed in I and we refer to that paper for a detailed presentation and the discussion of the relative merits and disadvantages of the approach. In table 1 we have reported the main ingredients of the calculation, i.e. the orbital exponents of the double- ζ Slater orbitals $\chi_a(\zeta)$, used to evaluate the atomic

wavefunction according to

$$R_{\alpha}(r) = C_1\chi_{\alpha}(\xi_1) + C_2\chi_{\alpha}(\xi_2) \quad (1)$$

where α labels the valence orbital of the atom under consideration while C_1 and C_2 are taken from tables of atomic wavefunctions. In the same table we give the parameters of the valence orbital ionisation potentials, defined by

$$I_{ap}(q) = C_{ap} + B_{ap}q_p$$

where q is the excess charge of the atom in the p th position of the unit cell. As discussed in greater detail in I, the use of charge-dependent potentials allows us to achieve self-consistency through an iterative procedure and to determine realistic values for the interatomic charge transfer.

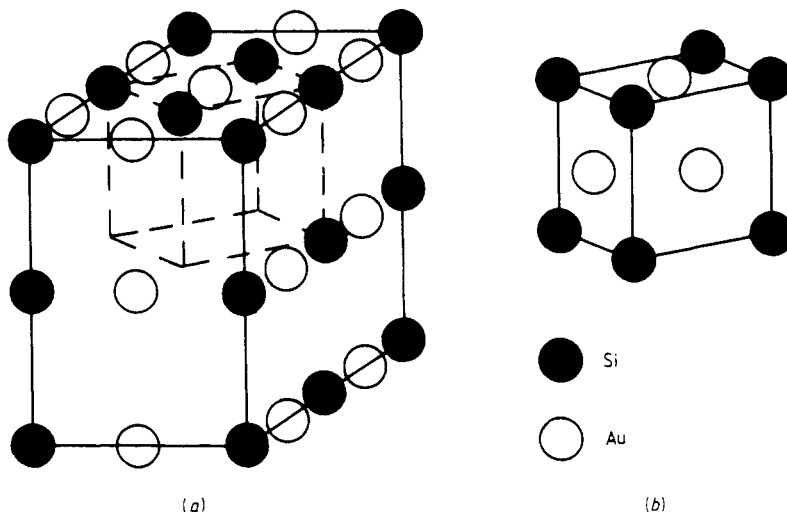


Figure 1. Sketch of the idealised crystal structure for the δ -phase of Au_3Si . The primitive cell, shown in figure 1(b), contains one unit of Au_3Si . The real orthorhombic structure is obtained by slight distortions of the cell of figure 1(a). The volumes of the real and ideal cell are 484.36 \AA^3 and 475.34 \AA^3 respectively.

As we did in paper I, we shall present the theoretical results by giving the total and partial densities of states, which allow a rather direct comparison with the experimental data and illustrate the main aspects of the chemical bond very clearly. The DOS were obtained by solving the secular problem in a grid of 28 k points of the irreducible part of the Brillouin zone. The results are displayed in figure 2, where the total DOS for Au_3Si is presented together with the contribution of Au d and sp states and the Si partial DOS.

Table 1. Input parameters for gold. The parameters for Si are given in paper I.

Orbital	6s	6p	5d
C_1	1.0	1.0	0.6480
$\xi_1 (\text{au}^{-1})$	2.80	2.20	3.84
C_2	—	—	0.3824
$\xi_2 (\text{au}^{-1})$	—	—	2.31
$C_{ap} (\text{eV})$	12.00	4.79	13.72
$B_{ap} (\text{eV})$	5.66	6.28	6.12

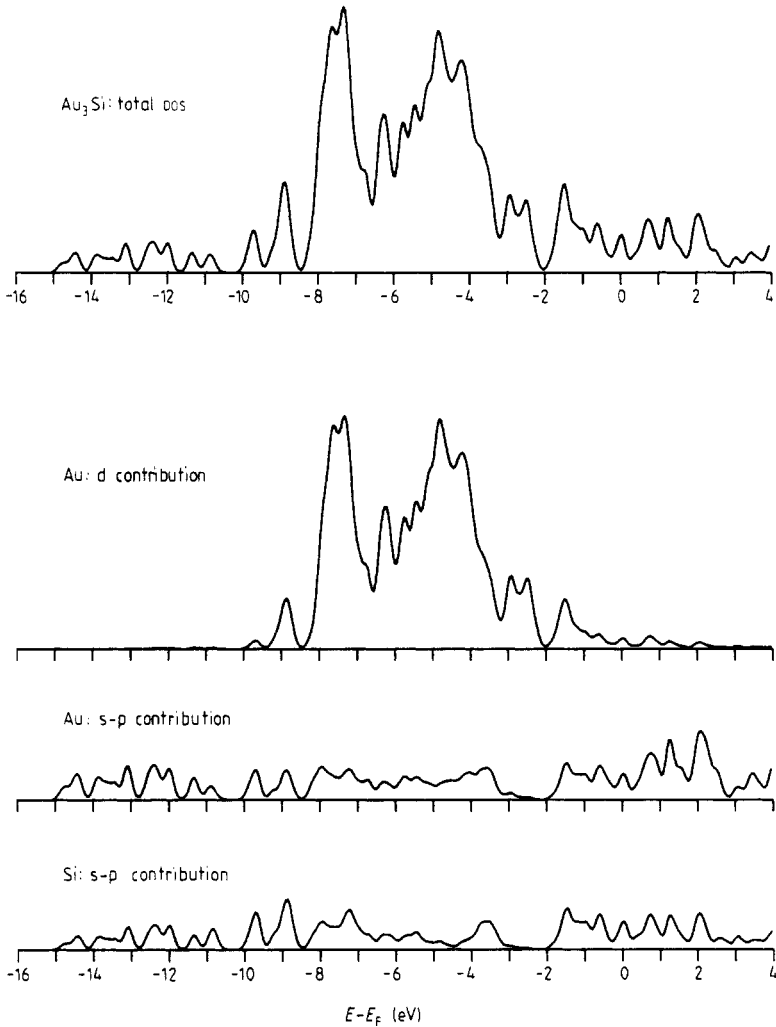


Figure 2. Theoretical total density of states and partial contributions for Au_3Si . The normalisation is to the number of electrons per unit cell. The sp contributions have been multiplied by a factor 2

Energies are referred to the Fermi level, so that the figure gives essentially the density of the filled states and of the first excited states, for which the theoretical method is reliable.

It is seen that the bulk of the gold d bands is located between -3.5 and -8.3 eV from E_F and consists of two pronounced structures. The broader one lies between -3.5 and -6.5 eV and accommodates 5.6 d electrons per atom; the other lies around -7.2 eV and accommodates 2.8 d electrons. The energy distance between the two maxima is 2.3 eV. The analysis of the overlap charge (Mulliken 1955) shows that the d - d antibonding states are located above -5 eV, so that the narrow structure at higher binding energies is due to bonding states between d metals orbitals only.

In the proximity of E_F we find two minor structures. The first one lies between -2 and -3.3 eV, where the sp DOS are nearly zero and the states have the character of d - d antibonding combinations. This structure is reminiscent of the d band edge found in

pure gold at approximately 2 eV below E_F . Upon alloying with Si the gold d band undergoes a considerable loss of structure near E_F and the sharp d edge of pure Au is smoothed and displaced at higher binding energies. Only a small fraction of d states are left in this energy region, giving rise to the structure under consideration.

The region between E_F and -2 eV is occupied by a structure due partly to sp Si and Au states and partly to d orbitals. It arises from antibonding combinations of sp states with d orbitals. Its bonding counterpart is found between -8.5 and -10 eV near the lower edge of the d band. The occurrence of these two structures straddling the d band is a common feature of all the compounds between silicon and transition metals. They are a consequence of the hybridisation of those conduction electrons residing primarily on Si sites with the metal site d electrons. Such hybridisation effects have been discussed with great detail in I in connection with the presentation of the electronic properties of nearly noble silicides. There are however significant differences in the hybridisation as it occurs in nearly noble silicides with respect to the present case. To illustrate these

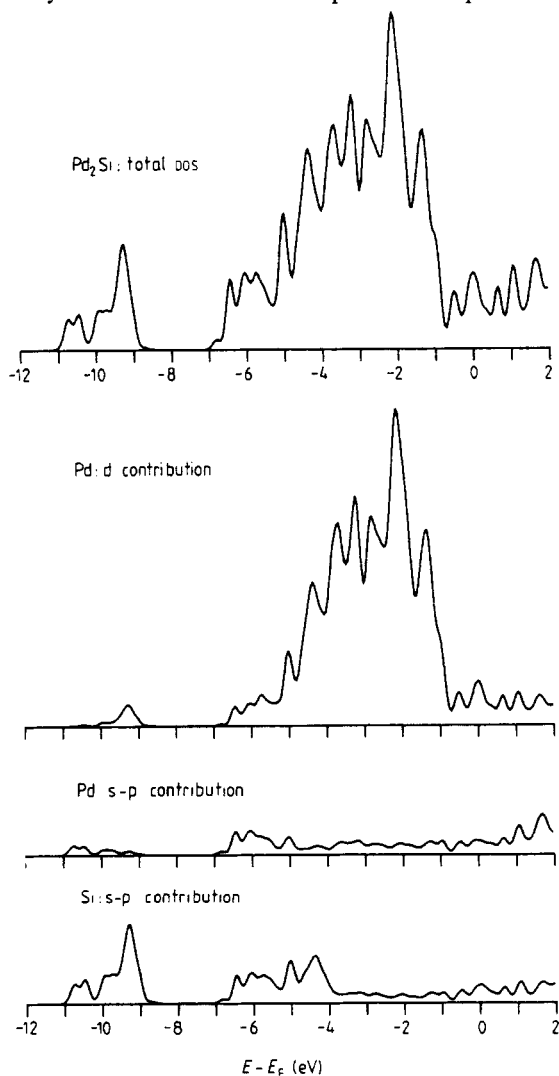


Figure 3. Theoretical density of states and partial contributions for Pd_2Si .

points we report in figure 3 the results of a calculation for Pd₂Si performed using the same theoretical approach. Comparison with figure 2 shows the following points.

(i) Unlike the Au₃Si case the s Si electrons in Pd₂Si give rise to a single band separated from the d metal states by a gap of nearly 1.2 eV. Such a feature is present in the theoretical DOS of all the nearly noble silicides and indicates that Si s states are not significantly involved in the hybridisation with d orbitals. In Au₃Si the sp partial DOS does not show such behaviour: the Si sp DOS has the same shape of the DOS contributed by sp metal states, being rather uniformly distributed from the shoulder at the lower edge of the d band down to -15 eV.

(ii) In nearly noble silicides the coupling of d orbitals with Si sp states is mainly responsible for the occurrence of the bonding and antibonding structures straddling the d band. Evidence for this fact is provided in figure 3 by the heaping up of Si p states between -4 and -6 eV, i.e. in the bonding states region, more pronounced than in Pd sp DOS. For Au₃Si there is a close correspondence between the two sp DOSs, so that there is no clear evidence of a strong preferential coupling between gold d bands with Si p states. Such a behaviour cannot be explained by the different crystallographic coordination found in Au₃Si with respect to Pd₂Si. Calculations for Pd₃Si using the crystal structure of figure 1 or other model structures (Ho *et al* 1980) give the same features of the electronic spectrum of Pd₂Si, except for a broadening of the part of the d band which is not directly involved in the bonding with Si p states. It is interesting to notice that the increased metal content leads to a silicon s band more separated from the p-d structures than in Pd₂Si. This trend agrees with the results of previous calculations for all nearly-noble metal silicides, assuming different structures, which have shown that the Si s band gets progressively deeper and less involved in the bond when the metal content is increased (Bisi and Calandra 1981). It seems therefore that the differences in the spectrum of gold-silicon systems with respect to nearly noble silicides are to be connected with the presence of a closed d shell. This difference in the electronic properties is probably the reason why a stable noble metal silicide cannot be produced, while nearly-noble metals give rise to a variety of stable compounds.

3. Experiments and comparison with the calculations

In this section we present new experimental data for the interfacial reaction products of Si (111)-gold and we compare our results with the calculations. In previous extensive work (Braicovich *et al* 1979) we have reported synchrotron radiation photoemission results for Si (111) 2 × 1 surface at increasing gold coverages at room temperature, giving spectroscopic information on the electronic structure of the products of the reactions occurring at the interface. It is known that in these conditions no ordered phase is formed (see for example Green and Bauer 1976); nevertheless we have found empirically that a general correspondence exists between the electronic structure of the interface products and that of bulk silicides (Braicovich *et al* 1979). In fact the basic features of the d states obtained theoretically are in excellent agreement with the results of our previous experiments, a fact that confirms the generality of our results and makes us confident in the comparison presented here between measurements on interface phases and theoretical bulk calculations. In particular the agreement is satisfactory in connection with the d band shift towards higher binding energies, the smearing out of the upper d band edge and the decrease of the energy separation between the two main d structures with respect to the pure metal.

However there are other results of the present calculations, as those concerning the hybridisation between Si and Au orbitals, which cannot be discussed on the mere basis of previously published experimental data. We have therefore done new measurements on valence photoemission at different photon energies with SSRL synchrotron radiation. We have already shown for Si-Pd and Si-Pt systems (Abbati *et al* 1981) that the partial contribution to a valence state in silicide can be pointed out very effectively by taking advantage of the energy dependence of 4d and 5d photoionisation cross sections, which are very low in correspondence with the Cooper minima. At these energies the fractional weight of sp contributions to the photoemission spectra increases considerably so that sp structures are clearly recovered. We have used this approach, measuring photoemission from Si (111) with increasing Au coverages (θ given in monolayer units) at $h\nu = 80$ eV, where the 5d contribution is dominant and at $h\nu = 150$ eV in the Cooper minimum region. Data were taken with the equipment described in our previous paper (Braicovich *et al* 1979) to which the reader is referred for experimental details.

The measurements have been done in the θ interval, where the surface region explored by photoemission is increasingly Au-rich, since the calculations refer to a gold-rich phase. For this reason we present the results at $\theta = 3$ and $\theta = 7$. We underline

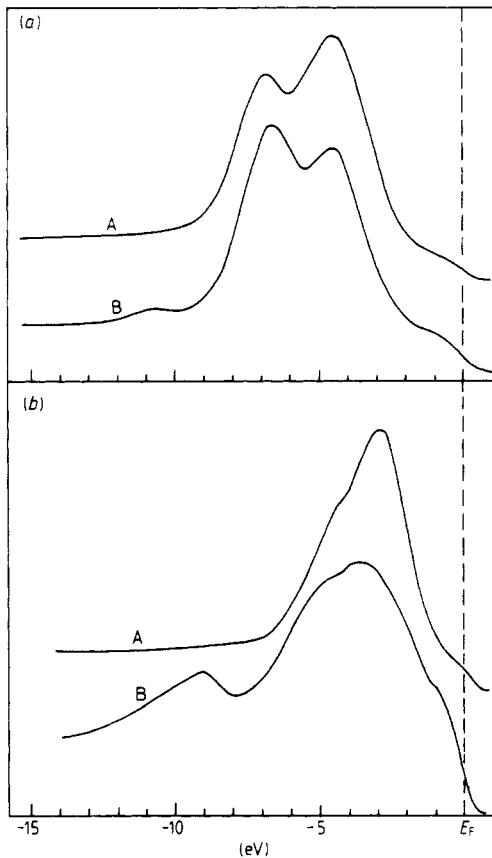


Figure 4. (a) Energy distribution curves for angle-integrated photoemission from the Si cleavage surface covered by 7 monolayers of gold at $h\nu = 80$ eV (A) and at the Cooper minimum $h\nu = 150$ eV (B); (b) Energy distribution curves at $\theta = 3.2$ coverage for Pd deposited onto Si (111) at $h\nu = 80$ eV (A) and at the Cooper minimum $h\nu = 130$ eV (B).

that this choice is not critical since the experimental features are extremely stable against coverage variation, as will be discussed below.

The valence photoemission at the two photon energies for $\theta = 7$ is given in figure 4(a). The EDCs are normalised to the same maximum height to better point out the shape modifications due to sp contributions outside the d band region. The most important of these modifications is the deep structure around -11 eV below E_F , which is recovered at $h\nu = 150$ eV and arises from sp states only.

The discussion on the nature of the chemical bond in these compounds is more significant if one contrasts the behaviour of Si–Au with the experimental data for the Si–Pd interface, where Pd₂Si is basically formed. For this reason we give in figure 4(b) the valence photoemission spectra from Si(111)–Pd $\theta = 3.2$ at $h\nu = 80$ and at the Cooper minimum $h\nu = 130$ eV. The comparison suggests the following comments.

(i) A deep structure is seen for both cases in the Cooper minimum EDC, but the orbital contributions are different, as can be seen from the different sensitivities of the structure to the photon energy choice. The enhancement of this deep structure with respect to the d peak which takes place upon going to the Cooper minimum, is smaller in Si–Au than in Si–Pd; the argument cannot be put forward quantitatively but the present knowledge of the cross sections for isolated atoms (Goldberg and Fadley 1981) strongly suggests that the fraction of sp character is considerably smaller in Si–Au deep structure than in Si–Pd, giving a smaller relative enhancement for Si–Au. This point agrees with the calculations presented above, showing that the deep structure contains bonding states between Si and Au, whereas in Pd₂Si it comes basically from Si s electrons. Moreover the absence in Si–Au of a rather localised s contribution from Si, suggested by the theory, is confirmed experimentally, since no other structure is seen up to -15 eV.

(ii) The modifications of the spectra which take place on going to the Cooper minimum in the d band region, are quite different in the case of closed d shell and of nearly-noble metal silicides. In the Si–Pd system the region around -5 eV decreases much less than the other d band region, since it contains a strong p contribution from Si, as a consequence of the bonding between the metal and Si states, as discussed in greater detail elsewhere (Rossi *et al* 1981). On the contrary in Si–Au the modifications of the gold 5d emission are a variation of the relative intensities of all the 5d structures: within the noise this is exactly what has been found for the pure metal (Johanson *et al* 1980), thus indicating little interaction between the gold d shell and Si. In other words there is no energy region where a preferential overlap of d states with Si p states takes place. This comes out very clearly from the experiments and is a strong factor in favour of the theoretical discussion given above.

(iii) In the region from -2 eV to E_F a Si p contribution to the photoemission spectra is evident from figure 4(a), if the EDC at 80 eV is compared with that at 150 eV. However the enhancement is definitely less pronounced than in the Cooper minimum EDC for Si–Pd, so that there is no conclusive evidence for a p silicon–d gold antibonding structure. The corresponding Si–Pd states are very clear from figure 4(b). We notice that the antibonding state structures in the theoretical DOS are rather broader in Au₃Si than in Pd₂Si: this fact could provide an explanation of the lack of this structure in Si–Au data.

Before concluding this section devoted to the experimental results we want to comment further on the stability of the above features versus coverage. This stability is particularly clear from figure 5, where we present Cooper minimum valence band spectra for two coverages ($\theta = 3$ and $\theta = 7$). These values belong to a coverage interval where

the composition in the region explored by photoemission varies considerably (Braicovich *et al* 1979), so that even the local coordination is expected to change. In the present experiments we have found by core line photoemission that Au enrichment by a factor 1.5–1.7 occurs on going from $\theta = 3$ to $\theta = 7$. Nevertheless the valence spectra show basically the same features in this θ interval, a fact that indicates the generality of the considerations presented above. This point is of paramount importance, since it shows that the comparison between theory and experiments is significant as far as the general features of the valence spectrum are concerned. For the purpose of the present investigation we do not deem it necessary to carry out more complicated experiments, which would be rather uncertain, since the formation of the stoichiometric phases by thermal treatment is far from being understood in the Si–Au system, as it is clear from the lack of agreement between different metallurgical investigations of the interfaces. It should also be noted in this connection that bulk Au–Si compounds are not stable.

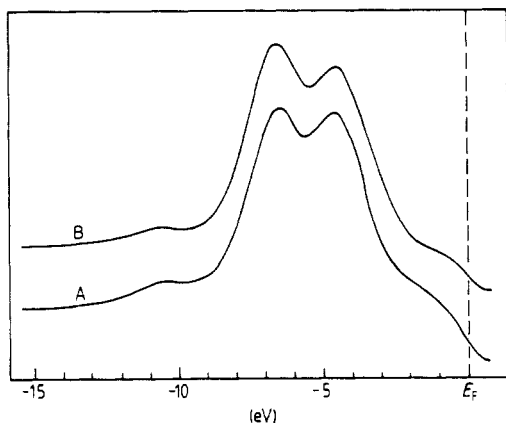


Figure 5. Energy distribution curves for (A) $\theta = 3$ and (B) $\theta = 7$ monolayers of gold deposited onto Si (111) at the Cooper minimum ($h\nu = 150$ eV).

The general shape of the EDCs is only weakly dependent on the coverage in Au-rich interfaces, mainly because the Au d photoemission is still important at 150 eV. Nevertheless some θ -dependence can be noted. More precisely: (i) the total d band width increases, as is clear from the upper edge shift in figure 5; (ii) near E_F , where an Si contribution is present, the emission is stronger in the $\theta = 3$ than in the $\theta = 7$ case, as expected from the composition change; (iii) also the deep structure around -11 eV is slightly weaker at $\theta = 7$.

We can provide an explanation of this behaviour on the basis of our theoretical results. Because of the lack of a strong preferential bonding between p–Si and d–Au states, the only effect of increasing the Si content in a gold silicide is a narrowing of the d band, due to the increased distance between the metal atoms. Even the shifts in the position of the centre of gravity of the d band, which occur in nearly-noble metal silicide upon varying the composition (Bisi and Calandra 1981) are not expected to be significant in Au–Si phases, since they arise from changes in the fractional occupancies of d states, not present in closed d shell systems.

4. Conclusions

We have presented the first joint theoretical and experimental investigation of the electronic structure of gold–silicon interfaces. In this way we have been able to point out the significant differences between the electron states in Si–noble metal systems and Si–nearly-noble metal systems. We have shown that these differences are essentially due to the presence of a closed d shell, which leads to a weaker interaction between Si p and metal d states. The trend is very general in interfacial compounds of different relative compositions and this indicates that the theoretical treatment based on model bulk band structure can be of great help in understanding the interface behaviour.

Acknowledgments

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Note added in proof. The main conclusions of the present paper are confirmed by comparison of the results for Au–Si with recently reported experimental data for Pt–silicon interfaces and compounds, taken at the Cooper minimum energy (1982 *Phys. Rev. B* **25**, 3627). The main differences in the electronic spectrum are those pointed out in §3 of the present paper and agree with our previous theoretical calculations.

References

- Abbati I, Rossi G, Lindau I and Spicer W E 1981 *J. Vac. Sci. Technol.* **19** 636–9
Andersen G A, Bestal J L, Johnson A A and Port B 1971 *Mater. Sci. Engng.* **7** 83–9
Bisi O and Calandra C 1981 *J. Phys. C: Solid State Phys.* **14** 5479–94
Braicovich L, Garner G M, Skeath P R, Su C Y, Chye P W, Lindau I and Spicer W E 1979 *Phys. Rev. B* **20** 5131–41
Cros A, Derrier J, Salvan F and Gaspard J P 1980 *Proc. 14th Int. Conf. on Solid Surfaces, 'La Vide, les Couches Minces'* suppl. **201** 951–4
Ho P S, Rubloff G W, Lewis J E, Moruzzi V L and Williams A R 1980 *Phys. Rev. B* **22** 4784–90
Goldberg S and Fadley J 1981 *J. Electron Spectrosc.* **21** 285–97
Green A K and Bauer E 1976 *J. Appl. Phys.* **47** 1284–91
Johanson L I, Lindau I, Hecht M H and Kollne E 1980 *Solid State Commun.* **34** 83–6
Magee T J and Peng J 1978 *Phys. Status Solidi* **49a** 313–22
Marchal G, Mangin P and Janot C 1980 *Phil. Mag.* **B 42** 81–94
Mulliken R S 1955 *J. Chem. Phys.* **23** 1833–40
Okuno K, Iwami M, Hiraki A, Matsumara M and Agayama K 1980 *Solid State Commun.* **33** 899–901
Ottaviani G, Tu K N and Mayer J W 1980 *Phys. Rev. Lett.* **44** 284–7
Perfetti P, Nannarone S, Patella F, Quaresima C, Savoia A, Cerrina F and Capozzi M 1980 *Solid State Commun.* **35** 151–3
Rossi G, Abbati I, Braicovich L, Lindau I and Spicer W E 1981 *Solid State Commun.* **39** 195–8