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Photoemission studies of the silicon-gold interface

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The early stages of the formation of the Au-Si interface have been studied with photoelectron spectroscopy of the valence-band and core levels. In this study, the Si sample was prepared by cleavage in ultrahigh vacuum and Au was deposited in a controlled manner at room temperature. By slowly increasing the Au coverage on the surface, the silicon surface states were depleted rapidly (by a factor of 2 at an Au coverage of 0.2 monolayers) without any observable change (>0.1 eV) in the Fermi-level pinning position. Furthermore, at low coverages, the binding energies of the Au core levels and the $5d$ peaks in the valence band were similar to those of atomic Au; however, the width of the structure indicated that the Au is strongly interacting with Si. Measurement of the strength of the Au core levels gives evidence for penetration of a fraction of Au into Si. Thus, at low coverages, the Au is probably dispersed in and on the Si, causing the removal of the surface states and production of new states in the band gap. As the Au coverage is increased, the Au $4f$ and Si $2p$ core levels shift in such a way as to suggest the formation of an alloy with variable composition at the Au-Si interface. At the highest Au coverages (above 15 monolayers), a small amount (less than 1 monolayer) of Si was observed on the surface of the deposited Au overlayer. Thermal annealing of a thin Au (50 monolayers of Au) on Si at 500 °C resulted in an increased Si concentration at the surface with the photoelectron spectra resembling those at low coverages (about 1.5 monolayers), thus indicating a high diffusion coefficient of Si through the Au layer. When less than 1 monolayer of O_2 was adsorbed onto the cleaved Si surface prior to the deposition of Au, the intermixing of Au and Si was significantly reduced.

I. INTRODUCTION

The study of the semiconductor-metal interfaces is of great importance both for fundamental and technological reasons, and a great experimental and theoretical effort has been devoted to the understanding of their electric properties and of their electron states. A common feature of all the theoretical models suggested until now is the assumption of a sharp interface. Within this scheme, the role of intrinsic surface states in the gap of the semiconductor in pinning the Fermi level has often been emphasized theoretically following the original suggestion by Bardeen.[1]

In the field of semiconductor-metal interfaces, an enormous quantity of information has been collected recently by using photoemission spectroscopy, both with conventional light sources and with synchrotron radiation. The results of these photoemission-spectroscopy investigations show that the physical situation in many interfaces is much more complicated than assumed in the usual models, so that the possibility of using these models is severely questioned for various reasons. A typical case is that of GaAs which has been recognized to have no surface states in the gap for perfectly cleaved faces.[2–4] In several (III–V) compounds, a severe disruption of the surface takes place[5,6] upon deposition of the metal with removal of anion and/or cation in different proportions in different cases. Furthermore, the research with Auger spectroscopy and energy-loss spectroscopy by Brillson[7] showed that disruption takes place also in (II–VI) semiconductor-metal interfaces. It appears thus that the electrical behavior of several interfaces is strictly related to the specific nature of this disruption mechanism with the possible formation of defect states at or near the interfaces.[6]

In view of this situation, it seemed timely to carry out a photoelectron spectroscopy investigation with synchrotron radiation on a simple chemical system in which surface disruption presumably takes place. This is the case of the Si(111)-Au interface which is important not only for technological reasons but because of (i) the fact of having a purely covalent elemental semiconductor simplifies the chemical problem, giving the hope that the analysis of the photoemission results provides a rather detailed picture of the various stages of the growth of the Si-Au junction and (ii) the Si(111) face is known to have intrinsic surface states in the gap[8] so that their role in determining the properties of the interfaces can be reexamined.

In this paper, we report on the electronic properties of the gold-silicon interface prepared by evaporating controlled amounts of Au under ultrahigh vacuum conditions onto a cleaved Si(111) surface. This paper addresses the question of the abruptness of the interface and the interaction between the metal overlayer and the semiconductor substrate. The analysis of the Au-Si interface should also be of interest as a starting point for comparative studies to other silicon-metal interfaces where the metal (transition metal) is more reactive and silicides are formed.

To the author's knowledge, this work is the first photoemission study of the Au-Si interface. Most information in the past has been obtained from Auger electron spectroscopy.[9–12] Narusawa *et al.*[9] reported that the Si *LVV* Auger transition at 92 eV was split for an overlayer of Au evaporated on top of a silicon substrate. This splitting was attributed to the formation of a silicon-gold alloy (rather than a silicide) since it remained the same when the Si-Au composition was changed. A further interesting result is the high-diffusion coefficient of Si in Au overlayers and the resulting broad interface, even at room temperature, as pointed out early in ion backscattering experiments.[13,14] The formation of a gold silicide after heat treatment of the surface of gold films deposited onto silicon substrates has been observed by Green and Bauer[12] (similar results have more recently been reported by Oura and Hanawa, see Ref. 50 for details). It has also been pointed out that oxidation and, in general, the passivation of the silicon surface strongly reduces the intermixing.[12–14] This is, of course, of great practical importance in device technology.[15] A systematic spectroscopic study of temperature and passivation effects is beyond the purpose of the present paper; nevertheless, some preliminary results will be given here since they are interesting in themselves and are useful to have a deeper understanding of the results on the clean Si-Au interface prepared at room temperature.

Thus, the paper is organized in the following way: after an experimental section, a detailed presentation of the results on the clean Si-Au interface at room temperature is given by discussing the results at low coverages ($\theta \lesssim 2$ monolayers), at intermediate coverages ($2 \lesssim \theta \lesssim 15$ monolayers), and at higher coverages (up to $\simeq 160$ monolayers). Before the conclusion, two short paragraphs are devoted to the temperature and oxygen effects.

II. EXPERIMENTAL

A. Sample preparation

Atomically clean Si(111) surfaces were produced by cleaving *n*-type degenerate Si samples in ultrahigh vacuum at a base pressure better than 1×10^{-10} Torr. The gold overlayers were produced by evaporation from beads on a tungsten wire. The deposited Au mass was measured with a quartz thickness monitor. The ratio of the masses deposited onto the quartz and onto the sample was determined in a previous calibration by inserting another quartz monitor in the place of the sample. The gold coverages up to ~15 monolayers were done by opening a shutter in front of the evaporator for a convenient time after having determined the evaporation rate with the quartz monitor; in the higher depositions, the thickness was measured directly. The accuracy in the determination of the coverages is about 0.05 monolayers at low coverages, below 2 monolayers, and better than 1 monolayer at high coverages. All the depositions were done at room temperature with the shutter closed periodically in order to minimize the heating of the sample due to the radiation from the evaporator. Great care was taken in degassing the bead and the evaporator to avoid any contamination of the sample. No trace of contaminants was seen in the core-level photoemission spectra and Auger spectra.

In the measurements on the oxygen effects, the Si(111) surface was covered with adsorbed oxygen, prior to the Au deposition, by successive exposures of 1, 9, 90, and 900 L (1 L = 10^{-6} Torr sec) as described elsewhere.[16,17] These exposures were obtained with oxygen pressures of 10^{-8} Torr for 100 sec, 10^{-8}, 10^{-7}, and 10^{-6} Torr for 900 sec, respectively. The pressure was measured with a cold cathode Redhead gauge to avoid any artifacts due to the production of excited oxygen by the ion gauge.[18]

The set of results presented here comes from several series of measurements; in each series, a freshly cleaved Si(111) face was exposed to successive gold depositions. All the energy distribution curves (EDC's) presented were measured a few minutes after gold deposition so that nothing can be said on long-term processes, if any, taking place at the interface.

B. Photoelectron spectra

The photoelectron energy distribution curves were measured with a double-pass cylindrical mirror analyzer (CMA) in a system described by Pianetta[18] elsewhere. Radiation from the Stanford Synchrotron Radiation Laboratory was used.[18] For photon energies <35 eV, the radiation was monochromatized by a Seya-Namioka monochromator described by Rehn *et al.*[19] A monochromator ("the grasshopper") described by Brown *et al.*[20] was used for higher photon energies. The surface of the sample was close to normal to the CMA axis, and the light was impinging on it at grazing incidence ($\simeq 15°$).

The combined resolutions of the CMA and of the monochromators are listed in Table I. The reproducibility of the measurements allowed accurate determination of the relative shifts of core lines. The relative shift accuracy is within ±0.05 eV, while absolute values of core-level energies are accurate within ±0.1 eV.

TABLE I. The combined resolution of the monochromator and CMA.

$h\nu$ (eV)	Combined resolution (eV)
10.2	0.15
21	0.17
32	0.32
130	0.34
150	0.38
200	0.50

III. CLEAN Si(111)-AU INTERFACE AT ROOM TEMPERATURE: RESULTS AND DISCUSSION

A. Energy distribution curves

Systematic measurements on the modification of the EDC's as a function of Au coverage (θ) were done at three photon energies (10.2, 30, and 160 eV); other photon energies were used when appropriate. Due to the relatively high value of the photoionization cross section, the 10.2 eV photon energy was very useful to study the Si surface states with high sensitivity and, in general, the region near the Fermi level. The 30 eV photon energy was selected to measure the entire valence band of the Au-Si system with great sensitivity to the Au $5d$ electrons. This is due to the fast decrease of the photoionization cross section of s and p states with increasing photon energy. The 160 eV photons were used to measure the emission from Si $2p$ and Au $4f$ levels with great surface sensitivity; in this case, the kinetic energy is around the broad minimum of the escape depth[21] which is of the order of a 5 Å.

Coverages from 0.15 to 160 monolayers were explored with small gradual increases at lower coverages (five steps up to 1.5 monolayers). In the present paper, one monolayer is defined as the number of Au atoms equal to the surface atomic density of the substrate ($\sim 7.8\times10^{14}$ atoms/cm^2). This is the most natural coverage scale at low coverages while, at high coverages, when a gold-rich phase is formed, it is probably most reasonable to rely upon gold atomic surface density which is $\simeq 1.5$ times higher. For this reason, the coverage is given also in these units in the figures at higher coverages (in brackets).

The EDC's measured with $h\nu = 10.2$ eV at increasing coverages are summarized in Fig. 1 and the EDC's measured with $h\nu = 30$ eV in Fig. 2. All the EDC's are normalized to the photon flux. The evidence of the modification of the valence states due to gold deposition is dramatic. The clean Si(111) EDC's are in excellent agreement with the literature[22] and show the well-known bulk structure together with the upper peak at $\simeq -0.7$ eV due to surface states.[23] The rapid decrease of the surface states, S in Fig. 1, is evident even at very low coverages and will be discussed later. At $h\nu = 30$ eV, the $5d$ emission from Au is clearly seen even at low coverages (peaks labeled A and B); this gold-induced structure rapidly becomes the dominant feature of the EDC's at increasing coverages (Fig. 2).

The core-level emission measured at a photon energy of $h\nu = 160$ eV is seen in Fig. 3 where a few representative EDC's are shown. At this photon energy, the coverage interval between 0.15 and 55

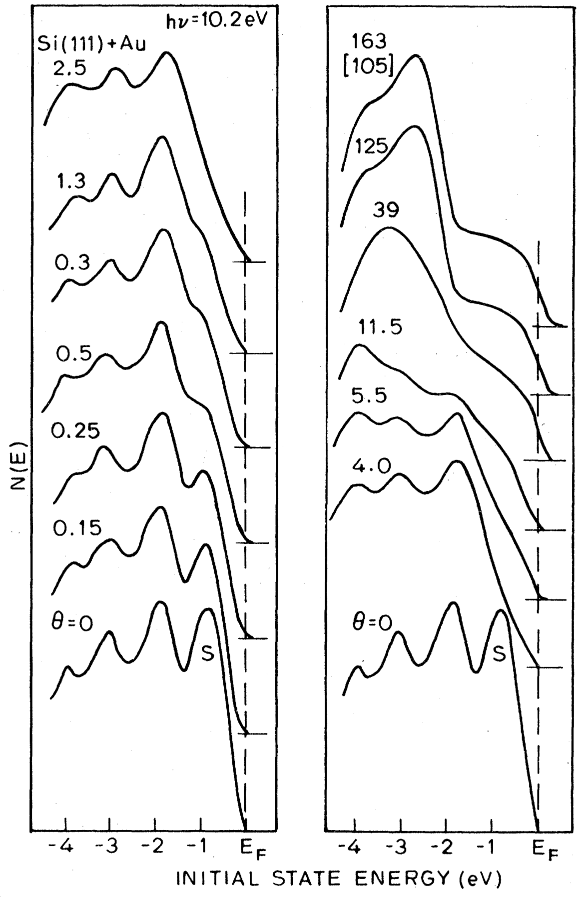

FIG. 1. Photoelectron energy distribution curves at $h\nu = 10.2$ eV at increasing gold coverages. The structure due to Si(111) intrinsic surface states is labeled with S. The initial energies are measured from the Fermi level. The coverage is measured in monolayers, i.e., in units of Si surface atomic density; the value in brackets is measured in units of Au surface atomic density (see text). The curves are normalized to the incident photon flux.

monolayers was explored. The EDC's are normalized to the same height of the Si $2p$ line. The dotted lines in the figure point out the shifts of the Si $2p$ and Au $4f$ lines at increasing gold coverages. The shoulder at the left of the Au $4f_{5/2}$ line is due to Auger electrons from gold. This assignment was confirmed by the fact that this structure appears at constant kinetic energy when the photon energy is varied.

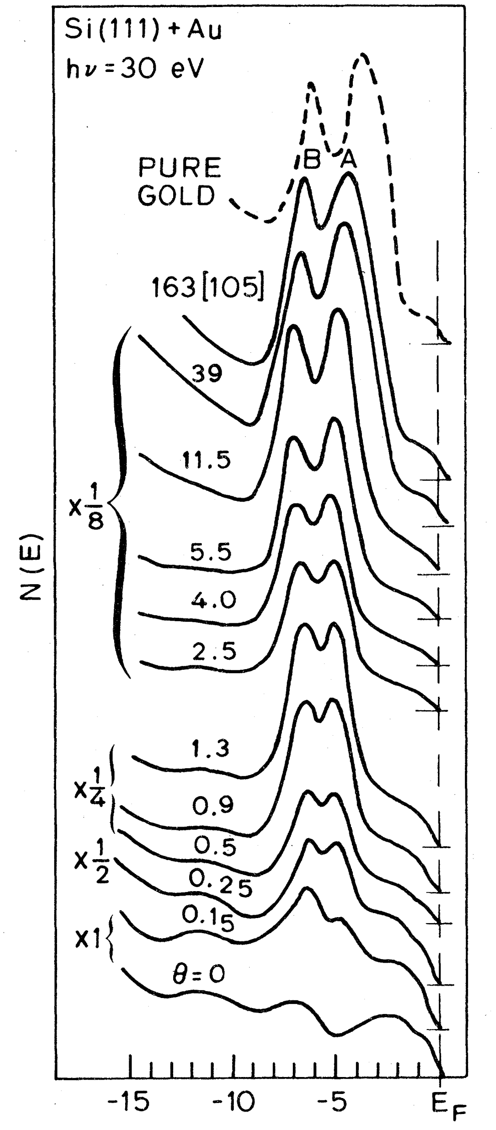

FIG. 2. Photoelectron energy distribution curves at $h\nu = 30$ eV at increasing gold coverages. The structures A and B are originated from gold $5d$ electrons. The initial energies are measured from the Fermi level. The coverage is measured in monolayers, i.e., in units of Si surface atomic density; the value in brackets is measured in units of Au surface atomic density. The curves are normalized to the incident photon flux.

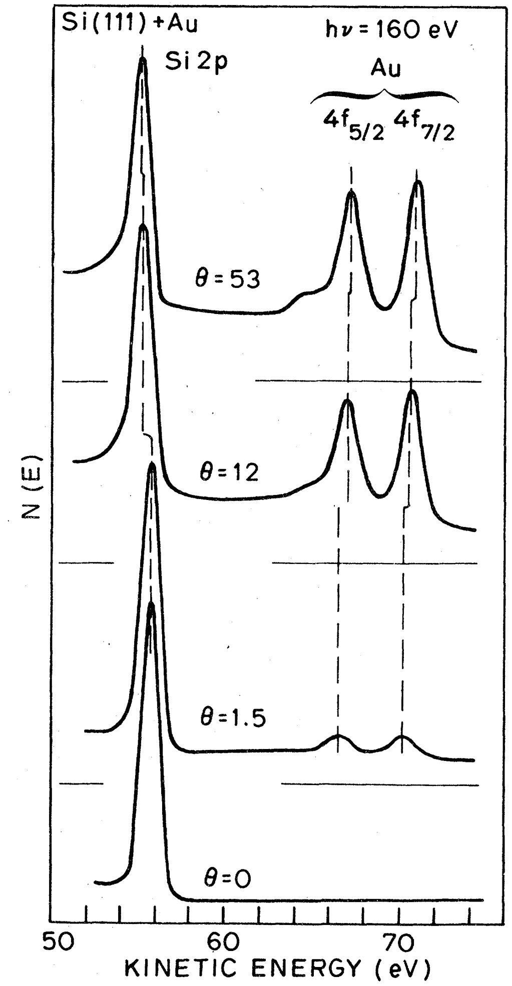

FIG. 3. Core-level photoemission at $h\nu = 160$ eV at increasing gold coverages. The Si $2p$ and Au $4f$ core lines are seen. The spectra are normalized to the same height of the Si $2p$ line and are plotted versus photoelectron kinetic energy. The coverage is measured in monolayers, i.e., in units of Si surface atomic density.

B. Main features of the coverage dependence of the EDC's

The EDC's of Figs. 1, 2, and 3 contain a great quantity of physical information on the Si-Au interface at increasing θ. It is thus necessary to provide some guidelines to organize the discussion. This is done on a purely phenomenological basis and without assuming any model, by considering the coverage dependence of the emission from gold $5d$ states and from Au $4f$ and Si $2p$ core levels.

In Fig. 4, the energy separation of the two prominent peaks (A and B) in the $5d$ region measured with $h\nu = 30$ eV (Fig. 2) is plotted against θ up to

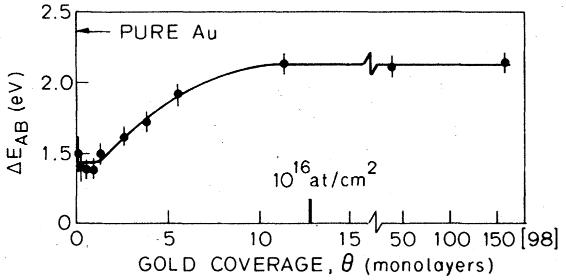

FIG. 4. Energy separation ΔE_{AB} between the two main peaks A and B from gold $5d$ states at $h\nu=30$ eV. The arrow indicates the value for pure bulk gold. The coverage is measured in units of Si surface atomic density (monolayers), and the value in brackets is measured in units of gold surface atomic density. The number of deposited gold atoms per unit area is also given.

about 160 monolayers (Si scale). In Fig. 5, the binding energies of Au $4f_{7/2}$ and Si $2p$ states are given as a function of θ; the energies are referred to the Fermi level as determined by photoemission with $h\nu=120$ eV. Since the spin-orbit separation of the two $4f$ lines does not depend on θ, an identical plot would be obtained by selecting the Au $4f_{5/2}$ line.

These figures point out the existence of three coverage intervals which must correspond to different physical situations, although no sharp clear-cut division can be made between these intervals. The θ dependence has also aspects which are not apparent from these figures, as will be shown later. The three intervals are: (i) a low-coverage interval up to approximately 2 monolayers in which the measured binding energy (BE) parameters are constant within the experimental accuracy, (ii) an intermediate-coverage interval between about 2 and 15 monolayers in which a rather rapid variation occurs in BE, and (iii) a high-coverage interval ($\gtrsim 15$ monolayers) in which the variation of the BE parameters is very slow, thus suggesting an asymptotic situation.

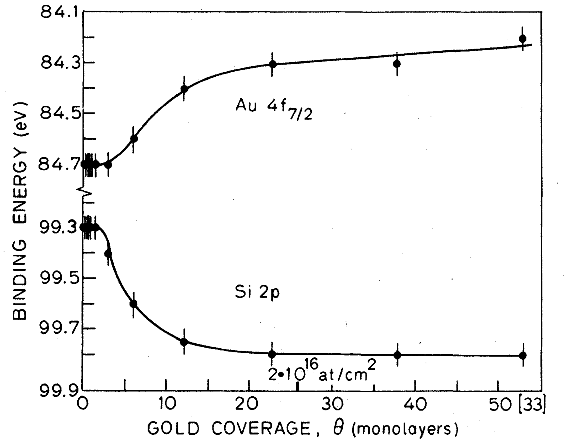

FIG. 5. Au $4f$ and Si $2p$ binding energies as a function of coverage. The binding energies are referred to the Fermi level. The coverage is measured in units of Si surface atomic density (monolayers). The value in brackets is measured in units of gold surface atomic density. The number of deposited Au atoms per unit area is also given.

In what follows, the physical situation in these intervals will be discussed in detail with the aim of obtaining a consistent picture of the electronic structure of the Si-Au interface.

C. Low-coverage interval ($\theta \lesssim 2$ monolayers)

In the low coverage interval, the most striking effect is the drastic modification of the emission from surface states. The peak due to Si(111) dangling bonds decreases very fast with θ and has been reduced by a factor of $\simeq 2$ at $\theta \simeq 0.2$ monolayers. This fast decrease does not imply that the gap emission disappears; in effect, gap states are always seen but the shape of the EDC's (for $\theta \gtrsim 1.3$ monolayers) close to the Fermi level is no longer reminiscent of the emission from clean Si(111) dangling bonds. Thus, one of the main problems is that of clarifying the physical situation at the interface when this type of gap emission is present. To this end, it is important to consider the intensity of the Au $4f$ lines versus coverage. In the absence of any atomic intermixing between the substrate and the adatoms, the fractional increase of the emission from Au $4f$ levels should be proportional to θ in the submonolayer region. In effect, an increase slower than that of the coverage is seen, as shown in Fig. 6, in which the ratio $R=I_{4f}(\theta)/I_{4f}(0.15)$ is plotted versus the reduced coverage $C=\theta/0.15$. The dashed line in Fig. 6 is the expected relation in the absence of intermixing while the solid line, which is a best fit of the experimental results for the $4f_{7/2}$ level, shows that there is a deficiency of roughly 30% of Au atoms, which must be accounted for by intermixing at a depth larger than 5 Å. It is worthwhile noting that this result is not affected by possible errors in the absolute calibration of the quartz thickness monitor. This result is a direct evidence of intermixing and confirms the previous suggestion by Narusawa, Komiya, and Hiraki,[9] based on Auger spectroscopy. Thus, the disappearance of the surface states is due to a disruption of the surface by the deposited gold atoms and the subsequent formation of a wide Au-Si interface. It is reasonable to attribute the gap emission, clearly evident around 2 monolayers, to this Au-Si interface.

As far as the nature of this Au-Si interface is concerned, it is interesting to note that:

(i) The monotonic increase (Fig. 6) of gold $4f$ emission with θ rules out the formation of only one

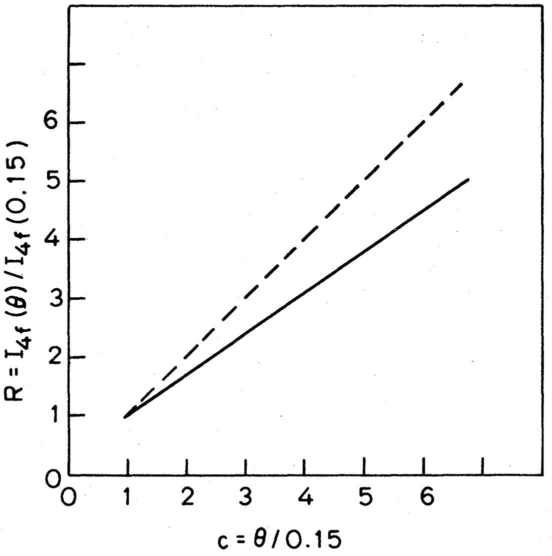

FIG. 6. Reduced intensity $R = I_{4f}(\theta)/I_{4f}(0.15)$ of gold $4f_{7/2}$ emission as a function of the reduced coverage $C = \theta/0.15$. The dashed line is the result expected in the absence of gold-silicon intermixing at the interface. The solid line is the best fit of the results of $h\nu = 160$ eV.

compound with a definite composition.

(ii) The gold is in a dispersed state since the $5d$ emission is basically "atomic" and the peaks A and B (Fig. 2) correspond to the $5d$ spin-orbit atomic states. The measured separation ΔE_{AB} ($\simeq$1.4 eV) is similar to that of isolated gold atoms ($\simeq$1.5 eV). The small difference is not considered to be significant and can be due to the background of substrate emission.

(iii) The $5d$ lines are rather broad, thus indicating some electronic interaction of Au atoms with the surrounding atoms which are mostly silicon.

Thus, the intermixed phase typical of the low-coverage interval may be thought of as an alloy rather than a compound. The disruption of the surface and the formation of this alloy is related to the heat of condensation of gold and the energy gain in the surface region is due to alloying. No low-energy electron diffraction (LEED) measurements were carried out. Thus, the degree of structural order at the surface is not known in our case.

Some other considerations on the electron states of this surface phase can be done by considering the gold emission. In effect, the $5d$ states appear to have higher-binding energy than the corresponding peaks from bulk clean gold, as is evident from Fig. 2. This is additional evidence of the dilution of Au, i.e., of the fact that gold is more "atomic" than in the metal in the sense pointed out by Hodges *et al.*[24] in their discussion of the d states of noble metals. This argument could also explain at least some of the shift of the Au $4f$ core lines with respect to the value typical of bulk gold ($\simeq$0.7 eV towards higher-binding energies). Needless to say, this discussion is highly speculative and some theoretical research on the electron states of gold-Si mixtures even by assuming simplified models (for example, ordered systems) would be very useful to obtain some qualitative indications.

As far as the thickness of the intermixed region is concerned, it is interesting to carry out an analysis similar to that summarized in Fig. 6 but with a longer escape depth (say, 10 Å), typical of the emission from Au $5d$ states at a photon energy of 30 eV. In this case, it is necessary to rely upon difference spectra where the uncertainty is higher. Nevertheless, it appears that the deficiency of gold is definitely lower than in the case of the measurements with $h\nu = 160$ eV. It is thus reasonable to state that the intermixed region extends, at most, up to about 15 Å beneath the surface at coverages $\lesssim$2 monolayers.

The fact that even at room temperature an interfacial reaction takes place in the gold-silicon system has been already established with Auger spectroscopy on the basis of the modification of the shape of the Si LVV transitions[9–11] (a splitting of the 92 eV peak). However, it is difficult to deduce the electronic structure of the valence band from Auger spectra, owing to the two-electron nature of the Auger process and to the fact that, in general, it is not yet completely clear whether a bandlike or quasiatomiclike picture holds for CVV transitions.[25,26] It is interesting to note that a progressive modification at increasing θ, in a sense parallel to that of the EDC's of Fig. 1, has been seen in the derivative of the LVV line.[9,11]

The present results are relevant in connection with the physics of the Si-Au Schottky barrier. The results of Fig. 1 show that, within the experimental accuracy, the Fermi level is pinned at approximately the same position as in the clean Si(111) surface. The above discussion shows that the pinning is not necessarily due to the Si intrinsic surface states but most likely to states associated with the alloy formed in the interface region. These gap states must not be confused with metal-induced states in a sharp interface which are reported to be typical of some Si—simple-metal interfaces.[27] The formation of a mixed phase with the disruption of the surface is established for the Si-Au interface. This means that the available theories of Schottky barriers which assume a sharp boundary between the semiconductor and the metal cannot be applied to the problem. This holds both for the models without bonding between the metal and the semiconductor[1,28–32] and for the models in which one attempts to relate the bonding at the interface to the stabilization of the Fermi level.[33–37] This fact is probably the origin of the difficulties in relating[38,39] the barrier heights of Si-transition and noble-metal barriers to the available theories.

D. Intermediate-coverage interval ($2 \lesssim \theta \lesssim 15$ monolayers)

The maximum thickness corresponding to this interval is of the same order of the escape depth at 10.2 eV, and larger than that at 30 and 160 eV. Thus, within this θ interval, the experimental information on valence states is a weighted average approximately over the whole interface region, with decreasing weights towards the interior. For 30 and 160 eV it is weighted toward the solid-vacuum interface.

All the EDC's give evidence that, when the surface region becomes richer in gold, the gold emission is less and less "atomic". In particular, the splitting between the two prominent structures *A* and *B* in the Au 5*d* region (Fig. 4) increases quite rapidly, and this must be regarded as the evidence of the "turning on" of a crystal field capable of producing a density of states which becomes closer to that of pure bulk gold. The great importance of crystal-field effects in determining the shape of the gold 5*d* bands and of the density of states is well known and has been pointed out, for example, by Christensen and Seraphin[40] whose results show that the two structures *A* and *B* cannot be given a one-to-one correspondence with the spin-orbit split 5*d* atomic levels as it can for diluted atoms at low coverages. The importance of crystal-field effects can be seen also from the similarity of the two density of states calculated by Smith,[41,42] with and without spin-orbit splitting included in the same calculation scheme.

Also in the intermediate θ interval, the gap emission is present. The increase of the average gold quantity produces a small shoulder at −0.8 eV in the EDC at $h\nu = 10.2$ eV with $\theta = 11.5$ monolayers (Fig. 1).

In the intermediate-coverage interval, the core lines from both Au and Si show an interesting behavior: the separation between the Au 4*f* and Si 2*p* lines increases since the Au 4*f* shifts towards lower-binding energies and Si 2*p* shifts towards higher-binding energies (Fig. 5). This opposite trend cannot be due to a band-bending effect and must be regarded as the evidence of the progressive modifications towards a different bonding between Si and Au. During the transition towards this new phase, the Si atoms sampled with $h\nu = 160$ eV are not all in equivalent environments, as can be deduced by the fact that the 2*p* linewidth increases, reaching a maximum [$\simeq$1.6 eV at $\theta \simeq 7$ monolayers to be compared with $\simeq$1.2 eV for clean Si(111)] and decreases again to a value ($\simeq$1.3 eV) which remains constant at higher coverages. It is very difficult to state if a band-bending mechanism is superimposed to this process: the comparison of the EDC's measured at 10.2 eV with 5.5 and 11.5 monolayers seems to suggest a slight variation of the band bending. In any case, it is worthwhile mentioning that this variation of bending, if any, begins at θ values which are definitely higher than the values at the beginning of the variation of core lines binding energies in Fig. 5. The core-line behavior in Fig. 5 for $\theta \lesssim 5$ monolayers is thus due only to a bonding effect. With these precautions in mind concermng band bending, it is interesting to note that the Au 4*f* line positions tend towards those of pure gold (84.0 eV for $4f_{7/2}$ level), giving a further spectroscopic evidence of the formulation of a gold-rich phase. The increase in Si binding energy would indicate a Au-Si interaction near the metal-vacuum interface. This results in a larger binding energy than for Si in bulk Si. Figure 7 shows that the Si concentration here is reduced by about a factor of 4 below that in bulk Si.

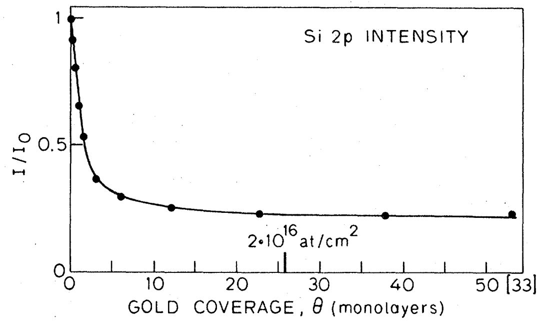

FIG. 7. Attenuation of the emission from Si 2*p* level as a function of gold coverage. The coverage is measured in units of Si surface atomic density (monolayers); the value in brackets is measured in units of gold surface atomic density. The number of deposited Au atoms per unit area is also given.

E. High-coverage interval ($\theta \gtrsim 15$ monolayers)

This coverage interval has been explored up to overlayer thicknesses definitely higher than the escape depth so that the experimental information which shows an asymptotic behavior refers to the top region of the sample. In this region, the interesting feature is that no pure gold is present, as it is clear from Fig. 2 ($h\nu = 30$ eV) where the gold 5*d* photoemission is considerably different from that of pure gold and from Fig. 4 which shows that the separation of the 5*d* peaks is $\simeq$10% lower than in pure Au. This provides evidence that silicon is dissolved in the gold. Although a quantitative discussion cannot be given, it is interesting to note that even about 25% of Si atoms results in measurable effects on the *d* states due to the great importance of the variations of crystal field discussed in the preceding paragraph. This phase is metallic since the EDC's at $h\nu = 10.2$ eV and at 30 eV show a progressive development of a well-defined metallic Fermi edge.

Although much work remains to be done, the literature reports an increasing evidence for the existence of various gold silicides[43–46] usually prepared by thermal treatment. It is thus plausible to consider the present Au-rich phase, produced at room temperature, as containing a stoichiometric silicide interdispersed in the Au-Si overlayer. This interpretation is in qualitative agreement with the Auger observations of Green and Bauer.[12] In their work, it was also suggested, on the basis of a sputter profile experiment, that a pure gold region is left beneath the silicide layer for depositions greater than 200 Å. With the present experimental method (i.e., without sputtering profiles), it is impossible to state if this happens also in this case. On the other hand, it is important to point out that recent channeling experiments[47] describe a situation with a uniform silicide layer extending up to the interface. In any event, the fact that the silicide formation[12] is seen immediately after the Au deposition strongly suggests the importance of the heat of condensation of Au in displacing some silicon already bound to Au and thus maintaining the silicide at the top of the sample. On the other side, the very high diffusion rate of silicon in gold overlayers even at room temperature[13,14] could supply some other silicon to form the silicide. It should also be recognized that Hiraki *et al.*[10] favors a picture of a pure gold overlayer with silicon segregated to the topmost layer, thus without any silicide formation.

As was discussed earlier, the present results do not provide any definitive evidence for the formation of an Au silicide with stoichiometric composition. Although only this or a Si-rich surface region is consistent with the data. The fact that the Au $5d$ peaks A and B shift towards E_F with increasing θ indicates that the material, on the average, becomes richer in gold (see Fig. 2), as seen with $h\nu = 30$ eV. On the other hand, the Si $2p$ line which originates from electrons with a shorter escape depth ($h\nu = 160$ eV; kinetic energy ≈ 55 eV) shows an almost constant intensity when θ is varied in the high-coverage region, as is shown in Fig. 7. A natural way to reconcile the increase of gold content and the constancy of Si emission is to assume that a small fraction of Si segregates at the surface. It is impossible to give quantitative statements, but it is apparent that its thickness is less than a monolayer. This silicon is present at the surface in a form distinctly different from bulk Si since no bulk Si $2p$ signal is present at $h\nu = 160$ eV. The Si enrichment of the surface is consistent with the fact that gold silicides are known to be definitely less stable than silicides of other d metals like Pt.

Another explanation could be that a richer-Au phase is formed without segregation beneath a top layer of a stoichiometric silicide. Since the escape depth is higher at $h\nu = 30$ eV than at $h\nu = 160$ eV, this Au-rich phase would be seen only at 30 eV. In such a case, the shift of the peaks A and B in the $5d$ region should be accompanied by a broadening of the same order of magnitude due to this Au-rich phase whose $5d$ states are less bound. Since it cannot be claimed that such a broadening is seen in the EDC's of Fig. 2, this possibility is less favorable than the preceding one based on Si enrichment of the surface.

As far as the composition of a possible surface silicide is concerned, values ranging from Au_3Si to Au_5Si have been suggested by AES work as reported in Refs. 12 and 46. The present results cannot be used to discriminate between these two possible cases in the absence of accurate measurements of the relative photoionization cross sections of Si $2p$ and of Au $4f$ states. A comparison of the core-lines emission around 2 monolayers in our data shows that the intermixed Au-Si phase present is silicon rich (typically $\approx 80\%$), i.e., very far from the eutectic composition (31% Si).

IV. SOME RESULTS ON THE TEMPERATURE EFFECTS ON THE CLEAN Si-Au INTERFACE

It has been pointed out[12] that several LEED patterns can be obtained by heating a Si(111)-gold sample and that formed silicides suffer decomposition with some gold agglomeration (island formation) if heated at temperatures around 450 °C. The effect of the treatment of a sample with 55 monolayers of gold for 10 minutes at 550 °C has been studied to gain a better understanding of the high-temperature behavior of the different Au-Si phases. However, a systematic study of the phases formed by thermal treatments has not been carried out. The effect of the thermal treatment is clearly demonstrated in Fig. 8 where the EDC's at $h\nu = 160$ eV show that the situation typical of low coverages is regained after heat treatment both in terms of relative peak positions and heights. It is thus possible to state that: (i) The heating leaves the surface region much more Si rich. (ii) The heating around 550 °C does *not* produce a phase similar to the eutectic (as deduced from the relative intensities of the Si $2p$ and Au $4f$ peaks). (iii) No simple gold agglomeration takes place after the heat treatment (the Au $4f$ binding energy is much less than that characteristic for pure gold, see Fig. 8).

This behavior can be explained by assuming that the diffusion of gold into silicon becomes sufficient, at these temperatures, to deplete partially the surface region from gold. In effect, the order of magnitude of the diffusion coefficient necessary to give the observed decrease of the gold $4f$ lines can be roughly evaluated from the EDC's of Fig. 8 in analogy with the method used by Abbati *et al.*[48] and is in agreement with the values reported in the literature[49] (10^{-9} cm^2/sec range). If this interpretation is

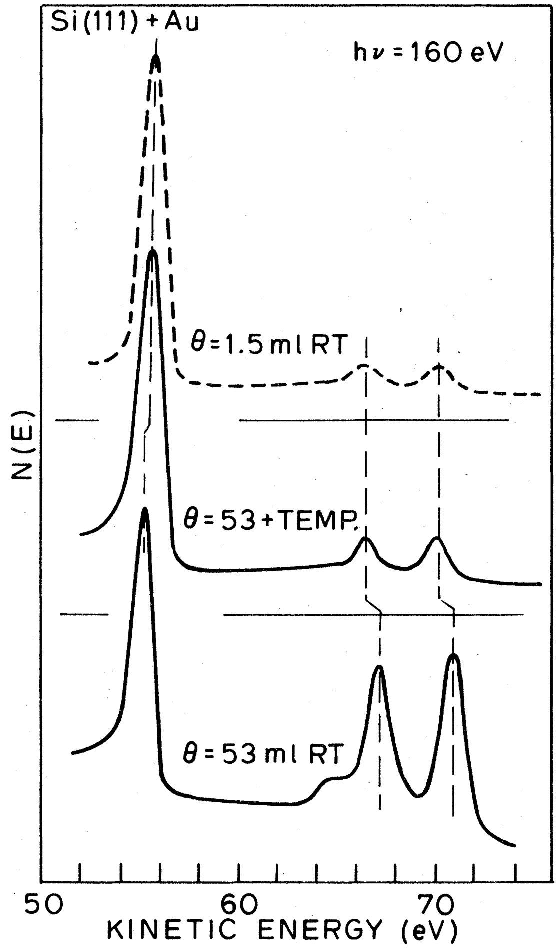

FIG. 8. Effect of a thermal treatment onto the Si $2p$ and Au $4f$ emission lines. The two solid lines are the spectra from a Si(111) + 53 Au monolayers sample before ($\theta=53$ ml RT) and after ($\theta=53$ +Temp.) a treatment at 550 °C for 10 minutes. The dashed line is the spectrum for Si(111) sample with 1.5 monolayers of Au without any thermal treatment. The spectra are plotted versus photoelectron kinetic energy and are normalized to the same height of Si $2p$ line.

correct, a situation more similar to the eutectic (i.e., richer in Au) may be obtained by heat treatment at lower temperatures where the diffusion coefficient is lower. This could explain qualitatively the results reported by Narusawa *et al.*[9] Extensive photoemission work still remains to be done on the temperature effects on the Si-Au interface.[50]

V. SOME RESULTS ON THE OXYGEN EFFECT ON THE Si-Au INTERFACE

It has been pointed out[12–14] that, if gold is evaporated onto an oxidized or passivated silicon surface, the intermixing is severely reduced.

The spectroscopy of the Au-Si interface after oxygen chemisorption and oxidation deserves a detailed study which is beyond the purpose of the present work. Only some preliminary results are given which are useful to answer an interesting point, i.e., if very low oxygen quantities (before bulk oxide formation) are sufficient to reduce to some extent the atomic intermixing. To this end, a freshly cleaved Si(111) surface was exposed to oxygen as specified in Sec. II A. This exposure procedure is known to produce[16,17] about half a monolayer of chemisorbed oxygen. Gold was deposited onto the sample after this treat-

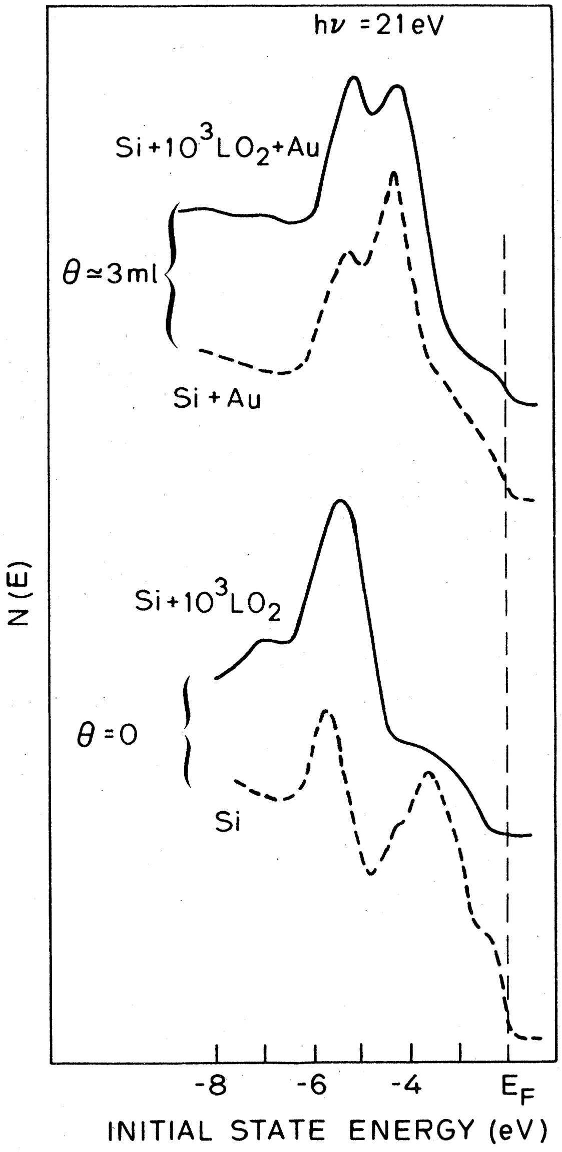

FIG. 9. Oxygen effect on the Si-Au interface. Dashed spectra refer to a clean Si(111) substrate, and solid spectra refer to a Si(111) substrate exposed to 10^3 L of oxygen with the procedure explained in the text. The photon energy is 21 eV, and the coverage is measured in units of Si surface atomic density (monolayers).

ment, and the EDC's were measured at $h\nu = 21$ eV. The most interesting results are given in Fig. 9 where it is shown that, with $\simeq 3$ monolayers, the intermixing appears to be lower. The most clear evidence is given by the metallic Fermi edge from the Au overlayer on the oxygen covered Si surface (solid line) which is not seen for a sample not exposed to oxygen (dotted line). Also, the shape of the *d*-band region shows less evidence of intermixing, although the presence of the $2p$ emission from oxygen complicates the analysis. The EDC's were measured immediately after the deposition so that no information can be given on a possible slow intermixing with a consequent broadening of the interface.

Thus, the main conclusion of these preliminary measurements is that even a very small quantity of oxygen without formation of oxide may reduce the atomic intermixing in the Si-Au interface. Further work is obviously required and is now in progress.

VI. CONCLUSION

The Si(111)-Au interface prepared at room temperature is not atomically abrupt. The Si(111) surface is severely disrupted upon Au deposition so that the photoemission peak from Si(111) surface states decreases very rapidly. An intermixed region ($\lesssim 15$ Å thick) is formed, as it is seen at low gold coverages (around 2 monolayers). This Si-rich phase, which may be thought of as an alloy, shows emission in the gap from states which are interpreted to be responsible for the pinning of the Fermi level. At increasing θ, a gold-rich Au-Si phase is formed which is always present at the surface of the sample at least up to a deposition of 160 monolayers. Only a slow increase of the gold content is observed from 15 to 160 monolayers, with evidence for segregation of a fraction of a monolayer of Si to the topmost surface layer. The Au-Si intermixing increases rapidly at elevated temperatures, with diffusion of Au towards the interior. The Si-Au intermixing is also very sensitive to oxygen overlayers, and a coverage of about half a monolayer of oxygen onto the Si(111) face at room temperature is sufficient to reduce it considerably.

The present results point out the importance of taking into account the formation of a broad intermixed region in the discussion of the Schottky-barrier behavior of the Si-Au interface. This may also be important for other Si interfaces, namely, those with transition metals where stoichiometric silicide formation takes place away.

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