

Rapid Communications

The Rapid Communications section is intended for the accelerated publication of important new results. Manuscripts submitted to this section are given priority in handling in the editorial office and in production. A Rapid Communication may be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the rapid publication schedule, publication is not delayed for receipt of corrections unless requested by the author.

Au-Si interface formation: The other side of the problem

A. Franciosi

Department of Chemical Engineering and Materials Science, University of Minnesota,
Minneapolis, Minnesota 55455

D. W. Niles and G. Margaritondo

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

C. Quaresima, M. Capozzi, and P. Perfetti

Laboratorio di Struttura della Materia, Via Enrico Fermi 38,
00044 Frascati, Italy

(Received 6 August 1985)

Most metal-semiconductor interface-formation studies investigate the chemisorption of metal adatoms on semiconductor substrates. We extended the investigation of the Si-Au interface to the chemisorption of Si atoms on Au. We found that the formation of an extended, alloyed interface region is a common feature of both interface-formation processes. Thus, the changes in the surface and bulk substrate thermodynamic parameters do not affect the qualitative morphology of the interface.

The crucial importance of metal-semiconductor interfaces has stimulated a large number of photoemission studies of their formation in the past decade.¹⁻¹⁴ These investigations have explored the chemisorption of metal atoms on semiconductor substrates. We present the results of what is to our knowledge the first photoemission experiment investigating the chemisorption of silicon atoms on a metal substrate—Si deposited on Au. These results demonstrate that the two processes—Au deposition on Si and Si deposition on Au—are essentially symmetric. In particular, we find a systematic correlation between formation of Au-Si alloys and change in Au 5*d* crystal-field splitting⁵⁻⁸ in both cases. We also find evidence that the formation of an extended alloyed interface region saturates at comparable coverages (atoms per unit surface) for Si deposited on Au and for Au deposited on Si.⁹

The experiments were performed at the PULS synchrotron radiation facility of the Frascati National Laboratory, with the beam line equipped with a Jobin-Yvon toroidal grating monochromator. Photoemission experiments were performed in the photon-energy range 20–60 eV with the experimental equipment described in Ref. 10. The overall resolution was of the order of 0.4 eV. The substrate was prepared by depositing a Au from a W coil on a Ta sheet *in situ*, at a pressure below 5×10^{-10} Torr. The thickness of the polycrystalline substrate was of several hundred angstroms. Si was deposited also *in situ* from an electron beam source at a rate of the order of 1 Å/min. The overlayer thickness was measured with a quartz thickness monitor.⁹ Data taking and processing were controlled by a CAMAC system interfaced with a Tektronix 4052 microcom-

puter.

Figure 1 shows a series of photoelectron energy distribution curves (EDC's) taken at a photon energy of 21 eV with the horizontal scale referred to the Fermi level. Figure 2 shows the corresponding spectra taken at a photon energy of 35 eV, which enhances the cross section of the *d-d* antibonding states. The bottom curve in each figure corresponds to the clean Au substrate. The other curves correspond to the same substrate covered by a Si overlayer of increasing thickness. Figure 3 shows for comparison a series of EDC's taken¹¹ at a photon energy of 40 eV for Au deposited on cleaved Si(111).

The most important conclusions obtained from Figs. 1, 2, and 3 are the following. First, when Si is deposited on Au the antibonding *d-d* state signal at ~ -2.6 eV is progressively attenuated.^{8,12} A symmetric increase in this signal is observed in Fig. 3 when Au is deposited on Si. Second, the *d* features shift to higher binding energies due to the Si adatoms on Au. This effect also has a symmetric counterpart in Fig. 3.

The similarity between the results for Si on Au and those for Au on Si is further demonstrated by a detailed comparison of the results of Figs. 2 and 3. The main effect of the Si adatoms in Fig. 2 is an apparent decrease of the energy splitting of the two main Au 5*d* features. We see in Fig. 3 a symmetric apparent increase of this splitting when the Au thickness increases. This effect has been explained⁷ by the formation of a Au-Si alloy in which the Au atoms are far from each other—and therefore the splitting becomes closer to that of atomic Au, 1.5 eV.

Calculations by Bisi *et al.*⁶ provided a detailed theoretical

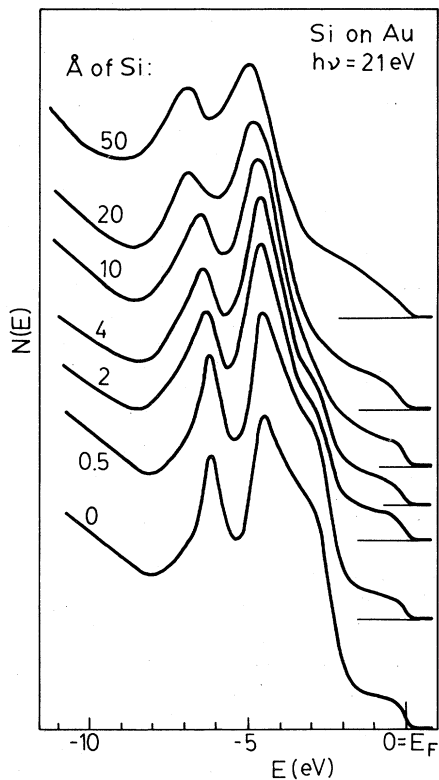


FIG. 1. Photoelectron energy distribution curves (EDC's) taken with a photon energy of 21 eV on a clean Au film and then on the same substrate covered with a Si overlayer of increasing thickness. The energy scale is referred to the Fermi level E_F .

background for the above explanation. The results of these authors indicate that the antibonding $d-d$ states are those mostly affected by alloy or compound formation. In the case of pure Au, these states correspond to the shoulder 2–3 eV below the Fermi level in Fig. 1. For photon energies of 35–40 eV, Figs. 2 and 3, the $d-d$ antibonding states dominate the shallowest-in-energy Au $5d$ feature.¹² Thus, their shift in energy is the main cause of the apparent change of the Au $5d$ splitting on going from pure Au to the Au-Si alloy.

Therefore, the behavior of the Au $5d$ energy splitting at photon energies of 35–40 eV is a good probe of the formation of a Si-Au alloy at the interface.⁷ We show in Fig. 4 this splitting as a function of the overlayer thickness (in equivalent monolayers; see Ref. 9), for Si on Au and for Au on Si. We see from this figure that most of the change occurs for equivalent coverages of 0–8 monolayers for Au on Si and 0–4 monolayers for Si on Au. To interpret this observation, one must consider the definition of the equivalent coverages in the two cases (Ref. 9). This definition implies that the interface layer formation is completed after depositing approximately the same number of atoms per unit substrate area in both cases, $(6-7) \times 10^{15}$ atoms/cm². This result is somewhat surprising, since the adatom chemisorption energy was considered⁷ the dominant promoting factor for the Si-Au intermixing. Thus, the extent of the intermixing should be proportional to the number of atoms per unit substrate area. This, however, is not consistent with the results of Fig. 4, since there are ap-

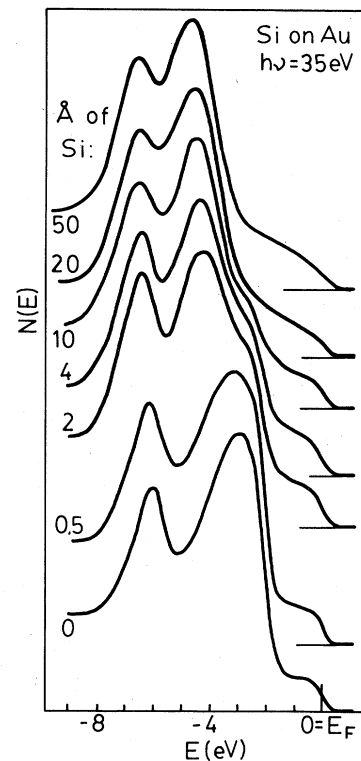


FIG. 2. EDC's similar to those of Fig. 1, taken at a photon energy of 35 eV.

proximately twice as many atoms per unit area for the Au substrate than for the Si substrate. The reason of this apparent discrepancy could be, for example, a different near-surface defect-formation enthalpy for the two cases.

We also see that the asymptotic values of the splitting for

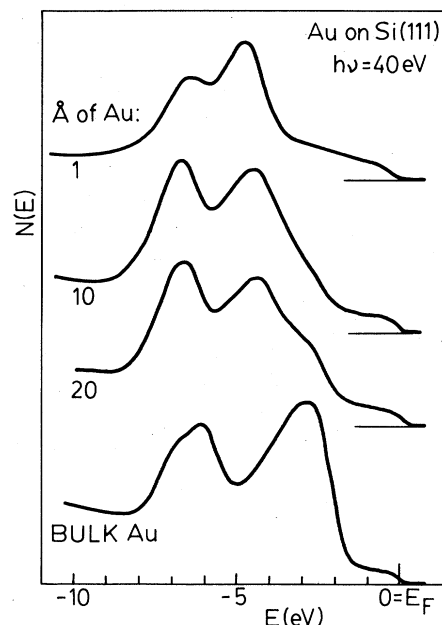


FIG. 3. EDC's taken for Au deposited on clean Si(111) at a photon energy of 40 eV. The data are from Ref. 11.

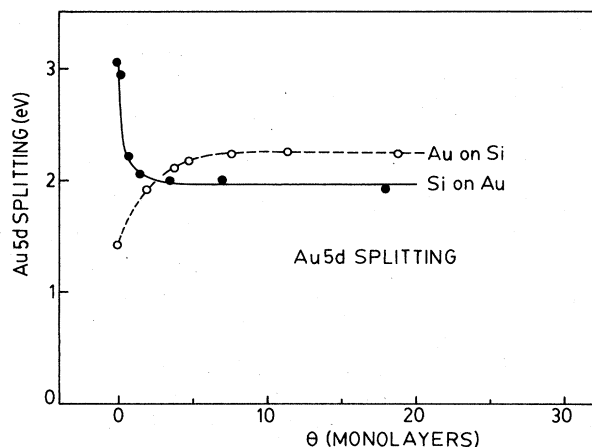


FIG. 4. The apparent Au 5d energy splitting as a function of the overlayer thickness for Au deposited on Si (Fig. 3) and for Si deposited on Au (Fig. 2 and Ref. 11). The overlayer thickness is expressed in equivalent monolayers in both cases, as discussed in Ref. 9.

large equivalent thicknesses are different by approximately 0.25 eV. This difference cannot be taken as evidence for a different average stoichiometry of the alloyed interface layer. In fact, the asymptotic value for Au on Si has been associated^{7,13,14} with the presence of segregated Si atoms at

the Au-vacuum interface. Similarly, in the case of Si on Au one could have segregated phases that give a constant Au 5d splitting for large coverages.

In summary, the most important result of our experiment is that interface alloyed species are formed both when Au is deposited on Si and when Si is deposited on Au. Processes of this kind, involving either alloys or interface compounds, have been observed in many investigations of metal overlayers on silicon.^{1-7,15-17} Several factors have been proposed to control the formation of these extended interfaces. Our results enable us to rule out some of these factors, at least in the case of Si-Au. For example, we can rule out an important role of mass transport, of the segregation energies, and of the adatom kinetic energy. We also find similar numbers of atoms involved in the alloyed interface species for both Au on Si and Si on Au. One important result is that the changes in bulk and surface thermodynamic parameters caused by interchanging substrate and overlayer do not affect the qualitative morphology of the interface region.

This work was supported by the Office of Naval Research and by the Center for Microelectronics and Information Science of the University of Minnesota. The international collaboration Frascati-Wisconsin is supported by the National Science Foundation under Grant No. INT-81-22013 and by the Italian National Research Council.

¹L. J. Brillson, *Surf. Sci. Rep.* **2**, 124 (1982).

²R. H. Williams, *Contemp. Phys.* **23**, 329 (1982).

³G. Margaritondo and A. Franciosi, *Annu. Rev. Mater. Sci.* **14**, 67 (1984).

⁴I. Lindau and W. E. Spicer, in *Synchrotron Radiation Research*, edited by H. Winick and S. Doniach (Plenum, New York, 1980), p. 159.

⁵I. Abbati, L. Braicovich, A. Franciosi, I. Lindau, P. R. Skeath, C. Y. Su, and W. E. Spicer, *J. Vac. Sci. Technol.* **17**, 930 (1980), and references therein.

⁶O. Bisi, C. Calandra, L. Braicovich, I. Abbati, G. Rossi, I. Lindau, and W. E. Spicer, *J. Phys. C* **15**, 470 (1982).

⁷L. Braicovich, C. M. Garner, P. R. Skeath, C. Y. Su, P. W. Chye, I. Lindau, and W. E. Spicer, *Phys. Rev. B* **20**, 5131 (1979).

⁸C. Calandra, O. Bisi, and G. Ottaviani, *Surf. Sci. Rep.* **4**, 271 (1984), and references therein.

⁹The definition of an equivalent monolayer thickness of Si on Au is made difficult in our case by the polycrystalline nature of the Au substrate. We assumed a prevailing (111) orientation for the mi-

crocrystallites, and used the surface density of Au(111), 13.8×10^{14} atoms/cm², to define the equivalent monolayer of Si on our substrate, 2.78 Å. The equivalent monolayer of Au on Si(111) is 1.32 Å.

¹⁰P. Perfetti, S. Nannarone, F. Patella, C. Quaresima, M. Capozzi, A. Savoia, and G. Ottaviani, *Phys. Rev. B* **26**, 1125 (1982).

¹¹A. Franciosi, D. G. O'Neill, and J. H. Weaver, *J. Vac. Sci. Technol. B* **1**, 524 (1983).

¹²A. Franciosi, J. H. Weaver, and D. G. O'Neill, *Phys. Rev. B* **28**, 4889 (1983).

¹³A. Hiraki, K. Shuto, S. Kim, W. Kamura, and M. Iwami, *Appl. Phys. Lett.* **31**, 611 (1977).

¹⁴A. K. Green and E. Bauer, *J. Appl. Phys.* **47**, 1284 (1976).

¹⁵P. S. Ho, *J. Vac. Sci. Technol. A* **1**, 745 (1983).

¹⁶J. Grunthaner, F. J. Grunthaner, A. Madhukar, and J. W. Mayer, *J. Vac. Sci. Technol. A* **19**, 649 (1983).

¹⁷P. Perfetti, S. Nannarone, F. Patella, C. Quaresima, A. Savoia, F. Cerrina, and M. Capozzi, *Solid State Commun.* **35**, 151 (1980).