To be submitted to
Solid State Comm.

ISTITUTO NAZIONALE DI FISICA NUCLEARE
Laboratori Nazionali di Frascati

LNF-80/13(P)
10 Marzo 1980

P. Perfetti, S. Nannarone, F. Patella, C. Quaresima, A. Savoia,
F. Cerrina and M. Capozi (PULS):

ENERGY LOSS SPECTROSCOPY (ELS) ON THE Si-Au SYSTEM.

Servizio Documentazione
dei Laboratori Nazionali di Frascati
Cas. Postale 13 - Frascati (Roma)

INFN - Laboratori Nazionali di Frascati
Servizio Documentazione

LNF-80/13(P)
10 Marzo 1980

P. Perfetti, S. Nannarone, F. Patella, C. Quaresima, A. Savoia, F. Cerrina and M. Capozi (PULS): ENERGY LOSS SPECTROSCOPY (ELS) ON THE Si-Au SYSTEM.

We report on the energy loss spectroscopy obtained on the clean cleaved Si(111) covered with different gold thickness. The results clearly indicate that in the Si-Au system the interface is characterized by a Si rich phase with a well defined electronic transition at 7.5 eV energy loss. Increasing Au thickness the main changes in the spectrum arise in the low energy loss region and a gold-like behaviour is observed for a gold coverage of 60 monolayers. The effects of annealing at 350°C are reported.

In one[1] of the first papers trying to find a chemical trend in the barrier height ϕ_B of transition-metal-silicide-silicon (tmSi-Si) interfaces, the silicon-gold system was included just for fiducial purpose. In fact, at that time, gold was not supposed to form a silicide when deposited on a silicon substrate. Now a large number of structural studies are available[2,3,4,5] and recently, ultraviolet photoemission spectroscopy (UPS), performed with synchrotron radiation[6] and with a helium source[7,8] is entering strongly into this subject.

One fact can be certainly stated: when gold is deposited on a clean Si substrate at room temperature (RT) an intermixing between the two materials occurs and an amorphous or disordered structure is detected at low coverages by a LEED analysis[5]. Auger electron spectroscopy (AES) depth profiles[2,5] and UPS[6] have pointed out that the intermixed region at the interface is approximately 20 Å thick.

On top of a thick Au deposited film ($\simeq$ 100 Å) a second intermixed region exists[2,5] (external region) and the system may be thought as a sandwich, where the intermediate region is almost pure gold. THis description is qualitatively valid both for Si(111)-Au[2] and Si(100)-Au[5] interfaces. When this sandwich is annealed in a temperature range between 200°C + 400°C an ordered phase is shown by LEED whose pattern is different for gold deposited on Si(111)[2] or Si(100)[5]. Even though the LEED pattern shows a well ordered phase a three dimensional crystal structure determination is needed in order to assign these patterns to specific silicides. Another important feature, common to the gold-silicide phase and to the mixed phase obtained after 30 Å of a gold deposition at RT is a splitting of the Si(LVV) auger peak at 92 eV into two peaks at 90 eV and 95 eV respectively. The aim of this paper is to add a piece to this mosaic and in fact these are the first energy loss measurements (ELS) on the Si-Au system. ELS as well as absorption spectroscopy, may be considered complementary to UPS and in fact it allows to observe transitions to final states under the vacuum level.

We used an ultrahigh vacuum chamber equippped for UPS at the synchrotron radiation center of Frascati. A manipulator allows the sample to be moved, out of axis, on circle in front of the different facilities. These are a cleaver, made with movable tungsten carbide blade in front of a flat copper anvil, and a PHI double pass CMA whose coaxial electron gun has been used either for AES or ELS. The sample annealing has been obtained with a joule heating system placed on the back of the sample holder. ELS data were taken on a "in situ" cleaved n-type Si(111) single crystal at different Au coverages obtained by thermal evaporation from a tungsten crucible and ranging from a fraction of monolayer (ml) to 100 mls. The film thickness has been measured by a piezoelectric film thickness monitor and one monolayer coverage (θ=1) has been defined as the number of Au atoms equal to the Si(111) surface density ($\simeq 7.8\ 10^{14}$ at./cm^2) corresponding to 1.3 Å thickness. This coverage scale is the most natural for low coverage while for the gold rich phase it should be better to refer to the atomic surface density of Au(111) which is $\simeq$1.5 times higher than Si(111). We used a 100 eV primary electron beam impinging on the sample at 45°. Fig. 1 and 2 show a set of selected ELS spectra referring to the clean Si(111) surface and to the Au-covered sample with different overlayer thicknesses. The dashed curve at the bottom of Fig. 2 has been obtained after 30 minutes of annealing at 350°C. On the right of the figures the most meaningful AES spectra of the Si-LVV and Au-OVV energy region are reported. These AES spectra are mainly reported to relate our ELS results with those obtained with other experimental techniques. Because we don't know to what extent the Si-LVV

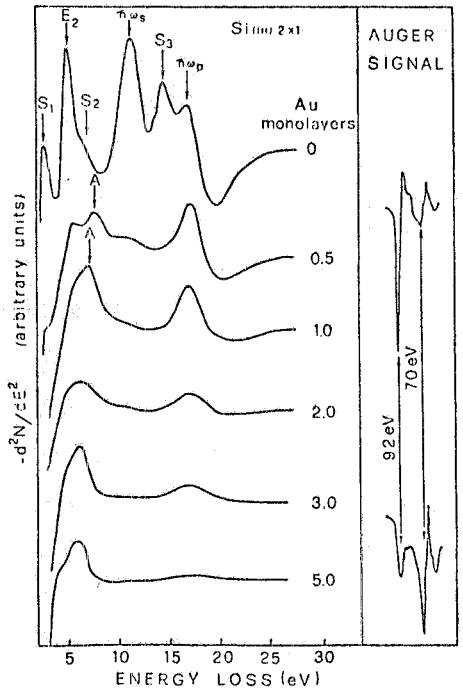

FIG. 1 - ELS spectra of cleaved Si(111) taken at different Au coverages. The most meaningful auger signals are reported on the right.

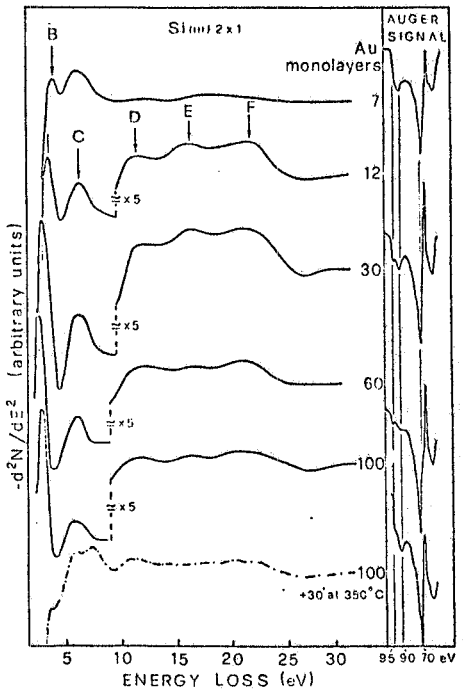

FIG. 2 - ELS spectra of cleaved Si(111) taken at different Au coverages. The dashed curve has been obtained after 30 minutes of annealing at 350°C.

peak is modified by the mixed phase formation we cannot extract from the AES signals a precise information on the relative amount of Si and Au in the mixed phase; nevertheless, if a ratio between the 90 eV auger peak, characteristic of the mixed phase, and the gold one at 70 eV is made, a trend of the intermixing process may be followed[2].

The first spectrum of Fig. 1 is reprentative of pure cleaved Si(111) and all the features have been already identified[9]. In particular peaks at 17.2 eV and 11.5 eV correspond to bulk and surface plasmon respectively. The peak at 5.2 eV is a one electron transition related to the bulk Si band structure. The remaining losses at 2.8 eV, 7.3 eV and 14.8 eV involve mainly transitions between back bonds and empty surface states. This spectrum is strongly modified after 0.5 ml of Au-deposition. The surface structures nearly desappear and a new peak "A" at 7.9 eV energy loss is clearly evident. After 1 ml coverage peak A shifts at 7.5 eV, it becomes dominant and only the losses at 5.2 eV and 17.3 eV remains of the old Si(111) spectrum. Increasing Au coverage an evolution of the spectrum occurs and the new structures B, C, D, E, F, are clearly evident at θ=12 of Fig. 2. The energy losses of these structures are reported in Table I.

TABLE I

Energy loss (eV) of the main features of Figs. 1 an 2.

θ	A	B	C	D	E	F
1	7.5					
12		3.7	6.0	11.0	16.0	22.0
60		2.7	6.0	11.0	16.0	22.0

Peack B is well defined for θ=7 ant its energy position is 3.7 eV. In the coverage range 0.5+ 7 mls the ratio between the Si (LVV) and Au(OVV) auger peaks drops from 3.8 to 0.13. For θ=7 the Si(LVV) peak bebings to change its shape, and it clearly splits into two peaks at 90 eV and 95 eV respectively at θ=30. At higher coverage the main changes in the ELS spectra arise in the low energy loss region. Namely, peak B shifts to lower energy and reach its final position at 2.7 eV at θ=60. The other strucures C, D, E, F, at 6 eV, 11 eV, 16 eV, 22 eV respectively remain unchanged. The ratio between the auger signals decreases at 0.06 for θ=100 indicating that a gold rich phase is present on the surface.

The sample annealing at 350°C for 30 minutes causes a strong modification of the spectrum (dashed curve of Fig. 2); peak B is replaced by a structure of 3.7 eV, characteristic of θ=7, and a feature at 7.5 eV, at the same energy of peak A (θ=1), becomes evident.

These results clearly indicate that at the interface (θ=1) a silicon rich mixed phase exists and this is characterized by a well defined electronic transition at 7.5 eV (peak A). The so called gold-siliced phase[2,5], characterized by the splitting of the Si(LVV) auger peak, and by the onset of peak B at 3.7 eV, arises at $\theta \simeq 7$; for coverages higher than θ=30 the surface becomes richer in gold and the only remarkable change in the spectrum is the shift of peack B towards lower energy. The spectrum at θ=100 is gold-like and all the features B through F may be accounted for in terms of structures of the gold surface loss function. In particular peak B at 2.7 eV is due to transition from the higher d levels to the Fermi energy[10]. This seems to indicate that the electronic configuration of the gold-silicide phase is similar to that of pure gold and that the bonding between the Si(sp) and Au(sd) electrons essentially affects the shallowest d-electrons as is confirmed by the shift of the peak B only going from θ=7 to θ=60.

The annealing at 350°C causes a further segregation of Si atoms from the substrate to the surface, the shoulder at 3.7 eV replaces peak B anf the Auger

spectrum is more likely to θ=7 (gold-silicide phase). On the other hand, the presence of a peack at 7.5 eV, at the same position of low coverage (θ=1) "A" peak, may suggest that the Si segregation at the surface is accompained by islands formation at 350°C and that the diluite Au phase (θ=1) may be present between islands.

We may conclude that in the Si-Au system the interface is characterized by a Si rich phase with a well defined electronic transition at 7.5 eV which is not present in the gold-silicide phase (θ=7). This last phase gives rise to ELS transitions similar to pure gold but with the highest initial states deeper in energy.

ACKNOWLEDGEMENTS

The authors are indebted to Prof. G. Ottaviani for having suggested this research. The technical assistance of R. Bolli, L. Siracusano, F. Campolungo, L. Moretto and M. Macrì is highly appreciated.

REFERENCES

(1) J.M. Andrews and J.C. Phillips, Phys. Rev. Letters 35, 56 (1975).
(2) A.K. Green and E. Bauer, J. Appl. Phys. 47, 1284 (1976).
(3) G. Le Lay, M. Manneville and R. Kern, Surface Sci. 65, 261 (1977).
(4) T.J. Magee and J. Peng, Phys. Stat. Sol. (a) 49, 313 (1978).
(5) K. Oura and T. Hanawa, Surface Sci. 82, 202 (1979).
(6) L. Braicovich, C.M. Garner, P.R. Skeath, C.Y. Su, P.M. Chye; I. Lindau and W.E. Spicer, Phys. Rev., to be published.
(7) I. Abbati, L. Braicovich and A. Franciosi, Sol. State Comm., to be published.
(8) I. Abbati, L. Braicovich and A. Franciosi, Phys. Rev. Letters, to be submitted.
(9) H. Froitzheim: Topics in current Physics (Spinger, 1977), vol. 54.
(10) N.E. Christinasen and B.O. Seraphin, Phys. Rev. B 4, 3321 (1971).