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Résumé. — Des films d'or déposés à température ambiante sur du silicium sont analysés par spectroscopie Auger et par pertes d'énergie, révélant ainsi l'existence de : 1) un interface diffus ; 2) un film d'or pur ; 3) une couche mixte or-silicium au-dessus du film. Les aspects des spectres de perte induits par la bande d de l'or sont reliés aux propriétés électroniques des alliages or-silicium. Une estimation de la composition à la monocouche donne environ l'eutectique $Au_{0.81}Si_{0.19}$. Les effets de recuits sont aussi examinés.

Abstract. — Gold films deposited at room temperatures on Si are analysed by Auger and electron energy loss spectroscopies which reveal the existence of : 1) a diffuse interface ; 2) a pure gold film ; 3) a mixed gold-silicon layer on top of the film. Loss spectra display gold d band features related to electronic properties of gold-silicon alloys. An estimation of the composition in the monolayer range gives nearly the eutectic $Au_{0.81}Si_{0.19}$. Annealing effects are also investigated.

The gold-silicon (Au-Si) interface is widely used in technology. In the past few years, it has been the object of many investigations. A good overview of its properties is of capital importance both on fundamental and technological points of view. Despite a large literature devoted to this subject, no definite understanding of its properties has been attained at the present time. The situation is very different from the Ag-Si interface which is very abrupt [1] or from the Pd-Si system whose properties are dominated by the formation of a definite compound [2]. However, some properties of thin gold films on Si are already well established. Bauer [3] and Le Lay *et al.* [4] studied the structural properties in the early stages of gold deposition on a Si (111) surface. The diffusion of Si through the gold films has been reported by Hiraki *et al.* [5] and Green and Bauer [6]. The electronic properties did not receive much attention up to now ; only recently published data from U.V. photoemission [7] and core level emission [8] gave some insight on this point.

The aim of this letter is to report some E.L.S. data on the Au-Si interface at the early stages of its formation and to relate them to its structural properties. The major features in the evolution of the spectra can be understood in terms of the electronic properties of gold-silicon alloys of varying composition. We also show as in the case of silver deposited on silicon that the E.L.S. spectra are very sensitive to the growth mechanisms which are different at room temperature and at temperatures higher than 400 °C [4].

Experiments were performed on p type Si surfaces (10^{16} boron atoms/cm^3). The sample was cleaved in air along the (111) face and introduced in an U.H.V. chamber having LEED, Auger electron spectroscopy (A.E.S.) and E.L.S. facilities. Repetitive short heat treatments at 1 000 °C gave a clean Si surface as monitored by A.E.S. LEED patterns revealed also well ordered surfaces with very sharp (7 × 7) spots. Gold was deposited onto the sample from a Knudsen cell and the coverage θ, defined as the ratio between the number of Au atoms and the number of Si surface atoms, was calibrated with a quartz microbalance. Coverage increments of 1/10 allowed us to characterize the interface at the very beginning of its formation. At each stage of the deposition, A.E.S. and E.L.S. spectra were recorded. The incident electron energy in E.L.S. was 100 eV and the back scattered electrons were analysed by means of a cylindrical mirror analyser (CMA) in the second derivative mode $- d^2N/dE^2$ of the reflected electron energy distribution. The energy resolution was 0.8 eV. LEED patterns were also checked.

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At room temperature, the evolution of the Auger spectra with increasing gold coverage gives the following results. The intensity of the Si peak at 92 eV associated to a LVV Auger transition decreases in the range $0 < \theta < 4$. Near $\theta = 4$, the peak splits into two components located at 90 eV and 94 eV. Its lineshape then remains unchanged but its overall intensity decreases while the intensity of the gold peak at 69 eV increases at higher coverages. Even at $\theta \sim 100$, A.E.S. indicates the presence of Si atoms on top of the gold film. In order to get some insight on the concentration profile, we proceeded to the sputtering of this film with argon ions and recorded the Auger spectra at fixed intervals during this treatment. The ion energy was 400 eV and the ionic current density was 5 $\mu A/cm^2$. From the calibration of the thickness of the deposit, we estimated the sputtering rate to fall at one monolayer/min. The profile obtained confirms the presence of : 1) a Si rich surface monolayer; 2) a pure gold film; 3) a diffuse interface of a few monolayers on top of the Si substrate.

The change in the Auger Si line reveals the modification of the electronic states in the valence electrons of Si surface atoms as in many Si-metal alloys [9] and allows an estimation of the composition of the top layer which is of the order of an Au-Si eutectic alloy. The value which is usually admitted now for the eutectic composition is $Au_{0.81}Si_{0.19}$ [10] while many authors still use the old value $Au_{0.69}Si_{0.31}$ given by Hansen and Anderko [11]. We remark that the splitting is observed only at $\theta = 4$ although the modification of the electronic states of Si surface atoms should already occur, as will be confirmed by E.L.S., at smaller coverages. In fact, its intensity is washed out by the large contribution of Si atoms in the subsurface. The progressive disappearance of the 7 × 7 LEED superstructure when Au is deposited suggests that the surface alloy is amorphous, a conclusion supported by the ability of Si and Au to form amorphous alloys.

The E.L.S. results are summarized in figure 1. For very low coverages, one sees immediate changes in the Si spectrum. The well-known bulk and surface structures corresponding to plasmon excitation and interband transitions [12] rapidly disappear when θ increases. Two peaks A (7.5 eV) and B (about 11 eV) are seen at $\theta = 1$. Somehow similar results are reported by Perfetti et al. [13]. Peak A shifts progressively towards 6 eV when θ is increased and its position does not change for $\theta > 12$. The unresolved and broad peak B remains nearly at the same position in this range of θ values. The dashed curve (f) in figure 1 is a loss spectrum of a clean polycrystalline gold ribbon mounted on the sample holder. The spectrum obtained at $\theta \sim 100$ is still identical to spectrum (e) but different from spectrum (f) although the 6 eV peak is present in both cases.
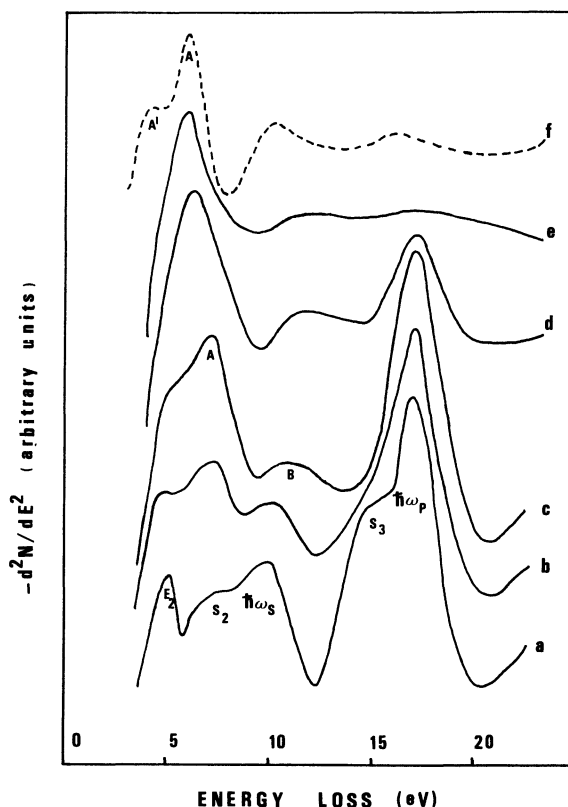

Fig. 1. — E.L.S. spectra of room temperature deposits. The primary electron energy was 100 eV. $N(E)$ is the reflected electron energy distribution. The modulation amplitude was 0.8 eV. Spectra were recorded in the second derivative mode of a CMA. (a) 7 × 7 clean surface; $\hbar\omega_p$ = bulk silicon plasmon; $\hbar\omega_s$ = surface plasmon; S_2 and S_3 = peaks due to electronic transitions from surface states; E_2 = bulk silicon interband transition. (b) $\theta = \frac{1}{2}$; (c) $\theta = 1$. Note the initial position of the A peak for this gold-silicon mixed layer is at 7.5 eV. (d) $\theta = 4$; (e) $\theta = 12$. The A peak has shifted now to its final position characteristic of pure gold. The spectrum remains unchanged at higher coverages. (f) Spectrum of a pure gold sample.

The final position of peak A corresponds to a characteristic loss of pure gold. The d band density of states in bulk Au displays two maxima (a) and (a') located respectively at 6 eV and 4 eV below the Fermi level. Peak A in pure gold corresponds to a transition from maximum (a) in the d band to the Fermi level in the sp conduction band. The expected transition A' from d band states (a') to the Fermi level is not seen even at high θ. Its energy is about 4 eV and in loss spectra the intensity of this transition is known to be very sensitive to the structure of the gold film. This is due to possible screening effects caused by the small size of Au crystallites in the gold layer [14]. Another possible screening mechanism could come from the gold-silicon surface layer.

It is worth mentioning that the progressive shift of peak A occurs during the build up of the mixed gold-silicon layers revealed by the film composition profile. Above $\theta \sim 12$, gold layers are deposited and then peak A remains located at the same energy position corresponding to the pure gold bulk value.

It is thus attractive to relate the observed shift to electronic properties of amorphous gold-silicon alloys. In these alloys, Si is known to be metallic and when the composition x of the system Au_xSi_{1-x} is varied, a displacement of the d band relative to the Fermi level is observed [15]. This causes the energy of the first interband transition from d band to Fermi level (A') to increase when some amount of Si is admitted in pure gold and we expect a similar behaviour for the A peak. Therefore looking at the shift of the A peak, we can estimate the composition of the alloy, by comparison with the shift of the A peak in photoemission data obtained on well-known composition Au-Si samples. This has been done using photoemission results of Hiraki et al. [5] where we compared the energies of the A peak for pure gold samples and for the eutectic alloy. In this manner, we found that the monolayer composition falls near the eutectic $Au_{0.81}Si_{0.19}$. This result seems to agree with the general behaviour of a metal semiconductor interface. Indeed Ottaviani et al. [16] have recently suggested that during the early formation of a Schottky barrier, an eutectic interfacial layer should play a large role. If θ is increased, further mixed gold-silicon layers are formed in which the Au concentration increases thus causing peak A to displace towards smaller energy up to $\theta \sim 12$. With overdose, gold layers are then deposited and peak A remains located at the same energy position, i.e. 6 eV.

Let us recall at this stage of the discussion that A.E.S. and E.L.S. signals integrate information on the electronic structure of atoms within an electron escape depth. Thus if spectral structures characteristic of both top layer and underlying layers within the probe depth are located at the same energy, subsurface effects will dominate. On the contrary, if no strong structure due to the underlayers is in the energy range analysed, outermost surface effects will prevail. This explains why the contribution of the surface alloy revealed by A.E.S. is hardly seen in the E.L.S. energy range of the strong interband transition near 6 eV which is dominated by the underlying gold film. On the other hand, we believe that peak B is due to the surface alloy because if we increase the escape depth by varying the incident electron energy, the intensity ratio I_B/I_A from peak B to peak A decreases so that peak B can be associated to the amorphous surface alloy. It is however impossible to assign it precisely either to a surface plasmon or to an electronic interband transition. Unfortunately, the band structure of gold-silicon alloys is not well-known so far to check this latter hypothesis. If on the contrary we assume that peak B is due to a surface plasmon, the value for the corresponding bulk plasmon should be 17 eV. This is very different from the 13 eV predicted by the analysis of Hauser and coworkers [15].

Anyway, we would like to point out that the analysis of these authors is based on the rigid band model for metallic alloys and assumes a full metallic character of the Si valence electrons. Although this can give the general features of the d band displacement in the sp conduction band, this cannot account for the results observed in photoemission [7]. In particular, Braicovich and coworkers report a change in the energy splitting of the two maxima (a) and (a') of the d band density of states when gold coverage is varied, which is unexplainable within this model.

If gold is deposited at temperatures > 400 °C, the intensity variation of Auger peaks is characteristic of a Stranski-Krastanov growth mode where 3D crystallites can be observed [4]. No splitting occurs in the Auger Si peak even at large θ. The evolution of loss spectra when θ increases is visible on figure 2. No more drastic changes in the spectrum are seen when θ is > 2. Spectra always present features characteristic of the monolayer range. This is due to the fact that even at high θ (> 100 layers), 3D clusters cover only 20 % of the whole surface as revealed by scanning electron spectroscopy [17]. Thus the E.L.S. signal comes mainly from the regions of the first adsorbed layer uncovered by 3D clusters. In the same manner, annealing at 400 °C for a few minutes a film ($\theta \sim 100$) previously deposited at room temperature, transformed this smooth film into 3D clusters on top of the first layer and the E.L.S. shows unambiguously this evolution [17]. This situation is very similar to that observed in Ag-Si [1].
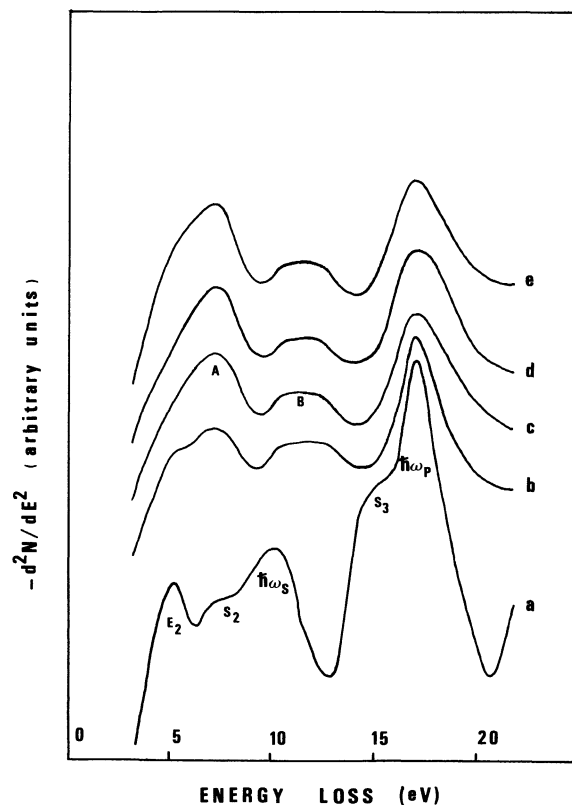

Fig. 2. — E.L.S. spectra at $T = 400$ °C. Above $\theta = 1$ almost no changes are observed. (a) $\theta = 0$; (b) $\theta = 1$; (c) $\theta = 2$; (d) $\theta = 10$; (e) $\theta = 20$.

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