



Temperature dependent early stages formation of the Au / Si (100) interface

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Abstract

Electron spectroscopies observations on morphological changes in gold deposited on Si (100) surfaces as a function of temperature have been reported. A detailed study of the Au/Si(100) interface is presented in the early stages of its formation at various temperatures in the low coverage region from zero to few mono-layers using LEED, AES and transmission electron spectroscopy. The Au / Si (100) system exhibits the Stranski- Krastanov growth mode where gold crystallites (without any apparent crystallographic face) on a 2D monolayers. The effect of temperature on the desorption of gold on silicon is discussed.

1. Introduction

The interface formed between metal and silicon is critical in determining its ultimate electronic properties. From an atomistic point of view the interface structure resulting from the deposition of noble metal atoms on the elemental semiconducting substrates is an important step towards a fundamental understanding of both the chemical nature and the electronic structure of the interfaces of these technologically vital systems. In this context since seven decades, the Au/Si interface has been a model system for investigating the Schottky barrier formation [1-3] as well as the nature of p-d hybridization process [4] and the subsurface interface electronic structure by ballistic electron emission microscopy [2,3].

However for such complex system, the interface structure is still under investigations and some controversy remains concerning the typical detailed characteristics of the interface. Many experimental results [5-7] support strongly that the Au/Si (111) interface grown at room temperature is fairly diffuse, containing an intermixing Au-Si alloy. In contrast to this diffusive interface model, other data [8] suggested that the room-temperature-grown interface is abrupt with the contact made metallic Au and bulk Si. Since these interface structures are mostly deduced from the results obtained using conventional surface sensitive techniques, the information of interest has been rather limited related to the poor spatial resolution and finite electron escape depth associated with these surface methods. According to its higher technological importance, the investigation of the formation of the Au/Si(100) interface [9,10] remains an attracting goal. Nowadays, metal nanoparticles on surfaces are being used effectively in nanofabrication, such as catalysts for carbon nanotube growth [11,12], as well as growth of inorganic nanowires [13-15] and for nanoelectronics applications [16-18]. The formation of nano-metal silicides, used as Schottky barriers and ohmic contacts in devices, is of fundamental interest in the domain of nanotechnology. The nature of these interactions, the range of temperatures required and the resulting composition of Au-Si alloy depend on whether these gold nanoislands interact directly with the substrate or have to deal with a barrier, e.g. a native oxide layer, before they could interact with the substrate.

Most of these studies were done under ultra-high vacuum (UHV) conditions and on systems where there was no oxide layer in between the metal film and the silicon substrate. Many of them have reported the formation of various metastable gold silicides due to the intermixing. There have been numerous interesting studies on the mechanism of relaxation of strain in such epitaxial layers. Strained epitaxial layers are inherently unstable and have interesting properties. It has been reported that dislocation formation and shape

transition are the important processes by which relaxation of strain occurs [19–22]. In recent years, it has been recognized that shape changes such as island formation constitute a major mechanism for strain relief [19, 21]. Below a critical size, islands have a compact symmetric shape. For larger sizes, they adopt a long thin shape that allows better elastic relaxation of the island's stress [23]. Metal silicide thin films on **Si (100)** have been studied in great detail for more than two decades due to the possibility of obtaining self-aligned epitaxial metal– semiconductor interfaces [21, 24].

The aim of this paper concerns the effect of temperature on the desorption of gold on silicon structures. We present experimental observations of the growth of gold on silicon structures during in situ thermal treatment in a heating stage for gold deposited on **Si (100)** surfaces. In particular, a detailed study of the **Au/Si(100)** interface is presented in the early stages of its formation at various temperatures in the low coverage region from zero to few mono-layers using LEED, AES and transmission electron spectroscopy. The discussion of the experimental data is focused on the onset of the intermixing reaction.

2. Experimental details

The experiments were performed in an UHV-chamber under a base pressure of $8 \cdot 10^{-10}$ Torr (down to $2 \cdot 10^{-9}$ Torr during Au evaporation). A four-grid LEED optics was also used as a retarding field analyzer for Auger electrons, which were excited by a grazing incidence gun operated at 2 keV (modulation voltage level 4V). The sample used have been cut from Si- epilayer covered Si (100) wafers to suppress the nucleation of etch-pits. They were cleaved by flash heating up to 1200°C.

Au was evaporated from a tungsten filament and the evaporation rate was carefully calibrated by using a quartz balance which could replace the sample. The substrate temperature was controlled within $\pm 1^\circ$ by a Pt PtRh thermocouple which could be pressed against the back side of the sample and removed during the sample cleaning cycles. For the ex-situ TEM studies a technique was developed to obtain micro cleavages permitting the direct observation of the as-prepared interface by TEM [25].

3. Results and discussion

3.1. Effect of annealing

We have gradually recovered a sample initially recovered by a rather thick layer of gold ($\theta = 180$ ML) at room temperature. In the case of temperatures lower than 300°C, the atoms of Si diffuse quickly towards the surface. This feature is translated from AES by an increase of the intensity corresponding to the doublet structure of the Si LVV at 92 eV (Fig 1) and a drop of the Au intensity. Above 300°C, a reappearance of the Auger transition (LVV) without the double structure of the Si at 92 eV occurs while the OVV Au peak at 69 eV continues to decrease mainly due to the formation of clusters of the gold film.

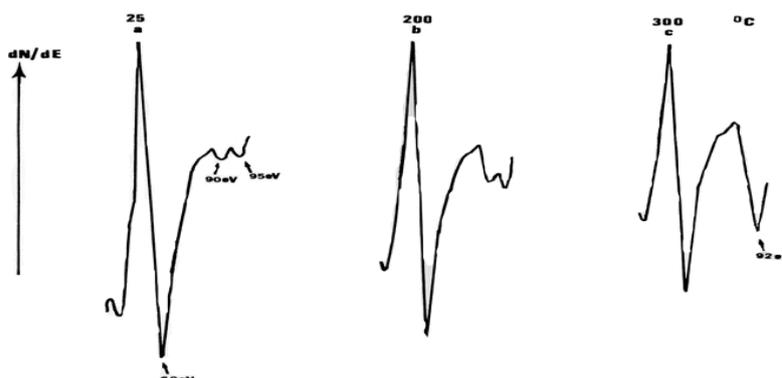


Figure 1: Deposit at different temperatures: evolution of the low energy Auger spectra versus the coverage.

3.2. Growth at high temperature

In the following, Au has been deposited on the clean 2×1 Si structure at various temperatures. Then, the different pictures of Fig. 2 have been realized after decreasing up to the room temperature. In Table 1, the main observations are summarized.

3.3. Effect of temperature

The deposit of Au atoms of about 26 monolayers obtained at $T_s = 550^\circ\text{C}$ has been observed ex-situ directly in the transmission mode by means the electron microscope. Fig 3 reveals the formation of 3D islands at high temperature but without any apparent crystallographic face.



Figure 2: Views of the surstructures as observed in LEED (for a voltage of 50 V)
 a- 2x1: clean Si(100) at room temperature; b- 4x2 : $\theta = 0.6$ ML, $T = 440$ °C ;c- 5x1 : $\theta = 0.3$ ML, $T = 730$ °C

Table 1: Different structures as function of temperature and for various monolayers

Θ (ML) T (°C)	0.5	1	1.5	2
440	2x1		4x2	4x2 + islands
550	2x1	4x2	5x1	5x1 + islands
730	2x1	5x1	5x1 + islands	

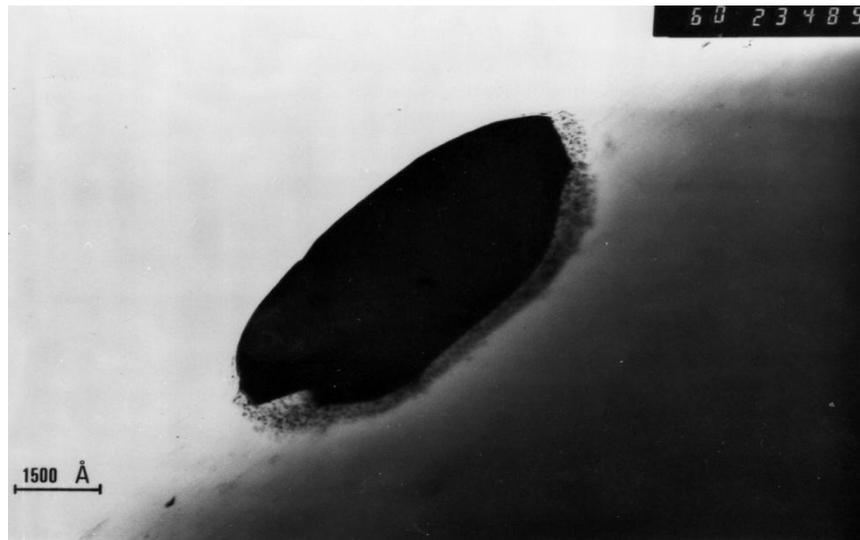


Figure 3: Au deposit at high temperature $T_s=550$ °C and $\Theta = 26$ ML.
 TEM view of micro cleavages (3D island).

3.3.1 Variation of the Auger signal

Condensation of Au on Si(100) has been realized within a range of temperature varying from $200^\circ\text{C} \leq T_s \leq 800^\circ\text{C}$. According to the results reported in Fig.4, two behaviors appear to be relevant in the variation of the Auger signal with respect to the temperature of the deposit.

- $200^\circ\text{C} \leq T_s \leq 700^\circ\text{C}$

In this domain, the curves of the Auger signal at different temperatures are similar: one can observe a linear decreasing of the Si signal with two regimes exhibiting a slight variation of the slope at $\theta = 1$ ML and then a drastic discontinuity at a critical value of θ above which the Auger signal becomes constant Fig 4b. The critical value of θ changes slowly with temperature: from $\theta = 1.6$ ML in the range $200^\circ\text{C} \leq T_s \leq 400^\circ\text{C}$ up to $\theta = 1.8$ ML at $T_s = 700^\circ\text{C}$.

The corresponding Au signal shows a linear increasing up to a threshold value θ similar to that of the value of the Si signal reaching also a plateau Fig 4a.

- $700^{\circ}\text{C} \leq T_s \leq 800^{\circ}\text{C}$

One observes an increase Fig4a (decrease) Fig4b in two linear parts of the Auger signal of Au (Si) with the presence of two discontinuities. The first one occurs at $\theta \approx 1$ ML. The second one depends on the temperature: it varies from $\theta \approx 1.8$ ML at $T_s = 700^{\circ}\text{C}$ up to $\theta \approx 2.2$ ML at $T_s = 800^{\circ}\text{C}$.

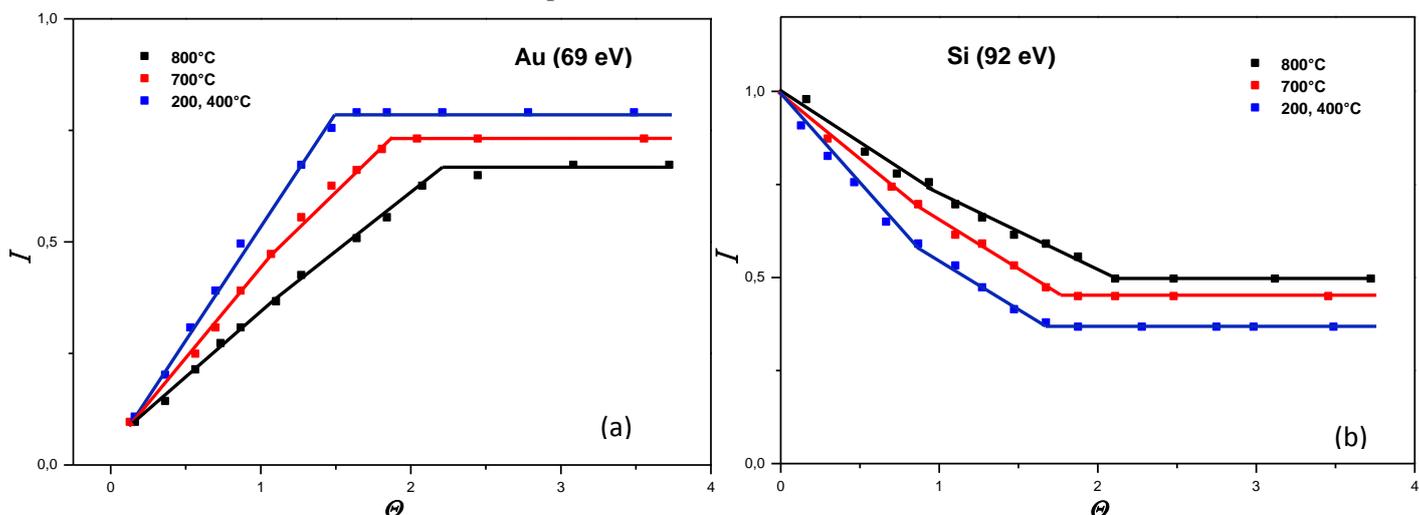


Figure 4: Variation of the peak-to-peak Auger amplitudes normalized to 1 as function of coverage and for various temperature of condensation: a) For Au ($\theta = 100$ ML) deposited at room temperature; b) For clean Si.

Above this discontinuity, the Auger signal reaches a plateau. This feature indicates the appearance of three tridimensional crystallites (Fig. 5).

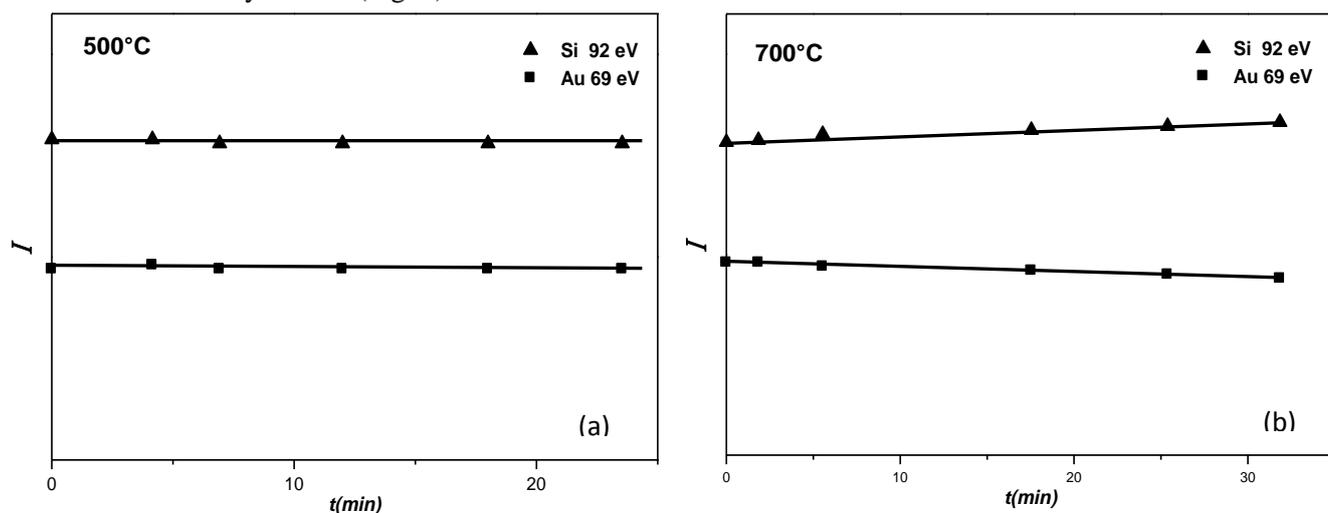


Figure 5: Evolution of the peak-to-peak Auger amplitudes versus time (deposit 1,5 monolayer at 200°C) a) At $T_s = 500^{\circ}\text{C}$; b) At $T_s = 700^{\circ}\text{C}$.

In order to determine the physical factor at the origin of the dependence on temperature of the variation of the second discontinuity, (i.e) the saturation of the bidimensional phase towards stronger coverage, we have investigated the evolution of the Auger peaks of Au and Si as a function of time at different temperature. Fig 5a shows clearly that for $T_s = 550^{\circ}\text{C}$ no variations of the Auger peaks are noticed.

However at $T_s = 700^{\circ}\text{C}$, a decrease (increase) of the Au (Si) peak Fig5b. Indeed $T_s = 700^{\circ}\text{C}$ is far from the desorption and these variations mean a penetration of the gold into the substrate.

3.3.2 Desorption isotherm

For a proper understanding of the significant role of the temperature, 3 monolayers have been deposited at $T_s = 200^{\circ}\text{C}$. Then, a quick increase of the temperature of the substrate is realized up to a constant value ($T_s = 900^{\circ}\text{C}$). The evolution of the Auger peaks of Si and Au as a function of desorption time is plotted in Fig. 6. During 9min the two amplitudes of the peaks of the substrate and the deposit remain constant (this corresponds to a desorption of the 3D crystallites) then a linear increase (decrease) of Si (Au) occurs.

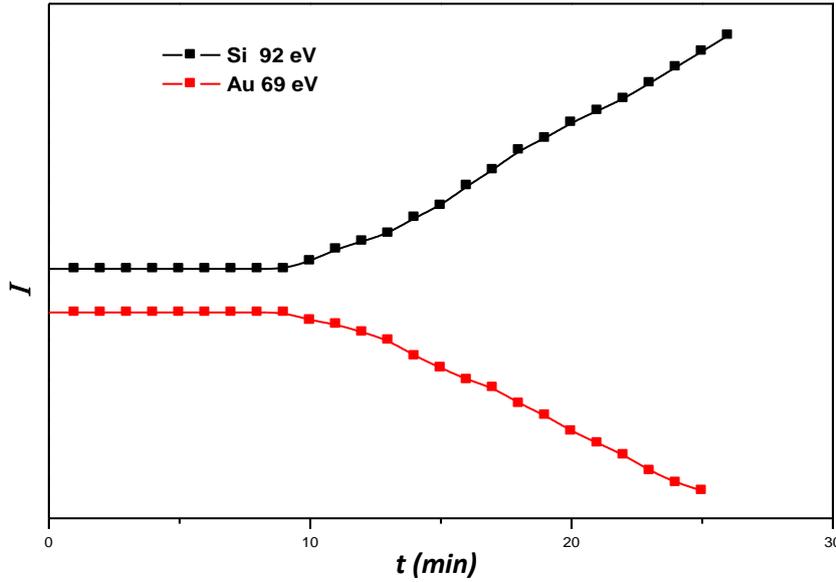


Figure 6: Variation of the peak-to-peak Auger amplitudes of Au and Si during the desorption. ($\theta = 3$ ML at $T_s = 900$ °C)

4. Interpretation

The general character of the curves $I = f(\theta)$ indicates that at high temperature $T_s \geq 200^\circ\text{C}$, the epitaxie of Au on Si is growing according to the Stranski-Krastanov mode as shown in Fig.4 where gold crystallites growth on a 2D monolayers. The curves $\theta(t)|T=C$ exhibit linear parts corresponding to a kinetic of desorption close to zero; each part being correlated to a well defined picture of surstructure in LEED The different kinetic steps show that each picture corresponds to a well defined 2D phase.

This finding may be transposed to our desorption isotherm realized at $T_s \approx 900^\circ\text{C}$. Then after a complete evaporation of the 3D Au islands (the signal being constant), the desorption of the unique adsorbed 2D phase (with 5×1 structure) according to a process close to zero (linear decrease (increase) of Au (Si)). The duration of the plateau of the isotherm $t_f = 9\text{min}$ allows us to determine the sublimation of the energy of the Au crystallites by means the formula:

$$\theta_i - \theta_0 = t_f B \exp\left(-\frac{A}{RT}\right) \quad (1)$$

for the 3D phase as used by Le Lay et al. [26] for the desorption of zero order of 3D crystallites (similarly to the Au/Si(111) interface).

In the present experiment, θ_i is taken to be equal to 3 which corresponds to the quantity of deposited Au at 200°C . θ_0 denoting the coverage rate of the adsorbed 2D phase is equal to 1.6 (the 2D phase saturates at 1.6 for $T_s = 400^\circ\text{C}$). $t_f = 9\text{min}$ describes the time of the desorption of the crystallites and B is the frequency of the desorption taken to be equal to the Debye frequency of Au: $B = 3,6 \cdot 10^{12} \text{ s}^{-1}$ [27].

With these physical values, one can deduce the sublimation of the energy $A = 82 \text{ Kcal mol}^{-1}$. This finding is in quite agreement with the value of the bulk of Au, namely: $\Delta H_{0^\circ\text{K}} \approx 88 \pm \text{Kcal mol}^{-1}$ [28].

Moreover the cohesion energy for the 2D phase may be also obtained from the model of Kern and al.[29].

The process of the desorption is formulated as follows:

$$-\dot{\theta} = a_0^{-2} n_s^{-1} \frac{kT}{h} \frac{f^*}{f_2} \exp\left(-\frac{E_2}{RT}\right) \quad (2)$$

where a_0 is the inter-atomic distance in the 2D phase, n_s the number of adsorbed sites of the substrate, f^* the partition function of the activated complex in the gaseous phase, f_2 the partition function corresponding to an atom in the 2D island and E_2 the energy of a semicrystal in the 2D phase.

The last expression may be rewritten as:

$$-\dot{\theta} = D \exp\left(-\frac{C}{RT}\right) \quad (3)$$

here C is the cohesive energy of the 2D phase, D the desorption frequency of atoms in the 2D phase which is taken as $D=B=3.6 \times 10^{12} \text{s}^{-1}$ according to reference [30] determined from the analyze of the spots (01), (04/5) and (4/5 0). Under these circumstances, it is found $C=83 \text{ Kcal mol}^{-1}$. This value is the cohesive energy of the phase 5x1 of the system Au/Si(100) and appears very close to the system Au/Si(111); i.e. ($C=85 \text{ Kcal mol}^{-1}$).

Conclusions

In summary, the description of the first stages of the growth of Au on Si(100) is as follows:

At room temperature, according to Hanbucken and al [31], Y.Haruyama and al [32] the very first golden layer form an amorphous alloy with the atoms of surface.

At high temperature, the epitaxie of Au on Si is growing according to the Stranski-Krastanov mode. In particular 2D ordered phases appear on which gold crystallites growth. The 5x1 is the intermediate layer at high temperature which desorbs according to a zero order process.

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