ELSEVIER

Growth and dissolution kinetics of Au/Pb(1 1 1): an AES-LEED study

H. Oughaddou[a], C. Léandri[a], B. Aufray[a,*], C. Girardeaux[b],
J. Bernardini[b], G. Le Lay[a], J.P. Bibérian[a], N. Barrett[c]

[a]CRMC2-CNRS, Campus de Luminy, 13288 Marseille Cedex 9, France
[b]L2MP, Campus de Saint Jérôme, 13397 Marseille Cedex 20, France
[c]LURE, Centre Universitaire Paris-Sud, Bât. 209D, 91898 Orsay Cedex, France

Abstract

The growth of Au on a Pb(1 1 1) surface is studied by AES-LEED at room temperature (RT). After deposition of 1/3 Au monolayer (ML), LEED observations reveal a $p(\sqrt{3} \times \sqrt{3})R30°$ superstructure. Beyond this coverage, no superstructure is observed. From Au and Pb Auger peak intensities, we deduce that the growth corresponds to the formation of an inter-metallic compound Au_xPb_y continuously growing under a floating Pb ML. The dissolution kinetics of one Au ML recorded at various temperatures systematically show a plateau (a slowing down) at a surface concentration corresponding to 1/3 ML. From a quantitative evaluation of the AES data we propose that the $p(\sqrt{3} \times \sqrt{3})R30°$ superstructure corresponds to a surface alloy with composition $AuPb_2$ buried under 1 Pb ML. Such a surface alloy has been previously measured after annealing of a Au(Pb) 0.45 at.% solid solution [Surf. Rev. Lett. 4 (1997) 1139], we propose that the slowing down observed during the dissolution kinetics is also the signature of this unexpected segregation behaviour of Au. It could be related to the fact that the surface energy of this inter-metallic compound ($AuPb_2$) is lower than the surface energy of both constitutive elements (Au and Pb).
© 2003 Elsevier Science B.V. All rights reserved.

PACS: 68.47.De; 68.08.De; 68.55.-a

Keywords: Metal adsorption; Surface segregation; Gold; Lead

1. Introduction

Generally, the prediction of thermal behaviour of thin films deposited on metallic substrates is a very important aspect for many technological applications. For very thin films (few monolayers), it has been shown recently that the kinetics behaviour i.e. the formation of a surface alloy followed by the dissolution process in the bulk, are strongly dependent on both surface segregation phenomena and chemical interactions. On one hand, when the deposited element presents the lowest surface energy, the dissolution kinetics in the bulk is always slower than the dissolution kinetics expected from the standard bulk diffusion parameters. This has been clearly observed for systems that present a chemical tendency to phase separation (e.g. Ag/Cu(1 1 1) [2]) as well as those which present an ordering tendency (e.g. Sb/Cu(1 1 1)) [3]. On the other hand, when the substrate presents the lower surface energy, the dissolution is then rapid for

* Corresponding author. Tel.: +33-491829204;
fax: +33-491829305.
E-mail address: aufray@crmc2.univ-mrs.fr (B. Aufray).

the same above reasons. This also has been theoretically predicted for systems which present a phase separation tendency as well as ordering tendency. In the first case, phase separation tendency, the deposit is quickly buried in the surface selvedge forming a distribution of small clusters buried under few monolayers of pure substrate, and then dissolved in the bulk (Ni/Ag(1 1 1) [4], Fe/Cu(1 1 1) [5], and Co/Cu(1 1 1) [6]). For ordered systems, the second case, one can expect a similar behaviour i.e. before the bulk diffusion, the formation of an (or more) inter-metallic alloys buried under one or two ML of pure substrate. In a surprising way there are very few experimental studies of this last case. Many have been performed for system for which the surface segregation driving forces as well as chemical effect are not very strong (e.g. Pt/Cu [7]). In this paper, we present a study of Au/Pb(1 1 1) system. Indeed lead presents a lower surface energy than the Au one and the bulk phase diagram is a prototype of a strong ordering tendency. We present an AES-LEED investigation of the Au growth on Pb(1 1 1) at room temperature (RT) and of the dissolution of a very thin film of Au at different temperatures. We show that the deposition of Au at RT induces the growth of an inter-metallic compound $AuPb_2$ under one pure Pb ML. The dissolution of this inter-metallic compound shows an unexpected slowing down which has been interpreted in terms of a surface segregation effect of the $AuPb_2$ compound.

2. Experimental

All the experiments have been performed in a UHV (ultra high vacuum) chamber equipped with a standard Auger spectrometer (CMA: cylindrical mirror analyser) and a classic four grid optics for LEED observations (low energy electron diffraction). The Auger intensities of the different elements on surface are acquired in a derivative mode and the data computerized. This way we easily record the surface concentrations variations as a function of the deposit/annealing time. The sample is heated with a standard heating sample holder. Temperature is measured via a thermocouple mechanically hold close to the surface of the sample. Au is deposited in situ by Joule heating of a crucible. The surface preparation consists of a standard cycle of argon

ions bombardment (800 eV) followed by heating the sample at 280 °C in order to get a clean surface (checked by AES) and a sharp (1 × 1) LEED pattern. The deposition kinetics consist in exposing the sample surface in front of the Au crucible for 3 min then to the Auger spectrometer to get the surface concentrations and then to the LEED optics in order to follow the surface structure evolution. The deposition rate was about 0.03 ML per minute. The dissolution kinetics consists in following at a constant temperature the time evolution of both Au and Pb Auger intensity signals.

## 3. Growth kinetics of Au on Pb(1 1 1)

3.1. Results

We present here the AES study at room temperature of the first steps (up to about 1.5 ML) of the Au growth on Pb(1 1 1) surface. The Fig. 1a gives the evolution of the peak-to-peak Auger intensities of both substrate (Pb, 94 eV) and adsorbate (Au, 69 eV) versus deposition time. The Au signal, presents a first linear part up to a maximum which is reached after about 20 min of deposition. The Pb signal is continuously decreasing up to a constant value. We have noted that the Pb and Au signals stayed constant even after a long time of exposition to the Au vapour. The Fig. 1b shows the intensity ratio (I_{Au}/I_{Pb}) variations versus Au deposition time. This representation, which is very convenient for comparison with different experiments, shows more clearly the constant value of the surface composition reached after about 20 min of Au deposition. The LEED observations performed during the growth reveals the formation of a p($\sqrt{3} \times \sqrt{3}$)R30° superstructure which appears slowly with the Au deposition, but is still observed after 35 min of Au deposition.

3.2. Discussion

It is generally difficult to propose a precise growth mode using only the Auger intensities variations of both substrate and adsorbate versus deposition time. Nevertheless the growth of Pb on Au(1 1 1) (the reverse system) has been studied in details elsewhere [8,9]. The main results of this study can be summarised as given
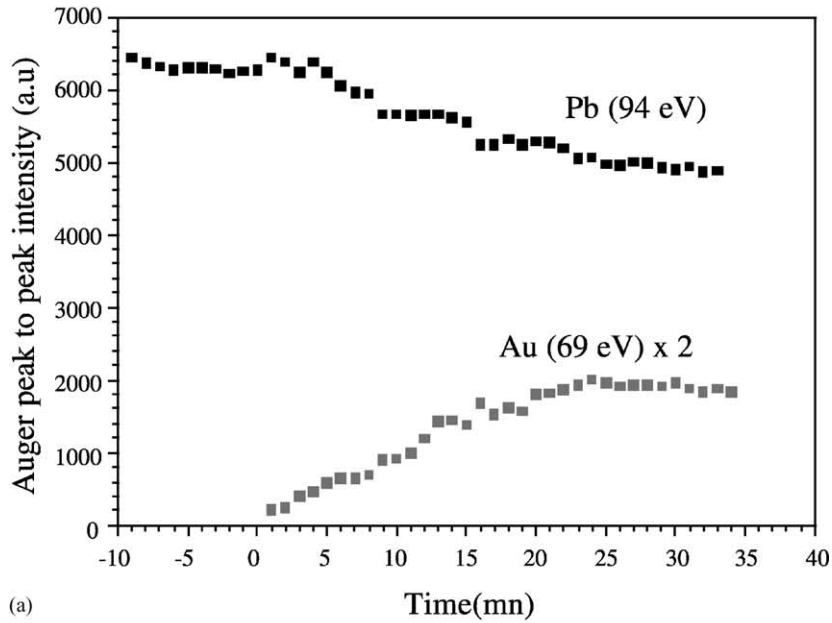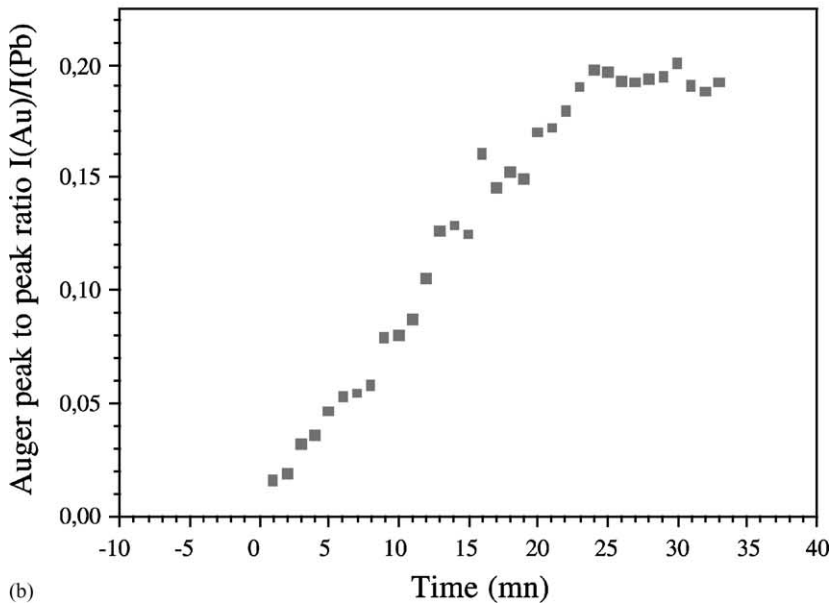
Fig. 1. (a) Auger peak-to-peak intensity signal of Au (I_{Au}) and Pb (I_{pb}) as a function of time during the deposition of Au on Pb(1 1 1); (b) Time evolution of the Auger peak-to-peak intensity ratio (I_{Au}/I_{pb}).

further. During the Pb deposition on Au(1 1 1) face there is a first formation of a pure Pb ML, followed by the formation of an inter-metallic compound. It has been shown that the structure of this inter-metallic compound is formed by alternate layers L1 and L2 corresponding respectively to a pure ML of Pb (L1) and a mixed layer Au_2Pb (L2) as follows: L1/L2/L1/L2/Au/Au/. . . . Using the attenuation coefficients of

Table 1
I_{Au}/I_{Pb} ratios corresponding to different models of inter-metallic compounds and compared with the experimental value measured at the end of the growth ($I_{Au}/I_{Pb} = 0.2$)

Model	Pb/L2/Pb/Pb	Pb/L2/Pb/L2/Pb/Pb
I_{Au}/I_{Pb}(L2 = Au$_2$Pb)	0.37	0.43
I_{Au}/I_{Pb}(L2 = AuPb)	0.27	0.30
I_{Au}/I_{Pb}(L2 = AuPb$_2$)	0.17	0.19
I_{Au}/I_{Pb} (experimental)	0.2	

Au Auger peak (69 eV) and Pb Auger peak (94 eV) through one ML of Pb (or Au) determined accurately elsewhere ($\alpha_{Au} = 0.3$ and $\alpha_{Pb} = 0.47$) [8], we evaluated the I_{Au}/I_{Pb} ratios corresponding to different models of inter-metallic compounds (see Table 1). Compared to the ratio I_{Au}/I_{Pb} experimentally measured at the end of the growth (i.e. on the plateau), the best fit is obtained for a composition profile L1/L2/L1/L2/Pb/Pb/... where L1 is still a pure Pb layer but L2 is, in this case, a mixed AuPb$_2$ layer. Let us note that this model is also in good agreement with the p($\sqrt{3} \times \sqrt{3}$)R30° superstructure which is observed in both cases Au/Pb(1 1 1) and Pb/Au(1 1 1) and coming from the second layer (L2) AuPb$_2$ and Au$_2$Pb, respectively.

4. Dissolution kinetics of Au on Pb(1 1 1)

4.1. Results and discussions

After a deposition of Au on Pb(1 1 1) up to the plateau observed on the growth kinetics (Fig. 1b), Au dissolution kinetics are recorded in a temperature range 75–120 °C. Fig. 2 shows the variations of the Auger intensities ratio (I_{Au}/I_{Pb}) versus annealing time at three different temperatures. The three dissolution kinetics present a characteristic shape which can be described as follows: at the beginning of the annealing, for about 2 min (which include the temperature rise), there is a rapid dissolution. For $I_{Au}/I_{Pb} = 0.17$, one can observe a slowing down of the dissolution followed by a continuous dissolution of Au. This slowing down varies with temperature: i.e. it is more and more important at lower temperatures.

It is well known that dissolution kinetics of thin films are driven by the surface segregation phenomena via a local equilibrium between the surface layers. In other words, the dissolution kinetics shapes are a signature of the surface segregation phenomena and of the reorganisations of atoms during the decreasing
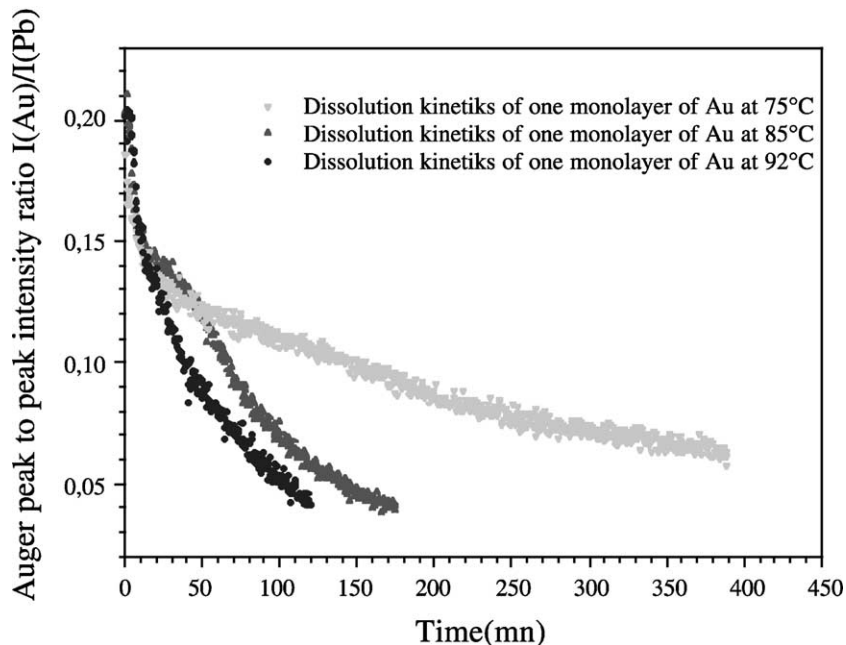

Fig. 2. Evolution of the Auger peak-to-peak intensity ratio I_{Au}/I_{pb} as function of the annealing time at different temperatures.

of surface concentrations. So the first part of dissolution kinetics corresponds probably to the dissolution of the deeper L2 layer. Indeed the flux of Au in the substrate which can be derived from the slopes of the first part of the kinetics are in good agreement with a Au dissolution derived from bulk diffusion coefficients and solubility limits of Au in Pb. The second part i.e. the slowing down, can be attributed to the dissolution of the L2 layer which forms the $p(\sqrt{3} \times \sqrt{3})R30°$ superstructure. This slowing down observed in the second part can be only explained by a segregation effect of Au close to the surface.

This Au segregation is unexpected since the main driving forces for segregation are all unfavorable for Au: surface energy of Au higher than the Pb one, Au atom size smaller than the Pb one and the tendency to the ordering which always favors the segregation of the main element (Pb in this case). Nevertheless, as remind in the introduction of this paper, this surprising segregation was first reported after annealing at 260 °C of a Pb(Au) (1 1 1) (0.45 at.%) solid solution [1]. Unfortunately, the Au segregation kinetics has not been recorded in this study. Only Auger spectra before and after annealing have been reported which limits the quantitative comparisons since, due to the rapid diffusion of Au, it is always very difficult to avoid surface precipitation during cooling of the sample down to room temperature. In any cases our dissolution experiments clearly confirm this surprising tendency of the Au segregation in $AuPb_2$ form. As in the previous paper, one can explain this result at the light of the bulk phase diagram Au–Pb. Indeed this phase diagram shows two inter-metallic compounds ($AuPb_2$ and $AuPb_3$) which both present a melting temperature lower than the Pb one. If one assume a direct correlation between surface energy of a compound and its melting temperature (which is generally accepted), the surface energy of both inter-metallic compounds $AuPb_2$ and $AuPb_3$ should be lower than the surface energy of pure Pb. We propose, that Au situated in the second layer, forms, on few surface layers, an inter-metallic compound close to $AuPb_2$ and then presents a tendency to segregate in order to minimise the total surface energy of Pb.

5. Conclusion

In summary, we have studied the growth of Au on Pb(1 1 1) at room temperature. We find that the fast diffusion of Au in Pb allows the formation of an inter-metallic compound on the surface formed by alternate layers L1 and L2 corresponding respectively to a pure monolayer of lead (L1) and a mixed $AuPb_2$ (L2) as follow: L1/L2/L1/L2/Pb/Pb/.... The dissolution kinetics of this compound confirms the tendency to segregate of an inter-metallic compound close to $AuPb_2$.

References

[1] H. Oughaddou, B. Aufray, J. Bernardini, J.P. Bibérian, Surf. Rev. Lett. 4 (1997) 1139.
[2] J. Eugène, B. Aufray, F. Cabané, Surf. Sci. 241 (1991) 1.
[3] H. Giordano, O. Alem, B. Aufray, Scr. Metall. 28 (1993) 257.
[4] B. Aufray, H. Giordano, B. Legrand, B. Tréglia, Surf. Sci. 307/309 (1993) 531;
   J.M. Roussel, A. Saul, G. Tréglia, Phys. Rev. B 55 (1997) 10931.
[5] K.E. Johnson, D.D. Chambliss, R.J. Wilson, S. Chiang, Surf. Sci. 313 (1994) L811.
[6] F. Nouvertné, U. May, M. Bamming, A. Rampe, U. Korte, G. Güntherodt, Phys. Rev. B 60 (1999) 14382.
[7] N.T. Barret, A. Senhaji, R. Belkhou, C. Guillot, B. Legrand, G. Tréglia, J. Elect. Spectrosc. Rel. Phenomena 68 (1994) 357.
[8] J.P. Bibérian, G.E. Rhead, J. Phys. F 3 (1973) 675.
[9] J.P. Bibérian, Surf. Sci. 74 (1978) 437.