

Initial Growth and Surface Alloy Formation of Ag on Pt(111)

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(Received November 20, 1995)

Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and ultraviolet photoelectron spectroscopy (UPS) were used to study the growth mode and the surface structure of a silver ultra-thin film deposited on a Pt(111) surface at 360 K. The AES and LEED results show that the growth of Ag/Pt(111) belongs to the Stranski-Krastanov mode. The growth mechanism is discussed. The electron density of states in the growth process was investigated by UPS. A splitting of Ag $4d_{5/2}$ and Ag $4d_{3/2}$ was observed as the absorbed Ag atoms changed from an atomic state to a solid state. In the LEED study, the intensity of the specular beam versus the surface temperature has an abnormal change and is irreversible between 550 K and 650 K, as the coverage is in the submonolayer range. These phenomena, and the Auger-intensity ratio of Ag and Pt varying with the temperature, show that a two-dimensional surface alloy develops at a temperature above 550 K, as the coverage is within one monolayer.

PACS. 61.14.Hg – Low-energy electron diffraction.

PACS. 61.66.Dk – Alloys.

PACS. 71.20.-b – Electron density of states.

I. Introduction

The growth of an ultra-thin film of metal overlayers on a solid surface is one of the central subjects of surface science. It offers an opportunity to explore the physics of a system with reduced dimensions. Simultaneously, it is of great technological interest, because of its relevance for electronic devices [1] and optoelectronic devices [2]. Usually the thin-film growth can be classified into one of three main distinct growth modes [3,4]: (a) the Franck and van der Merwe (FM) mode-monolayer-by-monolayer growth, (b) the Volmer and Weber (VW) mode-3D island growth, and (c) the Stranski and Krastanov (SK) mode-layer growth up to one or several monolayers followed by 3D island growth.

Recently, a number of experimental investigations discussed the surface structure of Ag ultra-thin films grown on a Pt(111) surface [5-9]. Most of them were observed by STM and He scattering at low temperatures. In this report, we used AES, LEED and UPS to study the initial growth and the formation of a surface alloy of Ag on the Pt(111) surface above room temperature.

II. Experiment

Experiments were conducted in a stainless steel ultra-high vacuum (UHV) chamber. The working background pressure was better than 3×10^{-10} Torr. The UHV chamber was equipped with a four-grid video-LEED, AES and UPS. The pressure within the UHV chamber was measured by an ion gauge and checked by a quadrupole mass spectrometer.

The electron energy analyzer for AES was a VG MICROTECH CLAM-2 hemispherical analyzer. In the AES experiments, a primary electron energy of 3 keV was used. The spectra were recorded in the derivative mode. The Ag growth process was monitored by the relative evolutions of the Ag 351 eV and Pt 64 eV Auger signals. The SYCON quartz balance thickness monitor was also used to double check the coverages of the Ag adsorbate.

The intensities of diffracted LEED spots were analyzed by a computer-controlled image processor. All LEED experiments discussed here were performed with a 66.2 eV electron beam. For this energy, LEED is very surface sensitive. The phase in our experimental conditions is $\Phi(0,0) = \Delta k_{\perp} h = 3\pi$ for 66.2 eV electron energy, where Δk_{\perp} is the momentum transferred perpendicular to the surface and $h = 2.26 \text{ \AA}$ is the step height of the adsorbed Ag adatoms. It is an out-of-phase diffraction condition which is suitable for studying the surface structure on a surface [10,11]

The photoelectron spectroscopy of the valence band region was performed by the use of an He I resonance line ($h\nu = 21.2 \text{ eV}$). The ultraviolet light has a spot size of about 1 mm in diameter. An electron emission angle near the normal direction was chosen. The electron energy analyzer for UPS, the same as in the Auger spectra measurement, is a CLAM-2 hemispherical analyzer MICROTECH VG but it was run in a different analyzing mode.

The Pt crystal was oriented within 0.5 degree of the [111] direction, checked by X-ray diffraction. The surface of the sample was cleaned by standard Ar ion bombardment and annealing cycles in the UHV chamber. To remove the residual carbon, the sample was heated to 850 K in an oxygen environment at a pressure of 5×10^{-7} Torr for about 3 minutes before sputtering. The annealing temperature reached 1100 K. The sputtering-annealing cycles were continued until a well-ordered (1×1) LEED pattern with bright, sharp spots and a low background were observed. The chemical impurity on the surface was checked by AES. The temperature of the crystal was measured by a k-type thermocouple.

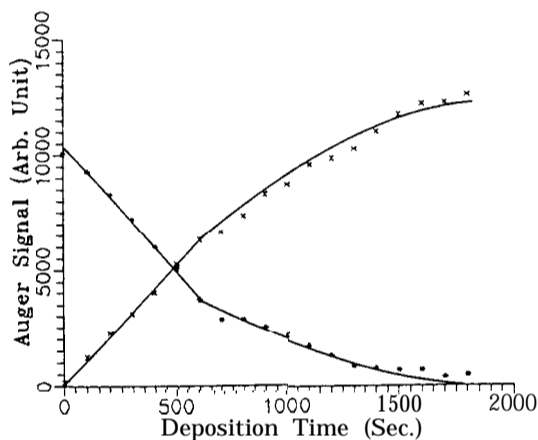
A ceramic crucible, resistively heated by a Ta wire, was used to evaporate the silver. The purity of the silver wire was 99.999%. During Ag dosing, the background pressure was about 1×10^{-9} Torr. With this evaporation source, Ag was evaporated from a distance of 30 mm at a rate of 1 monolayer (ML) per 600 seconds, by passing an electric current of 20 Amperes through it. One ML of deposited atoms is defined by the number of atoms in a bulk Pt(111) layer, i.e. 1.51×10^{15} atoms/cm².

III. Results and discussion

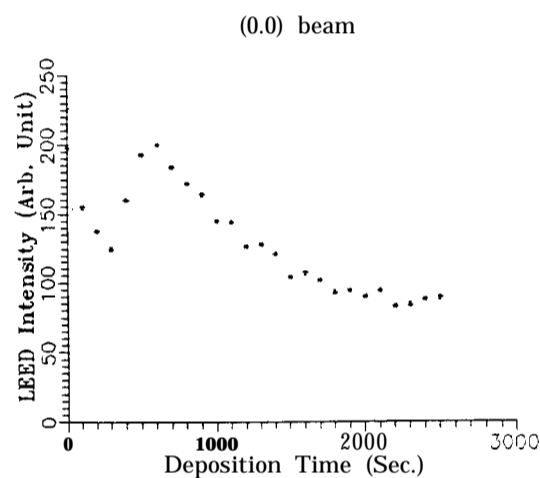
The plot of the Auger signal versus deposition time is usually used to distinguish growth modes [12,13]. The Ag overlayer growth was monitored by the evolution of the Ag 351 eV and Pt 64 eV AES signals at a substrate temperature of 360 K. The Auger peak-to-peak heights versus deposition times are shown in Fig. 1. Ag and Pt Auger intensities varied

with the deposition time linearly up to 600 s from the beginning. Then both curves followed an exponential form. The change in the slope on the Auger uptake curve is interpreted as a complete growth of each layer on a flat surface [13]. Fig. 1 shows that Ag atoms grow one complete monolayer then turn to 3D island growth. A coverage of 1 ML is located at 600 s. This result shows that the growth of Ag deposited on the Pt(111) surface at 360 K is the SK mode.

The oscillation of the LEED intensity has been used to measure the number of layers of material deposited during the molecular beam epitaxy of semiconductors and metal-on-metal growth [14]. The intensity of the LEED specular beam versus deposition time is shown in Fig. 2. The energy of normally incident electrons was 66.2 eV. The peak height intensity decreases before it reaches a maximum at $t = 600$ s. Since the specular beam is a direct measurement of the momentum change perpendicular to the surface, it is sensitive to the step formation. The maximum of the (0, 0) beam at $t = 600$ s indicates one complete monolayer of Ag. The peak height of this maximum is close to the original intensity of the substrate. It indicates that the first Ag layer is in an ordered state. The LEED pattern shows that the ordered state is the (1 x 1) structure. After this maximum, the intensity decreases monotonously to the background. This means that the growth turns to a disordered 3D island after an ordered state of 1 ML Ag is complete. These results are consistent with that in Fig. 1.



(Fig. 1)



(Fig. 2)

FIG. 1. The Auger uptake curves: * represents the Auger peak height of Ag 351 eV; x represents the Auger peak height of Pt 64 eV. The linear part is interpreted as a monolayer-by-monolayer growth. The break at $t = 600$ s corresponds to 1 ML of Ag. The growth changes to 3 D island mode after $t = 600$ s.

FIG. 2. The LEED intensity of the specular beam versus the deposition time. The LEED intensity decreases to a minimum, then resurges to a maximum at $t = 600$ s. After that its intensity decreases to a background value monotonously.

The growth mechanism of the Ag/Pt(111) can be considered from two different approaches. From the viewpoint of the surface free energy, $A\gamma = \gamma_{Ag} - \gamma_{Pt} + \gamma_{int}$, where γ is the surface free energy. γ_{int} , the interface energy, is small and usually neglected in the bimetal system. The three-dimensional island growth is favored as $A\gamma > 0$, while monolayer-by-monolayer growth is favored for $A\gamma \leq 0$. Since the difference of the surface free energy, $\gamma_{Ag(111)} - \gamma_{Pt(111)}$, is equal to -0.35 eV/atom [15,16], it favors the monolayer-by-monolayer growth. The other viewpoint is based on the lattice mismatch. The difference of the lattice constants is about 4% in this system. The non-uniform strain favors a 3D island growth. Considering these two factors together, monolayer-by-monolayer growth up to a coverage of 1 ML, followed by the three-dimensional island growth is reasonable in this system.

UPS is also very surface sensitive. The ultraviolet photoemission spectra corresponding to different coverages of Ag deposited on the Pt(111) surface at 360 K are shown in Fig. 3. The spectrum of the clean surface has a very sharp Fermi edge and there is one main peak located at 4.3 eV below the Fermi edge. A very broad peak around 8.0 eV below the Fermi edge can also be seen. The characteristic Pt(111) peaks agree with the report of A. Cassuto et al. [17]. After depositing Ag atoms, some interesting phenomena occur. At first the intensity at the Fermi edge lowers monotonously as the Ag coverage increases. The density of states at the Fermi edge of 1 ML Ag attenuates to 1/3 of its original value for the clean surface. This phenomenon is similar to that of the Ag/Pt(110) system [18]. Secondly, the 8.0 eV binding energy structure diminishes as the Ag coverage increases. Thirdly, the 4.3 eV peak gradually shifts to a higher binding energy and becomes steeper. This shift is up to 0.6 eV when the coverage of Ag is 1 ML, i. e. the binding energy becomes 4.9 eV. It is very interesting that the main peak of Ag located at 4.9 eV broadens and starts to split into two peaks due to the spin-orbital interaction when the coverage of Ag is larger than 1 ML. For example, in Fig. 3 (g) this peak splits into a 4.7 eV main peak and a 5.3 eV small peak when the Ag coverage is 3ML. The main peak, with a binding energy of 4.7 eV, is derived from Ag $4d_{5/2}$, while the small peak, with a binding energy of 5.3 eV, is derived from Ag $4d_{3/2}$. We believe that this is a sign of the change from an atomic state to a solid state of Ag.

The attenuation in intensity of a LEED specular beam as a function of temperature is usually used to investigate the atomic vibration of the surface layer. The surface Debye temperature and the root-mean-square displacement of the surface atom can be obtained. The logarithm of the LEED peak intensity ($\ln I$) of the (0, 0) beam versus the surface temperature (T) at different coverages (8) is shown in Fig. 4. The electron incident energy was 66.2 eV which is very surface sensitive. Each measurement was taken after thermal equilibrium was achieved. A very interesting phenomenon was observed in this study. From the $\ln I$ -T plot in Fig. 4 (a) at $\theta = 1/4$ ML, one can find that the specular beam $\ln I$ decreases linearly with T in experimental accuracy, when $T \leq 550$ K, but it has an abnormal drop between 550 K and 650 K. The linear part is just due to the Debye-Waller effect, $\ln I = \ln I_0 - \lambda T$, where λ is a constant relative to the surface Debye temperature. However, the dramatic decay between 550 K and 650 K indicates a major evolution of the film morphology. While slowly cooling this Ag ultra-thin film, the LEED intensity increases linearly, following a simple Debye-Waller behavior. Obviously, there is a thermal hysteresis in the $\ln I$ -T curve. This shows that the change of the surface morphology is irreversible

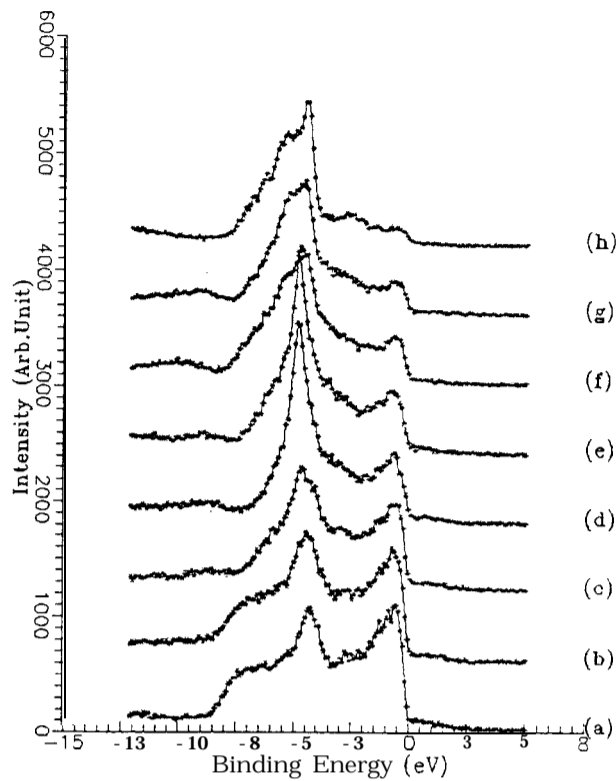


FIG. 3. UP spectra of Ag/Pt(111) corresponding to different Ag coverages: (a) Clean surface, (b) 1/4 ML, (c) 1/2 ML, (d) 3/4 ML, (e) 1 ML, (f) 7/4 ML, (g) 3 ML and (h) 5 ML.

during heating from 550 K to 650 K. Fig. 4(b) shows $\ln I$ versus T for the coverage of 3/4 ML. Comparing Fig. 4(a) and Fig. 4(b), we found that the area of the thermal hysteresis in Fig. 4(b) is smaller than that in Fig. 4(a). The phenomenon of the thermal hysteresis is not so significant as the coverage increases and will disappear after the coverage of Ag becomes larger than 1 ML. However, in the submonolayer range, all the of the logarithms of the LEED specular peak intensity versus the surface temperature have similar behavior. Each of them has a dramatic drop between 550 K and 650 K. These phenomena imply that some interesting structural change occurs on the Ag/Pt(111) surface. We believe that this first-order phase transition is due to the formation of a surface alloy. Roder et al. have reported a similar study of Ag on a Pt(111) surface by STM [5]. They have revealed that the growth at T above 600 K resulted in the formation of a 2D alloy that consists of Ag clusters dissolved in the Pt top layer or Pt clusters forming in the Ag matrix layer. Struber and Kuppers have also confirmed the formation of a surface alloy in this system using the XPS and TDS techniques [19]. So our results for LEED in Fig. 4 are also evidence of the formation of a surface alloy. The alloy develops at temperatures above 550 K.

Two-dimensional alloying at a free surface has an important implication for surface chemical processes such as heterogeneous catalysis. Recently the alloying of Au on Ni(110)

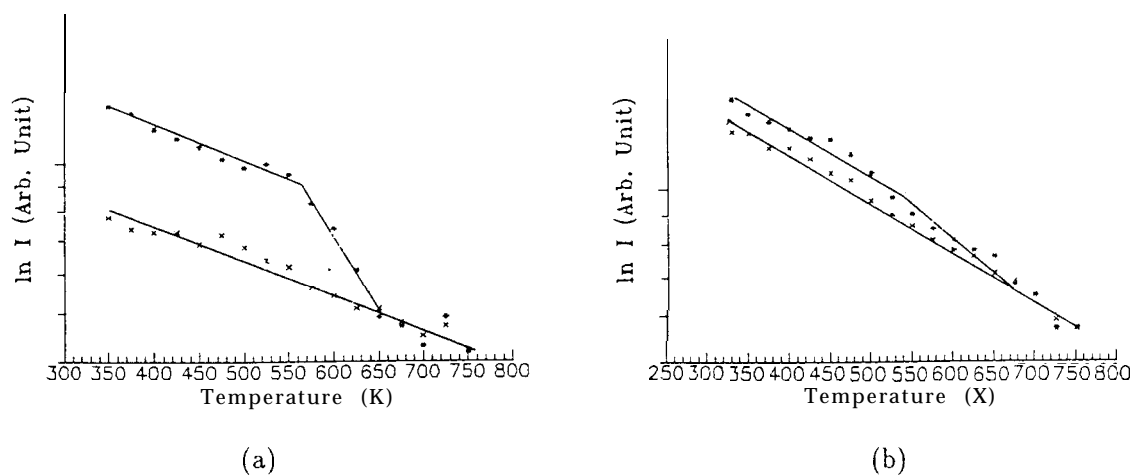


FIG. 4. The curve of $\ln I$ - T at different coverages: (a) $1/4$ ML and (b) $3/4$ ML. $\ln I$ decreases linearly but it has an abnormal drop between 550 K and 650 K during the heating up process, while it increases linearly in the cooling down process. A thermal hysteresis is observed, The area of thermal hysteresis of $3/4$ ML is smaller than that of $1/4$ ML.

and Sb on Ag(111) forming stable two-dimensional mixtures were also reported [20,21]. Theoretically, Tersoff [22] assumed that a pair-wise interaction between neighboring atoms showed that a surface-confined alloy is generally expected in systems dominated by lattice mismatch. To make sure the alloy is actually confined to the surface in this system, we monitored the Auger signals of Ag 351 eV and Pt 64 eV as a function of the temperature at $\theta=1/2$ ML. The intensity ratio versus T is shown in Fig. 5. The ratio is almost constant within $360 \leq T \leq 700$ K. Then the ratio drops dramatically and approaches zero at 1000 K. The constantancy of $R = I(\text{Ag})/I(\text{Pt})$ means that the Ag atoms always stay on the surface when the temperature is less than 700 K, but they start to desorb from the surface when the temperature is higher than 700 K. They are totally desorbed at a temperature of about 1000 K. This result shows that the Ag/Pt alloy is actually confined to the surface below 700 K.

IV. Conclusion

The Ag overlayer growth on the Pt(110) surface was monitored by the evolution of the AES signals and the intensity of the LEED specular beam at a substrate temperature of 360K. The results show that an ultra-thin Ag film grows one monolayer thick in an ordered state. After that it turns to three-dimension island growth. The growth mechanism was confirmed, by considering the surface free energies and lattice mismatch of the adsorbate and the substrate. The electron states in the growth process were studied using UPS. UP spectra of a clean surface and a coverage up to 5 ML of Ag on the Pt(111) surface show that the density of the states at the Fermi edge decreases and the d-band shifts toward a high binding energy as the Ag coverage increases.

In the $\ln I$ - T scan of the (0, 0) LEED beam in the submonolayer range, an abrupt

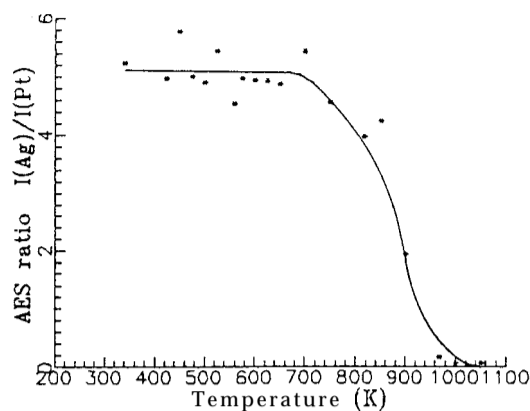


FIG. 5. The ratio of the Auger intensity $R = I(\text{Ag } 351)/I(\text{Pt } 64)$ as a function of annealing temperatures. A constant R indicates that Ag adatoms still stay on the surface before the temperature reaches 700 K. But Ag atoms start to desorb as the temperature goes higher than 700 K. No residual Ag atoms on the surface were observed after the annealing temperature reached 1000 K.

drop in the intensity occurs between 550 K and 650 K, but it follows the law of the simple Debye-Waller effect in the cooling process. It is obvious that an irreversible evolution in film morphology occurs at this temperature interval. These results in the LEED study indicate that an Ag-Pt surface alloy forms at temperatures above 550 K. Auger signals of Ag and Pt as a function of temperature also confirm this conclusion.

Acknowledgment

This work was supported by the National Science Council of the R.O.C. under grant number NSC 84-2112-M-003-007.

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