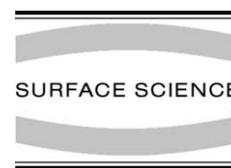




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Deposition of silver on the Pt(100)-hex surface: kinetic control of alloy formation and composition by surface reconstruction

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Abstract

Silver deposition on the Pt(100)-hex surface at 300 K leads to formation of a disordered Pt₂₀Ag₈₀ alloy in the first monolayer. This is due to lifting of the Pt(100)-hex-reconstruction which expels 20% of a monolayer of excess Pt atoms out of hex-reconstruction into the growing Ag film. Such mixing in the first monolayer may be expected generally for film growth on reconstructed surfaces at low temperatures. Our results are compared to a recently published article for Ag growth on Pt(110)-(2 × 1) surfaces [Surf. Sci. 478 (2001) L345]. For this system as well we suggest that a disordered monolayer-alloy forms with a Pt₅₀Ag₅₀ stoichiometry, instead of Ag growth proceeding by purely filling in the missing rows of the (2 × 1) reconstruction. © 2001 Published by Elsevier Science B.V.

Keywords: Auger electron spectroscopy; Scanning tunneling microscopy; Epitaxy; Surface structure, morphology, roughness, and topography; Platinum; Silver; Single crystal epitaxy

The growth of Ag on Pt(110)-(2 × 1) at room temperature was recently discussed by Huang et al. [1] They concluded that growth proceeds by filling in the missing rows of the (2 × 1)-reconstructed Pt(110) surface, thus resulting in alternating Ag and Pt rows at 0.5-ML Ag coverage. They proposed that further Ag deposition results in Ag growing on top of the Ag rows, resulting in Ag adrows at a total silver coverage of one monolayer. At 1.5 ML, the surface is covered with Ag. Thus, from this study, it would be tempting to propose

that missing-row reconstructions could be used as templates for forming nanopatterned surfaces with one dimensional, single-atom wide wires. An obvious alternative explanation for these results, which has not been discussed previously, is that the surface disorders and forms a random Ag₅₀Pt₅₀ surface alloy.

Herein we present results from scanning tunneling microscopy (STM) for Ag growth on Pt(100). These results suggest a more general phenomenon of monolayer confined alloying by epitaxial growth of heteroatoms on a reconstructed surface with altered atom densities compared to bulk terminated surfaces. Such a general description may also provide an explanation for the results by Huang et al. [1] for the Ag/Pt(110) system.

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Our experiments were performed in an UHV chamber equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES), rear-view low energy electron diffraction (LEED) optics, quadrupole mass spectrometer for residual gas analysis and temperature programmed desorption (TPD), homebuilt single-piezo-tube STM [2], an ion gun for sample cleaning, and precision leak valves for gas dosing. The sample was heated by electron bombardment from the backside of the Pt(1 0 0) single crystal. The sample temperature was measured by a chromel/alumel thermocouple that was spotwelded directly to the side of the crystal. The Pt crystal was cleaned by standard procedures of Ar^+ -ion sputtering at 500 eV, annealing to 1000 K in 5×10^{-7} -Torr O_2 and finally annealing to 1200 K in vacuum. Ag was evaporated from a resistively heated Ta boat. The evaporation rate was calibrated by AES measurements to obtain “uptake” plots on samples that were annealed to 800 K following Ag deposition. Under these conditions, Ag and Pt form a disordered nanophasic surface alloy confined to the topmost layer only. No Ag diffusion into the bulk occurs. With increasing silver content, Pt is replaced by Ag in the surface layer, until a complete pseudomorphic Ag layer forms [3]. There is a “break” in the AES uptake plot that occurs for this amount of silver and this is what we define as 1-ML Ag.

LEED observations showed that the spots from the hex-reconstruction decreased in intensity with increasing Ag deposition on Pt(1 0 0)-hex at 300 K and were only faintly visible at an Ag coverage of 0.7 ML. After Ag deposition at room temperature, and for samples that had been annealed to 800 K following this deposition, only sharp (1×1) spots were observed after the disappearance of the “hex” spots. This indicates that Ag grows pseudomorphically on the Pt(1 0 0) surface with no additional, long-range, ordered structure.

Two kinds of Ag deposition and growth experiments were performed and Ag-uptake plots were obtained by using AES. One was collected for Ag grown at 300 K, and another one collected after annealing the sample to 800 K following each Ag deposition. These two Ag-uptake plots are shown in Fig. 1. The break in the 300-K uptake plot occurs at 80% of the deposition time as that

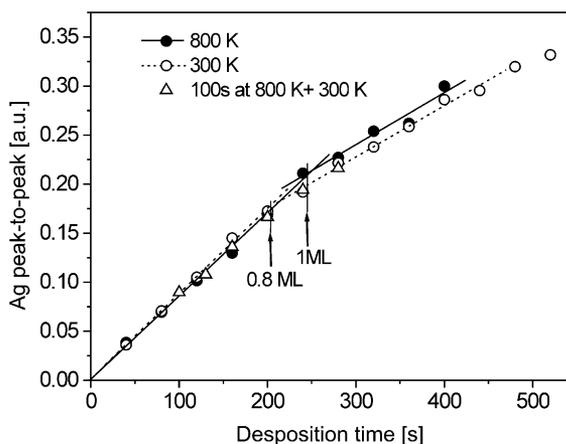


Fig. 1. Uptake plots obtained by using the Ag(351–356)-peak-to-peak intensity in AES. Three sets of data obtained for different sample preparations are shown: (i) Ag films grown at 300 K (open circles, dashed line); (ii) samples annealed to 800 K (full circles, solid line); and (iii) sample annealed to 800 K after 100-s Ag deposition followed by further Ag deposition at 300 K (open triangles). The lines drawn are linear fits for the appropriate data points. For the Ag-film deposited at 300 K, a change in slope or break occurs at 80% of the time for that observed when samples were annealed to 800 K.

for the Ag film which had been annealed to 800 K. This can be explained by Ag removing or “lifting” the Pt(1 0 0)-hex reconstruction. The hex-reconstructed surface contains about 20% more Pt atoms than the Pt(1 0 0)- (1×1) surface. Thus, lifting the reconstruction expels Pt atoms from the surface layer, which can then mix with the growing Ag film in the adlayer. The alloy that is formed can be observed by STM, as shown in Fig. 2. Consequently, the adlayer is completed after an Ag deposition of 0.8 ML if the Pt is crystal held at room temperature. Further Ag deposition causes nucleation and growth of a second layer. At moderately elevated temperatures, however, the surface evolves toward thermodynamic equilibrium that ultimately favors the surface to be completely covered with Ag because of the greatly reduced surface free energy of Ag compared to Pt [4,5]. Therefore, if enough Ag is available, Pt in the surface alloy will be replaced by Ag until a complete Ag monolayer is formed. This causes the break in the uptake plot to occur at 1-ML Ag coverage for samples that were annealed to 800 K.

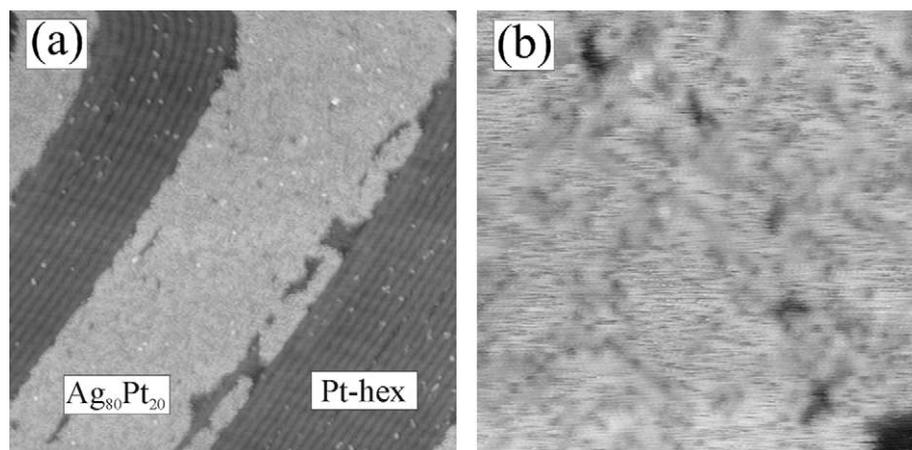


Fig. 2. STM images of 0.25-ML Ag deposited on the Pt(100)-hex surface at 300 K. (a) Scan area $(60 \text{ nm})^2$. Mixed Pt/Ag islands are separated from the remaining Pt(100)-hex reconstructed surface. (b) Scan area $(15 \text{ nm})^2$. STM image of an $\text{Ag}_{80}\text{Pt}_{20}$ alloy island. Ag is imaged brighter than Pt. This island shows a disordered structure with 20% Pt dispersed in 80% Ag.

These results are quite similar to the AES uptake plots reported for Ag growth on Pt(1 1 0) at room temperature [1,6], with the primary difference being that the removal of the surface reconstruction on Pt(1 1 0) provides 0.5-ML Pt to the adlayer and thus the formation of an $\text{Ag}_{50}\text{Pt}_{50}$ surface alloy. No results for annealed samples were presented for Ag/Pt(1 1 0) surfaces.

The different AES uptake plots expected for several possible thin film geometries are shown schematically in Fig. 3. These plots were derived by considering the contribution of first- and second-layer Ag to the intensity of the Ag signal in AES. The Ag intensity is proportional to the Ag concentration in each layer, with the contribution from Ag in the second layer attenuated by a factor α compared to that from Ag in the first layer, because the AES signal decreases exponentially with distance from the surface. Therefore we can express the Ag intensity I_{AES} as a function of the concentration of silver in the first layer (θ_{first}) and second layer (θ_{second}) as:

$$I_{\text{AES}} = \theta_{\text{first}} I_{\text{Ag}} + \alpha \theta_{\text{second}} I_{\text{Ag}}, \quad (1)$$

where α is a positive number smaller than one and I_{Ag} is the Ag intensity from a monolayer of Ag. The slopes depicted in Fig. 3 result directly from considering the changes in θ_{first} and θ_{second} for the

various growth scenarios. It is worth noting that no clear break in the uptake curve would be observed at 0.8- or 0.5-ML Ag on Pt(100) or Pt(1 1 0), respectively, if the initial growth of the second Ag layer proceeded by covering the remaining pure-Pt patches of the first layer (Fig. 3a). On the other hand, if Ag in the second layer initially grows only on top of Ag atoms in the first layer, as proposed by Huang et al. [1] for the case of Ag on Pt(1 1 0), then an additional break in the AES uptake is expected before completion of the second layer (Fig. 3b). This behavior was not observed in our Ag/Pt(1 0 0) studies nor reported for Ag/Pt(1 1 0). This implies that Ag adatoms in the second Ag-containing layer do not preferentially “cover” Ag or Pt atoms in the underlying layer. This is not surprising on Pt(1 0 0) since Ag and Pt in the alloy layer is not segregated into large monometallic domains, as can be seen in the STM images (Fig. 2b). Therefore, extended Ag adislands always cover both Ag and Pt in the alloy layer. Extended Ag adislands are thermodynamically favored over dispersed Ag adatoms because they increase the number of Ag–Ag bonds within the island and reduce the combined perimeter length of all the Ag islands.

If Ag and Pt were segregated into domains in the first layer, then one may hope to see preferential

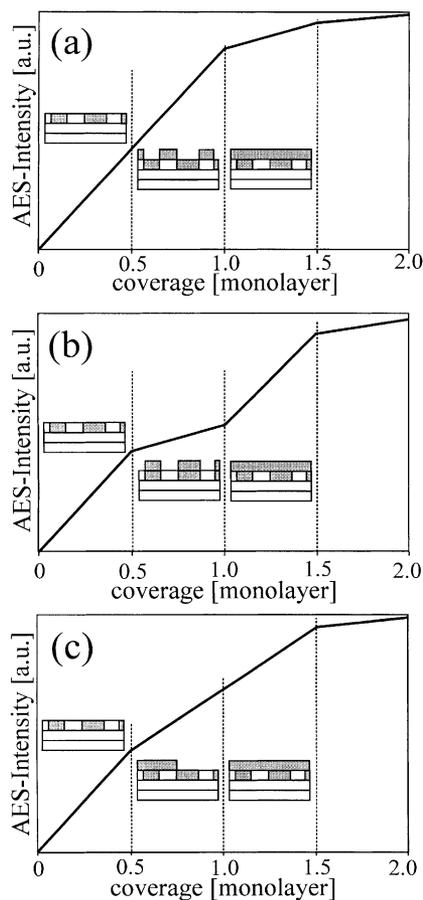


Fig. 3. Schematic uptake plots from AES for several possible configurations of second-layer growth on a mixed first layer with 50% heteroatoms: (a) preferential second-layer growth on top of heteroatoms; (b) preferential second-layer growth on homoatoms; (c) no discrimination by the growing second layer between homoatoms or heteroatoms in the first layer.

growth of the second layer Ag in the AES-uptake plots. To investigate this possibility, we performed the following experiment. First we deposited 0.4-ML Ag on Pt(100)-hex at 300 K and then annealed the sample to 800 K. After annealing to this temperature, all of the Ag has mixed with the Pt in the surface layer and no hex-reconstructed domains remain on the surface. The surface now consists of nanosized domains of Ag and Pt. The domain size has a characteristic length scale of ~ 1 nm. These structures will be discussed in more

detail in a forthcoming publication [3] and are similar to the structures observed for Ag/Pt(111) [7]. Additional Ag was grown on top of this surface alloy at 300 K and then the Ag peak-to-peak intensities in AES were measured. These results are also shown in Fig. 1 together with the other AES uptake plots. Initially, the slope of the Ag intensity in this experiment follows closely the slope obtained for monolayer-Ag growth. This indicates a growth mode as depicted in Fig. 3a where Ag grows on top of Pt domains rather than on Ag domains. If Ag covered all Pt sites first before it grew on top of Ag domains in the “substrate”, a “break” in the uptake plot at a total coverage of 1 ML would be expected. However, a deviation from this ideal growth was observed and a decrease in the slope of the Ag intensity was observed for a coverage of ~ 0.8 ML. This indicates that the situation is not as perfect as depicted in Fig. 3a, but that Ag islands also partially cover Ag domains in the “substrate” after initial nucleation and growth of Ag on Pt sites.

CO molecules can be used to titrate Pt sites at Ag-Pt surfaces effectively since CO does not adsorb on Ag above 35 K [8]. The peak areas from CO thermal desorption spectra are plotted against Ag coverage in Fig. 4 for both Ag films grown at 300 K and Ag films that have been annealed to 800 K. These results are entirely consistent with our conclusions drawn from the AES uptake plots. For Ag films annealed to 800 K, CO adsorption decreased linearly with increasing amounts of deposited Ag. The Ag film grown at 300 K shows an identical linear decrease up to 0.8-ML Ag coverage, at which point the first adlayer is completed but still contains 20% Pt. Depositing more Ag at 300 K caused a much smaller relative decrease in the amount of CO adsorption, consistent with the growth of Ag adislands that do not discriminate between Ag and Pt in the substrate. These results compare well with earlier studies by Strüber et al. [9].

The CO titration experiments reported by Huang et al. [1] for the Ag/Pt(110) surface are peculiar in that the amount of CO decreased by more than 50% for 0.5-ML Ag coverage. This implies that each Ag atom poisons more than one

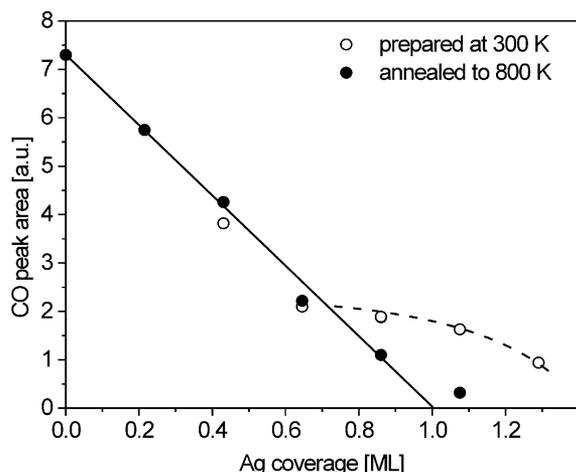


Fig. 4. Plot of the amount of CO adsorption as a function of Ag coverage on a Pt(1 0 0) surface for Ag films grown at 300 K (open circles) and samples annealed to 800 K (full circles) prior to CO dosing. The solid line gives a linear decrease of adsorbed CO from 0 to 1 ML coverage of Ag. The amount of adsorbed CO was obtained by integration of CO TPD curves.

CO adsorption site, which is in disagreement with observations for both Ag/Pt(1 0 0) and Ag/Pt(1 1 1) [10,11]. The constant amount of CO desorption from 0.5 to 1 ML coverage of Ag [1] suggests that Ag in the second layer preferentially nucleates and grows on top of Ag in the monolayer alloy, although the AES uptake plots do not show any evidence for such a growth mode. Nevertheless, preferential growth of Ag on Ag at 300 K could be explained by trapping of Ag at Ag sites because of stronger interactions between Ag and Ag compared to Ag and Pt, i.e., a positive exchange energy between Ag and Pt as was proposed by Röder et al. [7] for the Ag/Pt(1 1 1) system. For Ag/Pt(1 0 0) we did not observe any clearly preferential growth at Ag sites, neither from AES uptakes nor CO titrations for Ag growth at 300 K. On the contrary, we observed preferential growth of Ag on Pt for pre-annealed samples, as discussed in the previous paragraph. This behavior is consistent with a reduction of the surface free energy that favors a complete covering of Pt with Ag.

“As a final comment, alloy formation at room temperature should be expected generally for any

metal monolayer grown on a reconstructed metal surface”. The stoichiometry of this monolayer alloy is dictated by the differences in the atom densities of the reconstructed and bulk-terminated surfaces. This alloy structure represents a kinetically trapped structure, and thus no long-range ordering is expected. Local ordering with preferential neighbor constellations, however, may be established for systems with a negative exchange energy, i.e., systems that prefer hetero-neighbors.

The generality of the formation of monolayer confined kinetically trapped disordered alloys may be illustrated by the data presented by Huang et al. [1] for Ag on Pt(1 1 0). Although Huang et al. conclude that the growth proceeds by filling in the missing rows, their data can be interpreted alternatively in a way that is consistent with the formation of a disordered alloy. Unfortunately, no structural information was contained in either the AES uptake plots or in the CO thermal desorption experiments presented in the article by Huang et al. The only structural information is from LEED studies reported by Shern et al. [6] on this system. They observed a continuous decrease of the intensity of the half order spots with increasing Ag coverage until it vanished at ~ 0.5 -ML Ag coverage. The (0,1) beam on the other hand increased in intensity and reached a maximum at 0.5 ML Ag coverage. Shern et al.’s [6] interpretation of such a behavior is adopted from an article by He et al. [12] on the growth of Rh on Pt(1 1 0). They argue that by filling in the missing rows with Ag, two (2×1) sublattices exist on the same surface one for the Ag-rows and the other for the Pt-rows. The two sublattices have an antiphase relationship and thus interfere destructively for the half-order spots, causing their disappearance at 0.5-ML Ag coverage if the differences in atomic scattering factors for Ag and Pt are negligible. However, we point out that disordering of the surface and formation of a $\text{Ag}_{50}\text{Pt}_{50}$ monolayer alloy would also explain the decrease in the intensity of the half-order spots. Furthermore, the increase in the intensity of the first-order spots can also be explained if the substitutional Ag atoms are pseudomorphic with the Pt. Thus, the

possibility that the Ag–Pt(110) surface forms a disordered surface alloy rather than an ordered structure with two (2×1) sublattices is consistent with all the data presented by Shern et al. [6] and Huang et al. [1].

In conclusion, we observed that Ag deposition on a Pt(100)-hex surface at room temperature forms a monolayer consisting of a disordered Pt₂₀Ag₈₀ surface alloy following deposition of 0.8-ML Ag. We propose that the formation of a kinetically trapped, disordered alloy should be observed generally for submonolayer heteroepitaxial growth on reconstructed substrates, and the concentration of substrate atom species in the alloy is given by the atom density difference between the reconstructed surface and bulk lattice planes. Based on these results on Ag/Pt(100), we provide an alternative interpretation involving a disordered alloy for the recently reported data on Ag/Pt(110).

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