

## Monolayer-Confined Mixing at the Ag-Pt(111) Interface

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The present tunneling microscopy study reveals that the growth of silver on Pt(111) at substrate temperatures above 620 K results in the formation of a two-dimensional alloy consisting of Ag clusters dissolved in the Pt layer [ $\Theta_{\text{Ag}} < 0.5$  monolayer (ML)] and Pt clusters in the Ag matrix layer ( $0.5 \text{ ML} < \Theta_{\text{Ag}} < 1 \text{ ML}$ ), respectively. The embedded clusters have a narrow size distribution centered around 10 Å. The dissolution of silver into the Pt surface layer and vice versa proceeds from the step edges and is confined to the topmost layer. The second silver layer does not dissolve into the interface, but grows layerwise on top.

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The interface between two dissimilar materials in heteroepitaxy substantially influences the morphology of the growing film. According to Young's equation  $\Delta\gamma = \gamma_a + \gamma_i - \gamma_s$  [1], the thermodynamic behavior of epitaxial films is determined by the interface energy ( $\gamma_i$ ) and the surface free energies of substrate ( $\gamma_s$ ) and adlayer ( $\gamma_a$ ). Depending on the relation between the interface energy and the surface energies three principal growth modes are usually categorized: three-dimensional island growth ( $\Delta\gamma > 0$ ), layer-by-layer growth ( $\Delta\gamma \leq 0$  for each adlayer) and partial layer-by-layer growth with successive 3D islanding ( $\Delta\gamma \leq 0$  for a limited number of adlayers) [2].

The interfacial energy is, however, usually a poorly known quantity, and in many cases it has been disregarded, i.e., set to  $\gamma_i = 0$ . This approximation is justified only in the minority of cases when adlayer and substrate are very similar. A non-negligible positive interface energy results, for example, from interfacial misfit strain due to structural adlayer-substrate mismatch. In particular, a negative interface energy might have a substantial influence on the resulting film morphology: If  $\gamma_i$  becomes sufficiently negative the completion of at least the first layer can be favored even when  $\gamma_s$  is smaller than  $\gamma_a$ . Indeed, the interface energy  $\gamma_i$  must be negative if interdiffusion favors interfacial alloying [3]. In that case the system tends to minimize its energy by maximizing the surface of the interface, which is done by complete dissolution of the adlayer into the topmost substrate layers. Partial layerwise growth induced by interface alloying has recently been predicted theoretically [4] and also observed experimentally [5] for the Au epitaxy on the Ag(110) surface. The weakly positive surface energy balance  $\gamma_{\text{Au}(110)} - \gamma_{\text{Ag}(110)} = +0.12$  eV/atom has been found to be overridden by the heat of formation of  $-0.18$  eV/atom [4] of the Au-Ag substitutional monolayer alloy.

In order to shed light upon the microscopic process of interfacial alloying we have chosen to study the epitaxial system Ag/Pt(111). The completion of at least the first silver layer is expected for this system due to the large negative surface energy difference  $\gamma_{\text{Ag}(111)} - \gamma_{\text{Pt}(111)} = -0.35$  eV/atom [6,7]. In addition, as  $\gamma_i$  is supposed to

be negative as well, at elevated temperatures Ag and Pt are known to be miscible forming a substitutional bulk alloy [8]. Our tunneling microscopy studies reveal, indeed, that Ag/Pt(111) forms a two-dimensional *real* [9] interface mixture at  $T > 620$  K. Nevertheless, the dissolution of Ag into the Pt(111) matrix is not complete. The reason is the energy cost for the dissociation of Ag atoms from Ag clusters which counterbalances the energy gain by increasing the interface. The point where dissolution comes to a standstill is at cluster sizes which correspond to the most stable Ag clusters of 7, 10, or 12 atoms [10]. The interface mixing proceeds from step edges and is found to be confined to the topmost Pt surface layer. Therefore the second silver layer does not dissolve further into the interface, but grows layerwise on top.

The microscopy data contrast with recent conjectures of Becker *et al.* [11], who claimed that upon heating of Ag submonolayers on Pt(111) above 550 K the initially large Ag islands irreversibly fragment into small adsorbed 2D Ag clusters. The elastic strain due to the 4.3% lattice mismatch between Ag and Pt was discussed as driving force and the postulated isolated cluster fragments were even asserted to be "strain-free" relaxed 2D equilibrium structures. This interpretation was based on the observation of an irreversible decay of the specularly reflected He intensity upon heating above 550 K. As will become evident by the results presented here the island fragmentation hypothesis cannot be maintained. Instead the experimental He-scattering data of Becker *et al.* [11] are fully compatible with the confined interface mixing revealed by our tunneling microscopy study: The He-reflectivity decay is caused by the enhanced diffuse scattering of the *real* surface mixture.

The experiments were performed with a variable temperature UHV scanning tunneling microscope (STM) ( $25 \leq T \leq 600$  K) [12]. The clean Pt(111) surface was obtained by alternating cycles of Ar-ion sputtering, annealing in an oxygen atmosphere, and flash annealing to 1200 K. Ag was evaporated from a molecular beam epitaxy Knudsen cell at a rate of 1 monolayer (ML) per 900 s and a substrate temperature of 400 K. The background pressure in the UHV system was better than  $7 \times 10^{-11}$

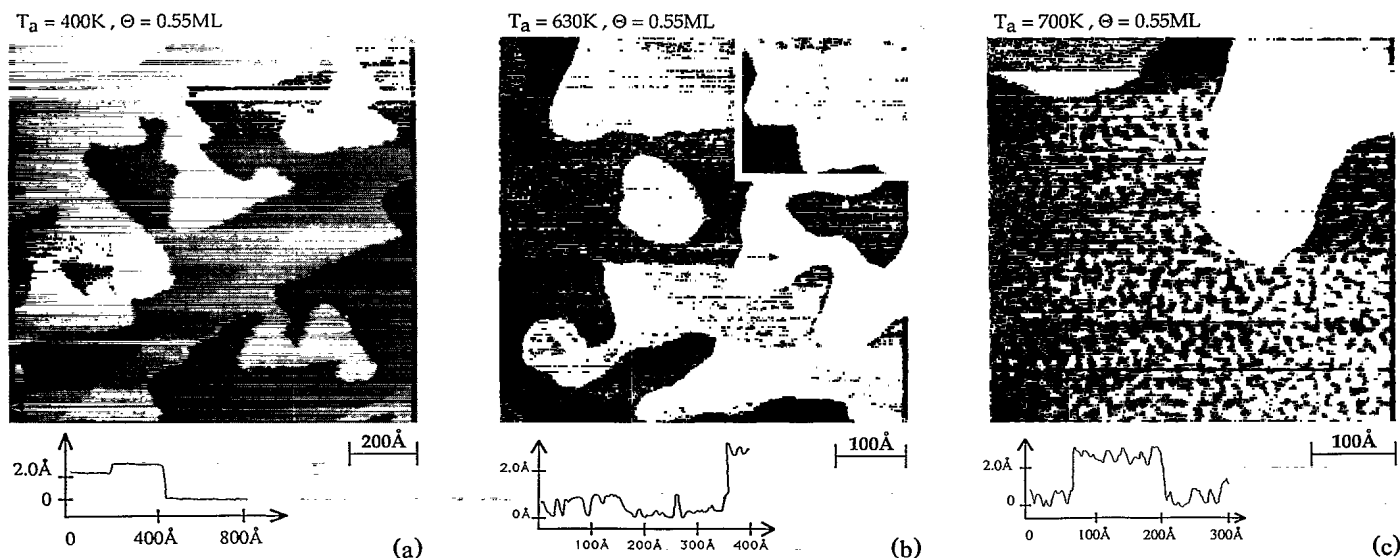


FIG. 1. STM top view images of Ag submonolayer films ( $\Theta=0.55$  ML) grown on the Pt(111) surface at 400 K (a) and annealed for 100 s to (b) 630 K and (c) 700 K. The line scans are taken along the bars in images (a) and (c). 0 Å corresponds to the height of the lower Pt terrace, 2.3 Å to upper Pt terrace height, and 2.9 Å to the Ag island height. Inset in (b)  $\Theta=0.55$  ML deposited directly at  $T=630$  K.

mbar, rising to  $2 \times 10^{-10}$  mbar during evaporation. After annealing the system to the temperatures indicated as  $T_a$ , STM images were acquired at a sample temperature of 350 K (constant current mode,  $-0.5 \leq V_t \leq -1.5$  V,  $1.0 \leq I_t \leq 3.0$  nA). The measured heights are found to be independent of the tunneling conditions applied.

Figure 1(a) shows the Pt(111) surface with a Ag coverage  $\Theta=0.55$  ML after annealing to 400 K. As shown in [12], the considerable mobility of the Ag adatoms at this temperature leads to the formation of large Ag islands, most of them wetting the ascending steps of the Pt surface. In the STM image the Ag islands are easily discernible from Pt due to their apparently larger height [ $h_{\text{Ag}}=2.9$  Å,  $h_{\text{Pt}}=2.3$  Å, see line scan in Fig. 1(a)] and their therefore brighter appearance. The difference in imaging height can only partly be due to a geometric effect [distances between (111) planes are 2.26 and 2.36 Å for Pt and Ag, respectively]. Most of it has to be ascribed to electronic effects, presumably to the decrease of the work function by Ag adsorption. Low energy electron diffraction images of this surface show sharp ( $1 \times 1$ ) spots, indicating a commensurate ( $1 \times 1$ ) Ag monolayer.

After annealing to temperatures above 620 K [Figs. 1(b) and 1(c)] the situation has drastically changed. The Pt terraces appear spotted with small protrusions of approximate diameter 10 Å, while the Ag islands are distorted by indentations of comparable width. Their apparent height ( $h=2.3$  Å) in the STM image is exactly that of the former Pt steps. On the other hand the height of the protrusions inside the Pt terraces ( $\Delta h=2.9$  Å relative to the underlying Pt terrace,  $\Delta h=0.6$  Å relative to surrounding Pt) is equivalent to that of the adsorbed Ag islands shown in Fig. 1(a) [see line scan in Figs. 1(b) and 1(c)]. Hence it is straightforward to identify the in-

clusions inside the Pt terraces with small two-dimensional Ag clusters, which have diffused into the Pt terraces, whereas the indentations in the Ag islands must be associated with Pt clusters, which mixed into the Ag islands [13].

The obvious roughening of the Ag-island-Pt-step interface and the increase of the density of the clusters towards the former step edges in Fig. 1(b) after annealing to 630 K indicates that the interdiffusion of Ag into the first Pt layer proceeds from the lower step edge side, and that of Pt into the Ag islands towards the lower terrace via the wetted Ag-Pt interface. In Fig. 1(b), the vicinity of the Ag island perimeter facing the underlying Pt terrace also reveals an increased cluster density with respect to the terrace far apart from any step. We therefore conclude that the steps present at the surface, predominantly the Ag-wetted Pt steps, are the active sites for the mixing process. The same inhomogeneous cluster distribution can be obtained by annealing to slightly lower temperatures with subsequently longer annealing times. This gives further support to the interpretation of Fig. 1(b) in terms of a quenched, incomplete mixing of Ag and Pt. It is interesting to mention that the same appearance of the binary Ag-Pt(111) interface mixture is obtained upon direct Ag deposition above 620 K. This is shown in the inset of Fig. 1(b) for  $T=630$  K. The uniformly impinging Ag atoms are mixed into Pt solely at step edges, which is obvious from the decreasing local Ag coverage with increasing distance from the step. (In the inset the local Ag coverage has reduced by 40% when going from 60 to 120 Å away from the step edge.)

Annealing to temperatures above 650 K for more than 50 s leads to completion of this mixing process. Figure 1(c) shows the same surface after annealing to 700 K.

Now the mixing is homogeneous over the whole surface. The apparent Ag concentration in the topmost layer, derived from the height distribution on the terraces, agrees within errors with the deposited amount of  $\Theta=0.55$  ML. For annealing experiments of 1 ML coverage it was found that the coverage remained unaltered within the experimental errors, which means that all of the deposited Ag remains in the topmost surface layer. This holds true up to the onset of thermal desorption of Ag at  $T \approx 900$  K. Annealing to temperatures below this threshold left the surface composition and the width of the Ag clusters unchanged, which gives further strong evidence that the intermixing is confined to the first layer and hence to intralayer mass transport. Diffusion into deeper layers must be kinetically hindered by an activation energy for interlayer mass transport which cannot be overcome before thermal desorption sets in.

Figure 2 shows two STM images at low and high Ag coverage after annealing to 650 and 750 K, respectively. In accordance with the situation in Fig. 1(c) at  $\Theta=0.55$  ML also at  $\Theta=0.22$  ML [Fig. 2(a)] and  $\Theta=0.95$  ML

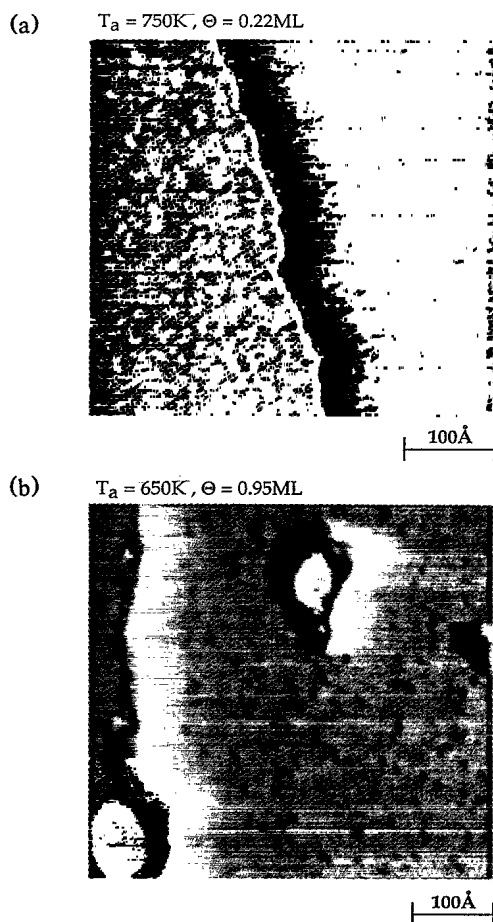


FIG. 2. STM images (the derivatives of the lines of constant current were recorded) showing Ag submonolayer films, (a)  $\Theta=0.22$  ML and (b)  $\Theta=0.95$  ML, grown on the Pt(111) surface at 400 K and annealed to 650 and 750 K, respectively.

[Fig. 2(b)] the Ag and Pt in the topmost layer have completely mixed. On the upper right part of Fig. 2(b), there are two small monatomically deep holes in the mixed Ag-Pt layer. Closer inspection reveals that the bottom of these holes also consists of intermixed Pt and Ag. The stability of these holes proves that the second layer must have a distinctly different constitution than the first: Before such a hole can be closed, the Ag atoms of the bottom of the hole have to be transferred into the first layer, which is strongly activated and hence stabilizes these holes. If the second layer would have the same constitution as the first, this activation barrier would be very low and the holes have to be closed at once, similar to the observations on clean metal surfaces.

At  $\Theta=0.22$  ML [Fig. 2(a)] small dissolved Ag islands are homogeneously distributed over the terraces. By counting islands and evaluation of their density, the average cluster size is determined for Fig. 2(a) via the coverage to  $9.5 \pm 1.0$  Ag atoms. The images of the clusters reveal a narrow distribution of the size centered at approximately 10–13 Å. Since isolated Ag dimers on the Pt(111) surface are imaged with an average size of 5–7 Å, this is in accordance with the value expected for clusters consisting of 7 to 12 atoms. The in principle inverted situation is shown in Fig. 2(b) at a Ag coverage of  $\Theta=0.95$  ML, where small Pt clusters are dissolved in the topmost Ag layer. The apparent width of these Pt clusters in the Ag surface equals that of the Ag clusters in the Pt surface. Therefore in both of these agglomerations 7 to 12 Ag or Pt atoms are involved. This is consistent with the symmetric enthalpy of mixing found for the liquid silver-platinum solution [8].

In a model binary mixture, including interaction between the particles, the thermodynamic equilibrium cluster size is determined by the minimum of the free energy of the system, i.e., the competition of the boundary energy, which in our case is the energy of the one-dimensional Ag-Pt interface, and the mixing entropy, which is proportional to the number of clusters. The variation of the boundary energy is supposed to be linear with the length of the boundary, or the width of the clusters, whereas the mixing entropy or the number of clusters is indirectly proportional to the squared cluster size. When this simple concept of a potential energy, only depending on the length of the boundary, would be applicable in our case, strong variations of the cluster size on the entropy term of the free energy, or the temperature, respectively, would have to be expected. That is why we performed a series of annealing experiments for the system at  $\Theta=0.2$  ML, where we heated the surface to 650, 700, 800, or 900 K for about 100 s and subsequently quenched to below 350 K. In these experiments we could not find any obvious dependence of the cluster size on the annealing temperature. Hence the simple concept of the internal energy of the clusters, depending simply on the boundary length does not apply here. There must exist an important contribution to this internal energy, strongly dependent on

cluster size which causes a local minimum at a cluster size of about 7 to 12 atoms. This term overrides the variation of the entropy with temperature. This is further supported by the observation that the Ag ( $\Theta < 0.3$ ) and the Pt ( $\Theta > 0.8$ ) cluster sizes are independent of the coverage. It may be speculated that one contribution to the stability of the clusters is due to a balance of the strain energy cost of the 4% misfit of Ag in Pt with the line tension of the increased Ag/Pt surface boundary length.

At medium coverages of  $0.3 < \Theta < 0.8$  ML the clusters touch each other and lead to an appearance depicted in Fig. 1(c). The width of this fingerlike agglomeration of clusters is again about 10–13 Å, which supports this interpretation of random agglomerations of single clusters. Because of the slight surplus of Ag in Fig. 1(c) the Ag clusters mostly percolate the terraces.

Recent theoretical [10,14] and experimental [15] studies support, indeed, the occurrence of “magic” numbers in the stability of small adsorbed two-dimensional clusters on the Pt(111) surface. In particular the clusters of  $n=7, 10$ , and 12 atoms, the smallest structures with at least threefold coordinations at the entire cluster perimeter, were found to be substantially stabilized. With respect to dimers,  $Ag_{7,10,12}$  clusters are energetically favored by 0.20–0.22 eV/atom [10], which clearly overrides the entropy term, i.e.,  $\Delta E \gg kT$ . The occurrence of magic 2D clusters is also consistent with our STM observation of the *real* Ag-Pt surface mixture. The observed medium size of  $9.5 \pm 1.0$  atoms of the dissolved clusters, as well as their imaging size are in good agreement with a distribution of  $Ag_n$  clusters with  $n=7, 10, 12$ .

Increasing the Ag coverage to one monolayer at  $T \geq 620$  K (or at room temperature and subsequent annealing) leads to a decreasing density of Pt clusters embedded in Ag until a complete demixing of the two metals is achieved and one is left with a completed monatomic Ag layer. The second Ag layer formed at coverages above one monolayer is identical to the one observed for Ag deposition without annealing, it forms a domain wall network.

In conclusion, Ag deposition on Pt(111) at—as well as after annealing to—temperatures above 620 K leads to a *real* binary mixture of Ag and Pt, which is confined to the topmost layer and therefore restricted to submonolayer Ag coverages. The surface mixing proceeds from steps which are present on the surface, namely, the Ag-wetted Pt step edges (predominantly) and the descending step edges of Ag islands. This observation is consistent with the result of a recent molecular dynamics simulation of Ni alloying into the Cu(111) surface [16]. Raeker and DePristo observed in their simulations that surface alloying only occurred at step edges but not on terraces. Those authors favor a mechanism of alloy formation through the incorporation of adatoms on the upper sub-

strate terrace near the step edge via displacement of the edge outwards. Our results for Ag mixing into Pt(111) steps, however, are more in favor of the alternative process of incorporation of adatoms directly at the steps.

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- [9] A *real* mixture (solution) of *A* and *B* is characterized by a nonzero enthalpy of mixing, which has the consequence that the equilibrium is not a random arrangement of atoms *A* and *B*. In our case the exchange energy  $\epsilon$ , defined by  $\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$  is positive (note that  $\epsilon$ 's are negative). Therefore clustering occurs [see, e.g., D. A. Porter and K. E. Easterling, *Phase Transformations in Metals and Alloys* (Van Nostrand Reinhold, Berkshire, 1982), p. 23]. We might likewise describe such a phase as a solid solution with a positive enthalpy of mixing, which leads to phase separation.
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