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Silver on $Pt(100)$: Alloying *vs.* surface reconstruction —two competing mechanisms to reduce surface stress

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Abstract. – Phase-coexistence of a Ag/Pt surface-alloy and a pure Pt-hex reconstructed phase has been observed for sub-0.3 ML Ag coverage on a Pt(100) surface by scanning tunneling microscopy and temperature-programmed desorption of Ag. We argue that, despite a stronger homoatom interaction, mixing at the surface is observed because the intrinsic tensile stress of the Pt(100) surface facilitates the incorporation of the slightly larger Ag atoms into the surface layer in order to minimize strain energy of the surface. Thus, surface-alloying presents an alternative to surface reconstruction as a means of strain minimization. Therefore, a competition between surface reconstruction and alloying to reduce the stress at the surface exists and, consequently, a two-phase coexistence of an alloy-phase and a pure Pt hex-reconstructed phase are observed.

Introduction. – Surface-confined alloying of elements that are immiscible or exhibit a low solubility in the bulk has been observed for several systems, such as alkali metals on Al [1,2], Au on Ni [3], Ag on Pt [4,5], and Sb on Ag [6]. It is accepted that stress minimization plays a crucial role in accounting for this phenomenon. Tersoff [7] explained it as a consequence of reducing the strain originating from the lattice misfit between the substrate and deposited element. Within this model, no difference between positive and negative misfit is predicted. However, in all experimentally known systems of surface-confined alloying, larger atoms are alloyed in a substrate with a smaller lattice constant. In this communication we explain this asymmetry in terms of the *intrinsic tensile stress* of a free surface favoring incorporation of larger atoms in order to reduce its strain energy.

It has been observed that for Ag deposited on a Pt(111) substrate, Ag alloys with the Pt(111) surface and forms a "nanophasic" structure [4,5], *i.e.* Ag nanoclusters rather than monodispersed Ag atoms are formed in the surface layer. These Ag clusters, however, disperse uniformly across the entire surface. Therefore, this surface can be described as a *single* alloy phase. The clustering and distribution of the clusters that comprise the micro(nano)scopic
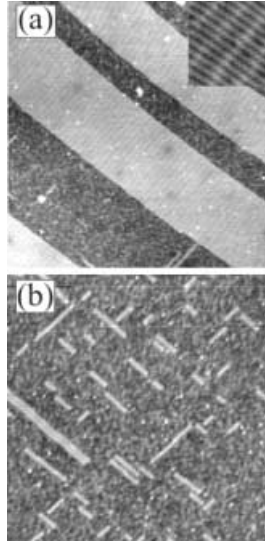
Fig. 1 – STM images of 0.25 ML Ag on Pt(100) after annealing to 900 K. (a) Scan area $(150\,\text{nm})^2$. An Ag/Pt-alloy phase, which appears darker, can be distinguished from the pure Pt(100)-hex reconstructed phase. The inset shows a $(15\,\text{nm})^2$ area of the hex-reconstructed phase that shows more clearly its characteristic structure. (b) Scan area $(75\,\text{nm})^2$. Small, single-unit-cell–wide Pt(100)-hex domains surrounded by the Ag/Pt alloy phase.

structure of the surface have been accounted for by preferred bonds between like atoms and "ordering" of these homoatomic clusters into stress-domain patterns [5, 7].

Here we present experimental results for Ag deposited on Pt(100) showing two-phase coexistence of an Ag/Pt alloy phase and a reconstructed pure Pt phase. We present a simple thermodynamic model to explain surface alloying for the bulk immiscible Ag/Pt system. This model is independent of the micro(nano)scopic structure of the surface alloy and may thus be applicable to a broader range of systems. The experimentally observed two-phase coexistence is treated by a thermodynamic model, which predicts this phase segregation as a consequence of two competing mechanisms to reduce the surface stress.

Experimental methods. –   Scanning tunneling microscopy (STM) of annealed Ag deposits on Pt(100) substrates and temperature-programmed desorption (TPD) of Ag from this surface were employed to identify surface alloying of Ag into the Pt surface and the presence of separate phases. A detailed description of the vacuum apparatus that was used to perform these experiments can be found elsewhere [8]. Ag was evaporated from a resistively heated, Ta boat onto a Pt(100) single crystal. θ_{Ag} was determined from Auger electron spectroscopy (AES) measurements that were calibrated by Ag growth curves [9]. All STM data reported here were acquired at 300 K after annealing the sample at 900 K for 10 s and rapidly cooling to room temperature.

Results. –   Figure 1 shows STM data for surfaces with 0.25 ML Ag coverage. Only one terrace is imaged in both images. Two phases can be distinguished in these STM images, with the brighter areas corresponding to a pure Pt-hex reconstructed phase, while the darker areas are an Ag-Pt alloy. The hex-reconstructed domains extend over several tens of nanometers in fig. 1a, while the hex-domains in fig. 1b are much narrower and often exhibit their minimum
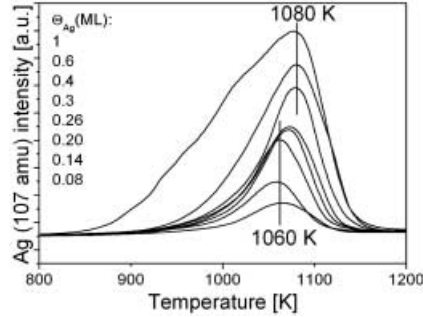
Fig. 2 – Ag desorption spectra acquired by using a constant heating rate of $5\,\mathrm{K/s}$ for different initial Ag coverages. The Ag desorption peak shifts by $20\,\mathrm{K}$ above $0.2\,\mathrm{ML}$ Ag coverage.

possible width of 5 atoms, *i.e.* the width of one unit cell of the reconstruction. However, we only distinguish two phases, independent of the size of the domains.

The contrast in these STM images is mainly topographical. The hex-reconstruction appears brighter because of the incommensurate nature of this pseudohexagonal overlayer. The alloy, on the other hand, is pseudomorphic with the substrate and thus appears darker. Substructures can also be imaged in both phases. The Pt-hex reconstructed phase shows a pattern with a characteristic (5×20) periodicity. This can be more clearly seen in the inset of fig. 1a that shows a magnification of this phase. The alloy phase consists of darker (Pt) and brighter (Ag), elongated features a few atoms wide that form a labyrinthine-like network. This structure has a surface morphology similar to the Ag/Pt(111) system [4,5]. Therefore, it is reasonable to conclude that the alloy structure of both surfaces has the same origin. We support the hypothesis that this surface morphology is explained by stress domains, *i.e.* the formation of alternating compressive and tensile stressed "nano-domains" in order to minimize the total stress in the film [5,7,10–12]. For $\theta_{\mathrm{Ag}} > 0.3\,\mathrm{ML}$, no hex-reconstructed phases remain at the surface and addition of Ag results in an increase in the Ag content of the 2D Ag-Pt alloy [9]. The disappearance of the hex-reconstruction from the surface at $\theta_{\mathrm{Ag}} > 0.3\,\mathrm{ML}$ can also be observed in low-energy electron diffraction (LEED) and was previously reported by Strüber *et al.* [13].

In addition to these direct observations at $300\,\mathrm{K}$, we have evidence for phase coexistence from Ag TPD, even at the desorption temperature of Ag. Ag TPD traces for different initial Ag coverages are shown in fig. 2. The Ag desorption peak continuously shifts to higher temperatures for increasing Ag coverages between $0.2\,\mathrm{ML}$ and $0.6\,\mathrm{ML}$, while the peak temperature maximum remains unchanged at $1060\,\mathrm{K}$ and $1080\,\mathrm{K}$, respectively, below $0.2\,\mathrm{ML}$ and above $0.6\,\mathrm{ML}$. Shifting of the desorption peak below $0.7\,\mathrm{ML}$ Ag coverage on Pt(100) was reported previously [13]; however, no data were presented for the coverage regime below $0.2\,\mathrm{ML}$. The $20\,\mathrm{K}$ shift of the Ag desorption peak corresponds to a difference in the desorption activation energy of $\sim 6\,\mathrm{kJ/mol}$ assuming first-order desorption and the same pre-exponential factor in the rate constant. For $\theta_{\mathrm{Ag}} > 0.7\,\mathrm{ML}$, the constant desorption temperature for Ag can be explained by the formation of a contiguous Ag film with Pt clusters alloyed into it (droplet phase). Thus Ag essentially evaporates out of the same local environment for a coverage range of $0.7\,\mathrm{ML} < \theta_{\mathrm{Ag}} < 1\,\mathrm{ML}$. Similar effects were previously observed for desorption spectra of bimetallic monolayers on immiscible substrates [14]. In the Ag-coverage regime of phase coexistence, the Ag/Pt ratio in the alloy phase is constant and does not change with the global Ag coverage on the surface. An increase in the Ag coverage results in a spreading of the

alloy phase on expense of the hex-reconstructed phase. Therefore, Ag desorbs out of the same local alloy structure for $0 < \theta_{Ag} < 0.2\,\text{ML}$. Consequently, the activation energy for desorption is unaltered. This agrees with our observation for Ag coverages below $0.2\,\text{ML}$. The Ag desorption peak shifts to higher temperatures for larger Ag coverages, indicating an altered composition of the alloy phase as θ_{Ag} changes. At the Ag desorption temperature ($\sim 1000\,\text{K}$), the critical Ag coverage at which the entire surface consists of a single Ag-Pt alloy phase is $0.2\,\text{ML}$, about $0.1\,\text{ML}$ lower than the value deduced from STM data at $300\,\text{K}$. This may be an entropy effect that favors the more disordered alloy phase at elevated temperatures.

Discussion. –   To explain the coexistence of two phases in thermodynamic equilibrium at a surface we first address the problem of why elements that are immiscible or exhibit only a small solubility in the bulk phase may alloy at surfaces. In a simplified description, alloying is observed for elements that prefer hetero-neighbor atoms, *i.e.* stronger A-B bonds than A-A and B-B bonds. This is not the case for the Ag/Pt system and is indicated by the fact that Ag and Pt tend to cluster to form the observed nanophasic alloy structure, *i.e.* Ag and Pt form preferred homobonds rather than heterobonds. The thermal desorption of Ag at fairly low temperatures, rather than formation of a bulk alloy, is a further indication of the weak Ag-Pt bonds. Therefore, the formation of AgPt surface alloys observed on Pt(111) and Pt(100) cannot be explained by interatomic interactions alone. Another component that is important to explain phenomena at surfaces is surface-strain energies. In the following we argue that this component is the critical factor to explain the observations described in this communication. The importance of stress in alloy formation at surfaces can be seen from a closely related phenomenon —the alloying of bulk-immiscible elements in supported, bimetallic monolayer films [14–17]. This has been explained by the stress caused in a monolayer film due to lattice mismatch with the substrate. Using two components, one with a larger and the other with a smaller size than the substrate, the strain in the bimetallic monolayer film can be reduced by alloying the two components. Such a strain-induced alloying may even occur if two components are immiscible in the bulk. Clustering of the constituents of the film and ordering in stress domains were also observed for such systems. Furthermore, two-phase coexistence for such films has been observed with a mixed two-component phase and a single-component phase that releases stress by formation of dislocations [17]. Thus the phenomenological similarity to the Ag/Pt system suggests similar mechanisms at work.

Free surfaces of many bulk materials are under tensile stress [18, 19]. This arises from the low coordination number of surface atoms, *i.e.* missing bonds at the surface, but phenomenologically it is the same as the stress induced in pseudomorphic monolayers. In some cases, free surfaces, like the Pt(100) surface [20, 21], readily reduce their stress by forming a more densely packed, reconstructed surface layer [19]. Although the Pt(111) surface is not reconstructed at room temperature, it is still under considerable stress. This causes the surface to spontaneously reconstruct at elevated temperatures [22, 23].

Schmid *et al.* [24] calculated a theoretical, ideal size of a surface atom that would minimize the stress in a surface layer. They found that atoms of 1.014 and 1.029 times their actual size for the Pd(111) and (100) surface, respectively, were needed to solve this problem. Although the atom size cannot be varied, we argue that the experimental observation of other, larger atoms being alloyed into the surface layer agrees with this theoretical treatment. Thus, alloying of Ag into the Pt surface is a consequence of the *tensile* stress of the Pt surface.

In order to understand the phase equilibrium at Ag/Pt surfaces, we examine how the free energy varies with Ag concentration. Segregation into phases with different stoichiometries results from a double-minimum dependence of the free energy with variation of the Ag concentration. This is usually represented by a common-tangent construction in a plot of free energy

vs. density. The free energy (per unit area) of the surface F can be separated into two terms: the surface energy F_{surface}, which can be approximated by random mixing contributions of the two surface elements, and the strain energy F_{strain} that arises from the stress in the surface layer. Both free-energy components depend on the Ag concentration and we can write

$$F(\theta_{\text{Ag}}) = F_{\text{surface}}(\theta_{\text{Ag}}) + F_{\text{strain}}(\theta_{\text{Ag}}). \tag{1}$$

The surface free energy can be written (in random mixing approximation) as the weighted sum of the surface energies of Pt and Ag:

$$F_{\text{surface}}(\theta_{\text{Ag}}) = (1 - \theta_{\text{Ag}})\gamma_{\text{Pt}} + \theta_{\text{Ag}}\gamma_{\text{Ag}}, \tag{2}$$

where γ_{Pt} and γ_{Ag} are the surface energies of Pt and Ag, respectively, and θ_{Ag} is the Ag coverage (with $\theta_{\text{Ag}} = 1$ corresponding to one monolayer of Ag).

In order to derive an expression for the strain energy term in eq. (1), we approximate the effect of alloying a larger atom into the surface layer by a uniform increase in the size of all surface atoms. If the interaction between atoms is assumed to follow Hooke's law, then the tensile stress decreases linearly with increasing atom size until the surface is under no stress. Continuing to increase the atom size causes the stress to become compressive and this increases the stress linearly. This linear change in the surface stress results directly in *quadratic* change in the strain energy and has a minimum for atom sizes at which the surface is under no stress.

This simplified approach neglects differences in Pt-Pt, Pt-Ag, and Ag-Ag interactions and the discreteness of atom sizes. If the atom-size difference is very large, then the approximation of a uniform change in the surface stress will fail. In the case of Ag on Pt, however, where the lattice constants differ by only 4.3%, one should be able to use a weighted mean-atom size a, given by $a = \theta_{\text{Ag}}a_{\text{Ag}} + (1 - \theta_{\text{Ag}})a_{\text{Pt}}$, as the atom size in the surface layer in order to estimate the surface stress. *Consequently, the tensile stress of the free surface is compensated for a critical* Ag *concentration* $\theta_{\text{Ag}}{}^{+}$ *in the surface.* What would be the value expected for $\theta_{\text{Ag}}{}^{+}$? The lattice constant of Ag is larger than that of Pt by a factor of 1.043. If we simply assume that the surface stress for Pt surfaces was the same as that deduced by Schmid *et al.* [24] for Pd, then values for $\theta_{\text{Ag}}{}^{+}$ can be obtained for which the tensile surface stress is compensated. These values are $\theta_{\text{Ag}}{}^{+} = 0.33$ and $\theta_{\text{Ag}}{}^{+} = 0.48$ for the (111) and (100) surfaces, respectively. It follows that the strain term in eq. (1) can be expressed as

$$F_{\text{strain}} = \varepsilon(\theta_{\text{Ag}} - \theta_{\text{Ag}}{}^{+})^{2}, \tag{3}$$

where ε is the strain energy per unit area.

The above discussion allows us to account for the dependence of the free energy on the Ag coverage, upon substituting from eqs. (2) and (3) into (1). A schematic graph for eq. (1) is drawn in fig. 3a, taking into account the fact that the surface energy of Ag is about one-half that of Pt [25]. It is apparent from this that F *vs.* θ_{Ag} has only a single minimum and therefore one would not expect phase-segregation into domains with different stoichiometries. Observations for the Ag/Pt(111) system [4,5] are consistent with this expectation.

If the pure Pt(100) surface did not reconstruct, the free-energy curve for Pt(100) would be similar to that for the Pt(111) surface, apart from a different value of the critical Ag coverage $\theta_{\text{Ag}}{}^{+}$ in the strain term. Reconstruction of the (100) surface, however, provides an alternative mechanism to reduce the intrinsic strain in the surface and therefore to reduce the free energy. This phenomenon has to be taken into account if the free energy of the system is to be described correctly. Reconstruction of the clean Pt(100) surface causes a second
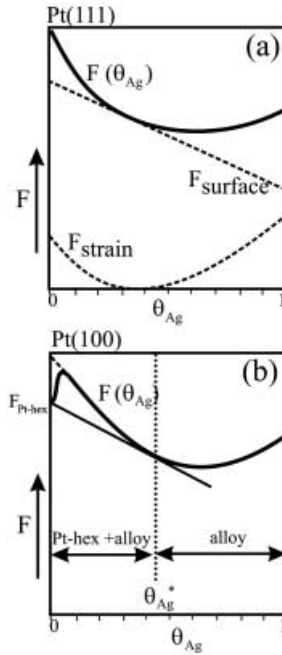
Fig. 3 – Free energy *vs.* coverage curves for Ag on Pt surfaces. (a) The strain and surface energy components are indicated by dashed lines. (See text for explanation of the curve shapes.) The free energy of the surface, indicated by the solid line, is given by the sum of the two dashed lines. The free energy varies monotonically with θ_{Ag} and thus no phase segregation is expected. (b) The free-energy curve is similar to (a) with the exception that the free energy is reduced at $\theta_{Ag} = 0$ by the presence of a surface reconstruction. This results in two minima in the energy. A common tangent construction indicates the presence of a two-phase coexistence regime.

minimum in the free-energy curve at the pure Pt surface ($\theta_{Ag} = 0$). Studies by Yeo *et al.* [26] showed that the reconstructed surface has a free energy that is lower by $\sim 17\%$ compared to the unreconstructed surface. This results in an additional minimum for the free energy as is indicated in fig. 3b. *Consequently, phase segregation can be predicted for* Ag *deposited on* Pt(100). This can be quantified by a common tangent construction in the free-energy diagram. Figure 1b shows that two phases coexist at the surface below a critical Ag coverage θ_{Ag}^*: i) a pure-Pt, reconstructed phase and ii) an Ag/Pt-alloy phase with a Ag concentration of θ_{Ag}^*. For $\theta_{Ag} > \theta_{Ag}^*$, only a single alloy phase exists at the surface with a uniform stoichiometry dictated by the Ag coverage, in agreement with our experimental observations.

In conclusion, we propose that reduction of the intrinsic tensile stress of free surfaces is primarily responsible rather than the stress introduced by the lattice mismatch for the alloying of bulk-immiscible Ag with Pt at its surface. This mechanism is not just limited to bulk-immiscible elements but may also act to stabilize surface alloys of miscible systems. For surfaces that can reduce their intrinsic stress by reconstructing as well as alloying, the competition between these two mechanisms results in a phase segregation. This has the consequence, for example, that no Ag/Pt surface alloy phase can exist with a lower Ag concentration than $\theta_{Ag}^* \approx 0.3\,\mathrm{ML}$ on Pt(100), at $300\,\mathrm{K}$.

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