VOLUME 77, NUMBER 1 PHYSICAL REVIEW LETTERS 1 JULY 1996

Giant Surface Stress in Heteroepitaxial Films: Invalidation of a Classical Rule in Epitaxy

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(Received 23 January 1996)

The first few monolayers of silver deposited on the Pt(111) surface bear a giant compressive surface stress. The stress is more than an order of magnitude larger than the stress caused by the lattice mismatch and results presumably from the charge transfer from Ag to Pt. Upon annealing to 600 K, the stress relaxes by the formation of a mixed Ag-Pt interface. The result shows that the consideration of surface energies and lattice mismatch is not sufficient for the prediction of the growth mode. [S0031-9007(96)00525-X]

PACS numbers: 68.55.–a, 68.65.+g

The structure and morphology of heteroepitaxial systems is determined frequently more by kinetic constraints rather than by the principle of minimization of the free energy. However, when the temperature is sufficiently high or the deposition rate is low, the system has time to relax towards its equilibrium structure during the growth. Under such conditions, the growth modes are determined by the specific free surface energies of the substrate γ_s, the deposited material γ_a, and the specific free energy of the interface γ_i. Complete wetting of the first monolayer occurs if $\gamma_s > \gamma_a + \gamma_i$ [1,2]. When the misfit between the lattice parameters of the deposit and the substrate is small, the near equilibrium growth should proceed as a layer by layer growth, at least up to a critical thickness where the strain energy in the film is so large that formation of dislocations, light or heavy domain walls, or the continuation of growth in the form of three-dimensional clusters (Stranski-Krastanow growth) becomes energetically favorable. As the interfacial energy γ_i is typically small, good candidates for layer by layer (Frank–van der Merwe) growth are deposits of low surface energy on substrates bearing a large surface energy. Frank–van der Merwe growth is expected, in particular, when the substrate and the deposited material have the same crystallographic structure and when the lattice constants differ only by a few percent. Following these criteria, the near equilibrium growth of Ag on Pt(111) should be of the Frank–van der Merwe type. It was indeed found in previous investigations [3–6] that at 300 K the first monolayer of Ag wets the Pt(111) surface and that this monolayer is pseudomorphic with the Pt lattice. Subsequent growth appeared to be kinetically hindered as Ag was found to grow in the form of islands, and islands on top of these islands [6]. This three-dimensional growth is not surprising, however, since even the homoepitaxial growth of Ag on Ag(111) is three dimensional at 300 K [7] because of a relatively large Schwoebel-Ehrlich barrier for the hopping of silver atoms over a step edge. As for the Ag/Ag(111) system, annealing of an Ag film of a few monolayer thickness deposited on Pt(111) should lead to a smoothening of the roughness. Because of the mismatch of the lattice constant of 4.2% (with Ag having the larger lattice constant), one might expect some relaxation of the elastic strain by the formation of discommensurate domain walls, as observed for the reconstructed surfaces of Au(111) or Pt(111) at high temperature [8–12]. The formation of a two-dimensional network of domain boundaries was indeed found in a recent scanning tunneling microscopy (STM) study [13] for the annealed two monolayer Ag film on Pt(111). No atomically resolved images were presented, however, in this work. Guided by the observations on the clean, reconstructed Au(111) and Pt(111) surfaces, the STM images were interpreted by a plausible model of light domain walls separating pseudomorphic domains. According to this model, the silver film would have nearly the density of bulk silver, on the average. Hence, in this model, the elastic strain in the film is considered to be the driving force for the restructuring of the film upon annealing.

By means of a direct measurement of the bending of a thin Pt(111) crystal, we show in this Letter that the stress in thin Ag films deposited on Pt(111) is about an order of magnitude larger than expected from the lattice mismatch of 4.2%. Hence, the classical rules used for the prediction of the (near equilibrium) growth mode and the critical thickness based on surface energies and lattice mismatch are not valid for the Ag/Pt(111) and possibly other systems. The reason for this large compressive stress is probably the considerable charge transfer from Ag into the *d* holes of Pt. The stress and the strain energy associated with the stress make the system unstable, which invalidates the classical criteria for near equilibrium growth modes. The stress in the Ag films disappears almost completely when the films are annealed to 600 K. The observed stress relaxation is incompatible with a model of an only slightly perturbed film after annealing. A considerable increase in the ratios of the Pt 237 eV to the Ag 351 eV Auger signals during annealing provides evidence for a mixed interface.

The stress in the Ag films was experimentally determined by a measurement of the radius of curvature of a 0.29 mm thin platinum crystal. The Pt crystal is part of a

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composite sample holder in which the Pt(111) substrate is mounted between two Mo extension sheets [14,15]. One Mo extension sheet serves as a capacitor plate, the other one for mounting. The variation of the surface stress upon the deposition of adatoms on one side of the Pt substrate causes a bending of the crystal (see inset in Fig. 1). The radius of curvature R is measured as a change of the capacitance using the three-terminal method [16]. The relation between R and the change in the surface stress $\Delta\tau_s$ is calculated using Stoney's formula [17]

$$\Delta\tau_s = \frac{Et^2}{6R(1-\nu)}, \tag{1}$$

where t, E, and ν are the thickness, the elastic modulus, and the Poisson ratio relevant for the (111) oriented Pt substrate, respectively. We note that $\Delta\tau_s$ may alternatively be interpreted as a change in the surface stress of the sample or as the stress in the silver film integrated over the film thickness.

An example of the capacitance measurement is shown in Fig. 1. After the shutter was opened, 0.6 monolayer (ML) of silver was deposited on the clean Pt surface. The rise in the capacitance signal by 3.7×10^{-4} pF corresponds to a compressive surface stress of -3.25 N/m. The small overshoot of the capacitance signal observed immediately after closing the shutter is attributed to an ordering effect in the silver film. A detailed analysis of this phenomenon will be given in a forthcoming paper [18]. Prior to the experiments, the surface was cleaned by subsequent cycles of Ne sputtering and annealing to 1000 K until no impurities were detectable above the Auger electron spectroscopy (AES) noise level. Ag adlayers were deposited on the Pt(111) crystal at temperatures between 300 and 620 K from a carefully degassed Mo crucible using a water-cooled evaporating source [19]. The typical flux rate was 5×10^{-3} ML/s. The base pressure during the evaporation was lower than 3×10^{-10} mbar. Ag coverages were calibrated using a plot of the Auger-signal intensities (351 eV) and Pt (237 eV) versus the evaporation time. The pronounced change in the slope of the plot was used to determine the completion of the first Ag layer [6]. According to our calibration, 1 ML Ag corresponds to an AES ratio (Ag_{351}/Pt_{237}) of 5.1 which is close to the value reported in Ref. [20].

The surface stress induced on Pt(111) by the Ag coverage is shown in Fig. 2. At 300 K, Ag deposition causes a compressive stress which increases almost linearly up to 2 ML with a slope of -8.8 N/m per monolayer and levels off after a deposition of about 4 ML. A more detailed investigation shows that the initial rise below 1 ML has a reduced slope (inset in Fig. 2). This behavior is not unexpected since below 1 ML Ag grows in islands, and the induced stress should relax locally to some extent as long as the islands have not coalesced. Stress relaxation at higher temperatures was investigated by deposition of Ag on Pt(111) after the crystal had been equilibrated at various temperatures between 300 and 620 K [21]. The result for $T = 580$ K is shown as an example (Fig. 2).

The large compressive surface stress induced by the room temperature deposited Ag film exceeds by far the amount which could simply arise from a reduction of the tensile surface stress of clean platinum which is 5.6 N/m [22]. Another possible source of the stress could be the elastic deformation of the pseudomorphic Ag film. The surface stress arising from the elastic deformation should vary linearly with coverage, as indeed observed for the first three layers. It is easily seen, however, that the observed surface stress exceeds also by far the stress which could arise from the elastic deformation. With the boundary condition that the stress vertically to the film, τ_{33}, be zero, one obtains for the stress parallel to the plane of the

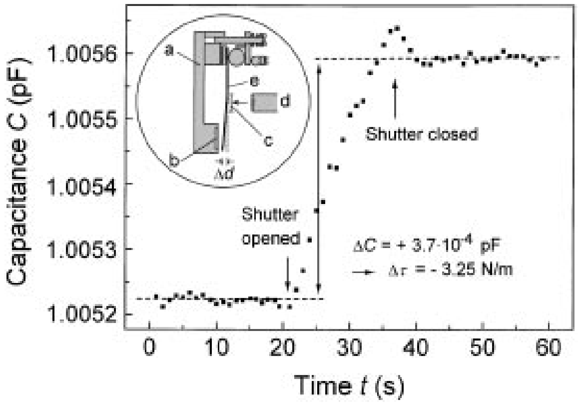

FIG. 1. Capacitance signal measured during the deposition of 0.6 ML of silver at 300 K. Inset: Schematic drawing of the cantilever bending setup [(a) sample holder, (b) electrode, (c) sample length, (d) evaporation source, (e) composite substrate holder]. The capacitively determined change of distance Δd between the lower part of the sample holder and the inner electrode is converted into the surface stress change $\Delta\tau$.

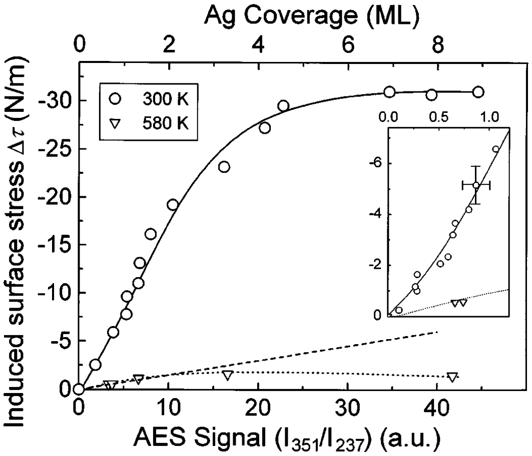

FIG. 2. Measured surface stress versus silver coverage with the Pt(111) sample held at $T = 300$ and 580 K. The dashed line indicates the stress expected from the lattice misfit.

film τ_{11},

$$\tau_{11} = \left(c_{11} + c_{12} - 2\frac{c_{12}^2}{c_{11}}\right)\varepsilon_{11}\,. \tag{2}$$

After inserting the elastic constants c_{11} and c_{12} of silver [23] and the misfit of -4.2%, a surface stress of -0.75 N/m per ML is calculated from the elastic deformation which is more than an order of magnitude smaller than the observed value. In other words, the observed surface stress cannot have its origin in the elastic deformation of the silver film. This invalidates the standard concept in heteroepitaxy which relates the stress in thin films and the critical thickness of a thin pseudomorphic film to the elastic deformation. With the stress being as high as it is, the elastic energy stored in the film also becomes quite high. The variation of the elastic energy density is

$$\delta u_{\mathrm{el}} = 2d\tau_{11}\delta\varepsilon_{11} = 2d(s_{11} + s_{12})\tau_{11}\delta\tau_{11}\,. \tag{3}$$

If one assumes the elastic coefficients s_{11} and s_{12} of the Ag film to be at their bulk value, one obtains an energy of 1.75 eV per atom in the Ag film for the coverage range below 3 ML where the surface stress rises linearly with the film thickness. This elastic energy exceeds the surface energy of Ag (0.55 eV/atom [22]) and of Pt (1.05 eV/atom [22,24]), and therefore necessarily becomes a decisive factor for the near-equilibrium growth mode [25].

In the calculations above we have used bulk elastic constants for the ultrathin Ag films. To test this approximation, we have performed effective medium theory (EMT) calculations for a self-supporting, three-layer Ag film [26]. Specifically, we calculated the change in total energy as the film is subjected to a series of compressive and tensile strains. From this simulation, we obtain a value for the quantity $c_{11} + 2c_{12}$. For a fully relaxed film, this value is equal to that of bulk Ag (both calculated within the EMT and measured [23]). If the film is subject to a 4% compressive strain, the value increases by 35%. Thus, changes to the elastic constants which arise from compression of the film increase the surface stress, but are insignificant compared to the effect needed to explain the measurement.

The huge surface stress observed for the Ag/Pt(111) system is probably related to the charge transfer from Ag film to the Pt substrate. Charge transfer must occur because of the lower work function of Ag [4 eV for Ag(111) [27]] compared to Pt [5.7 eV for Ag(111) [28]], or in another terminology, the transfer occurs because of the lower electronegativity of Ag. For single Ag atoms on Pt(111), this charge transfer was, in fact, already observed in a first principle local density functional calculation [29]. For Ag, the electrons at the Fermi level are nearly free electrons. The reduction of electron density in the Ag film causes an increased repulsion of the ion cores in the Ag film, and therefore a compressive stress. While a full explanation of the measured stress clearly must await a more rigorous treatment of the total energy of the Ag/Pt(111) system, we may estimate the surface stress induced by the charge transfer from a crude continuum model [30]. In this continuum model, the charge transfer is assumed to be homogeneous parallel to the surface. The electrostatic energy is then

$$E_{\mathrm{estat}} = \frac{\Delta q^2}{2\varepsilon_0 A}\, d_{\mathrm{eff}}\,, \tag{4}$$

where Δq is the amount of charge transfer, A is the surface area, ε_0 is the absolute dielectric permeability, and d_{eff} is an effective thickness of the capacitor. Using the definition of the surface stress,

$$\tau_s = \frac{1}{A}\,\frac{\partial E_{\mathrm{estat}}}{\partial \varepsilon}\,, \tag{5}$$

one obtains

$$\tau_s = -\frac{\Delta q^2}{2\varepsilon_0 A^2}\, d_{\mathrm{eff}}\,. \tag{6}$$

The effective thickness d_{eff} depends on the charge distribution in the silver film perpendicular to the interface. If one assumes that for the first few monolayers the silver film is homogeneously depleted of the charge and that the counter charge sits in the localized d holes of the first layer of Pt atoms, then the effective thickness of the capacitor d_{eff} would be half the thickness of the Ag layer. In that case, Eq. (6) would describe the initially linear increase of the stress correctly, as well as the sign of the surface stress. According to this model, the experimentally observed surface stress would require a charge transfer of 0.43 e/atom. Considering the number of d holes in Pt (0.65 e/atom [31]), this number appears to be in the regime of reasonable charge transfers.

It was shown in a previous study [13] that annealing of a 2 ML Ag film deposited at room temperature leads to the formation of a network of domain walls. Although no atomically resolved STM images were presented, it was concluded that the domain walls separate patches of commensurate Ag islands. The small change in the interatomic distances associated with this proposed structure could not relax the huge surface stress. In order to exclude a large change of the lattice parameter of the 2 ML Ag film upon annealing which could have escaped the attention of previous researchers, we have looked at the low energy electron diffraction pattern before and after annealing and found that the mean lattice constant of the surface does not change by more than a few percent at the most. As seen above, such a small change in the lattice parameter could not relax the huge surface stress. It is furthermore unlikely that the charge transfer could be affected considerably by a minor restructuring of the surface since the charge transfer reflects atomic properties of Ag and Pt. We propose therefore that the relaxation of the surface stress upon annealing is caused by an intermixing of Ag and Pt, in a similar way as was indeed observed for submonolayer coverages [4]. This model of an intermixing is corroborated by our observation that, upon annealing of a 2 ML

Ag film to 600 K, the ratio of the Pt 237 eV peak to the Ag 351 eV Auger peak increases by 40%. An additional stringent argument for the intermixing of Ag and Pt arises from the coverage dependences of the stress at 300 and 580 K itself (Fig. 2). According to [4,13], continuous deposition at 580 K should lead to an intermixed surface for coverages below 1 ML followed by a restoration of a flat nonintermixed Pt surface and a layerwise deposition of further Ag layers. In that case, one should find for coverages beyond 1 ML the same stress as for the room temperature deposited films, since a possible elastic relaxation for the annealed films could produce a significant change in the stress, as shown above.

In summary, we have established that thin heteroepitaxial films may bear a large stress of a value far beyond the stress induced by the misfits of the lattice. This stress constitutes a new parameter which determines the growth modes in heteroepitaxial growth much more significantly than the lattice mismatch. It is proposed that the stress arises from the charge transfer between the adlayer and the substrate. In the specific case of Ag/Pt(111), both the charge transfer and the lattice misfit work in the same direction of a compressive stress within the Ag film. It is conceivable, however, that the charge transfer induced stress could balance the stress induced by the misfit so that a heteroepitaxial, near equilibrium growth of a few monolayers could occur even when the misfit is rather large.

The skillful preparation of the thin platinum crystal by U. Linke and partial financial support from the Fond der Chemischen Industrie are gratefully acknowledged. The authors benefited from stimulating discussions with M. Hohage, P. Zeppenfeld, M. A. Krzyzowski, and the critical reading of the manuscript by M. Giesen-Seibert and G. Rosenfeld. We are also indebted to P. Stoltze for providing us with his EMT codes and potentials.

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[30] This model is rather popular in electrochemistry. Since the energy is necessarily quadratic in the charge transfer, the model fails to describe adsorbate induced tensile stresses. The latter are a result of a laterally inhomogeneous charge transfer and a redistribution of the charge in the surface layer. We have also estimated the charge transfer induced stress in the Ag film by considering the total energy of the film in the free electron approximation. While a charge transfer from Ag to Pt produces the correct sign of the stress the model fails to deliver the experimentally observed values of the stress for reasonable charge transfers.
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