

## Changing morphology of metallic monolayers via temperature controlled heteroepitaxial growth

Holger Röder, Harald Brune, Jean-Pierre Bucher and Klaus Kern

*Institut de Physique Expérimentale, EPF-Lausanne, CH-1015 Lausanne, Switzerland*

Received 23 July 1993; accepted for publication 19 August 1993

Variable temperature scanning tunneling microscopy at substrate temperatures between 25 and 550 K reveals a transition from diffusion limited aggregation to thermodynamic equilibrium in the two-dimensional (2D) monolayer growth of Ag on the Pt(111) surface. Via deposition temperature control the “nanostructure” of the grown 2D-Ag-films can be tuned in a very defined way: from randomly distributed adatoms and small clusters, through highly dendritic islands, dense large islands with irregular or smooth boundaries to an equilibrium 2D condensate-gas mixture.

The epitaxial growth of thin films vapour-deposited on solid substrates has been a topic of much interest [1], ever since the pioneering studies of I.N. Stranski and W. Kossel in the twenties. Today numerous modern technologies rely on the routine fabrication of ultrathin, atomically structured epitaxial layers. The progress in the growth of these epitaxial films is ultimately related with the improved understanding of the microscopic mechanisms of the nucleation and growth processes involved. The application of improved and novel surface science techniques in the last decade [2], in particular spatial resolving techniques like field ion microscopy (FIM) [3] or scanning tunneling microscopy (STM) [4], has indeed revealed many atomic details of the film growth, which have been inaccessible to direct experimental observations before.

It is generally accepted that there are three principal types of growth possible. Detailed phenomenologic theories predicting these growth modes have been developed [5,6] and applied with some success. These theories are based on the thermodynamic properties of the film–substrate system, i.e. they are only valid in the thermodynamic limit (at high deposition temperatures) where the film is able to reach its thermo-

dynamic equilibrium configuration. At all temperatures below, the film growth and the resulting film morphologies will be governed by kinetic effects. Many novel and fascinating phenomena, which are related to the growth kinetics have, indeed, been discovered in recent experiments [7–9].

In this paper we present an STM study of the initial stages of silver heteroepitaxy on the Pt(111) surface, demonstrating for the first time, the transition from kinetic to thermodynamic growth of a two-dimensional system. Vastly different submonolayer film morphologies are observed in the kinetic growth regime ( $T \leq 270$  K). These morphologies can be tuned by a careful control of the substrate temperature during deposition (at constant deposition rate).

The experiments were performed with a new variable-temperature UHV-STM, which operates in the temperature range from 25 to 600 K. The instrument is a home-built modified “beetle” type tunneling microscope which is combined with a specially designed cryogenic sample holder. After the initial cooling down of the liquid He-cryostat ( $\sim 10$  min) any sample temperature can be stabilized for subsequent STM measurements within 5–10 min. A detailed description of the instru-

ment will be given elsewhere [10]. The Ag (purity 99.995%) submonolayer films were evaporated with an MBE-Knudsen-cell at a background pressure better than  $2.0 \times 10^{-10}$  mbar. The deposition rate was fixed to  $R = 1.1 \times 10^{-3}$  ML/s. All STM images have been acquired in a constant current mode with tunneling currents from  $I = 1.0$  to 3.0 nA at sample voltages from  $U = -0.5$  to  $-1.5$  V. No influence of the tunneling parameters on the imaging of the film morphology was observed. The lateral thermal drift was determined to be lower than 5 nm/min at cryogenic temperatures. Images were acquired in 2 min; the images shown here are not corrected for lateral drift and not filtered. All images except fig. 2d were recorded in differential mode, which means that the derivative of the lines of constant tunnel current is recorded, whereas fig. 2d shows an STM image with the grey scale representing the absolute tip height. In this absolute image a pla-

nar background has been subtracted to tilt atomic terraces in such a way that they are represented as horizontal areas.

Single Ag-adatoms are observed only at the lowest temperatures studied, i.e. at  $T \leq 40$  K. At these temperatures their mobility is low enough to prevent clustering on the time scale of the STM experiment. At deposition temperatures above 40 K, Ag-adatoms are found to cluster on the Pt(111) surface, forming two-dimensional (2D) monolayer thick islands. Clustering is observed down to the lowest coverages studied ( $\theta_{\text{Ag}} \approx 0.01$  ML). This behaviour is consistent with attractive mutual interactions between adsorbed Ag-atoms and a high degree of lateral mobility. At temperatures of 40–50 K the typical cluster size is  $\text{Ag}_2$ , as determined by the ratios of coverage and island density for various coverages. These dimers have indeed been found to be the stable nucleus for temperatures up to 100 K.

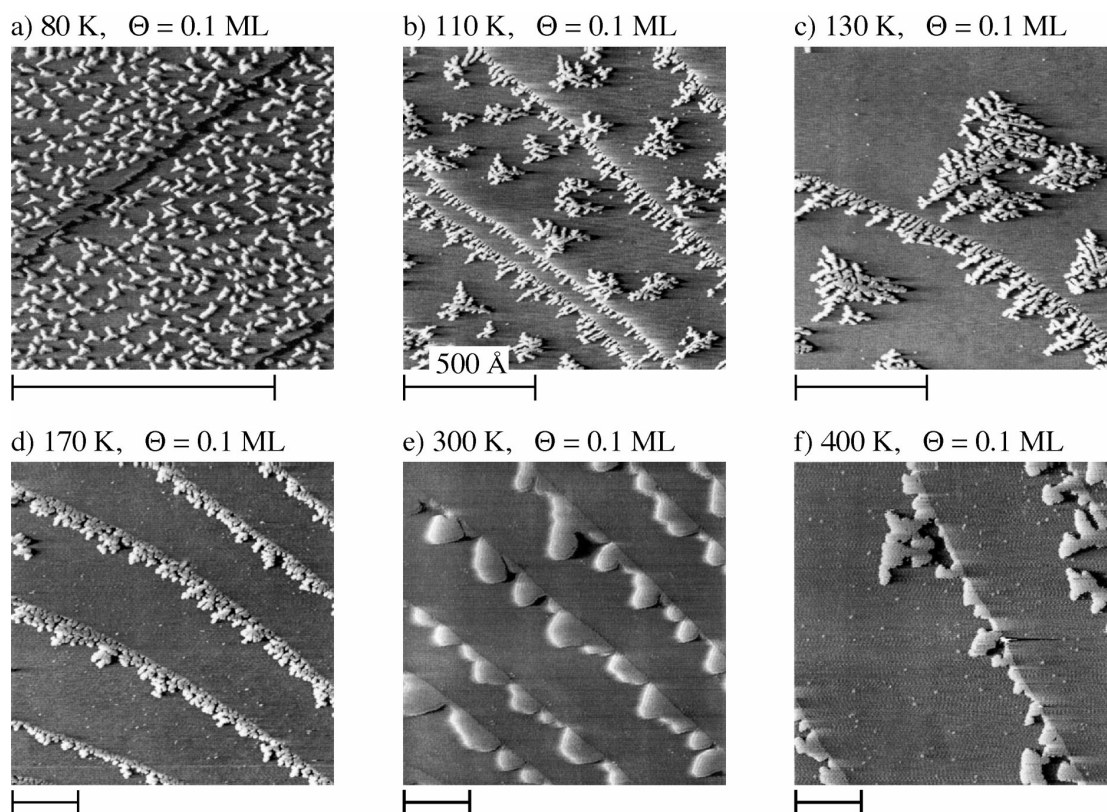


Fig. 1. STM topographs of low coverage Ag submonolayer films ( $\theta = 0.1$  ML) on a Pt(111) surface, grown and imaged at the temperature indicated. The lateral scale is given by the bar, representing a length of 500 Å.

Submonolayer Ag-films grown at different substrate temperatures exhibit a wealth of characteristic nanostructures, which is illustrated in figs. 1 and 2. In the temperature interval from 50 to 70 K, the Ag-adatom mobility is still low and only small compact clusters (2–20 atoms) grow. At 80 K (fig. 1a) the adatom mobility is already sufficient to grow larger clusters, their average size is 19 Ag-atoms at a coverage of 0.1 ML in fig. 1a. The small islands are randomly distributed on the Pt-terraces and exhibit a characteristic Y-shape. The arms of the Y's show preferred orientations roughly  $120^\circ$  apart, reflecting the trigonal symmetry of the Pt(111) substrate. Surprisingly, only one of the two symmetrically equivalent Y-orientations is formed during growth. In all experiments performed so far, exclusively clusters with one arm perpendicular to the preexisting Pt(111) steps

(probably  $\{11\bar{1}\}$  running along the  $\langle 1\bar{1}0 \rangle$  azimuth) are present on the surface. We have presently no explanation for this striking observation. Increasing the temperature above 90 K the Y's grow larger and start to branch (fig. 2a).

At deposition temperatures above 110 K the preexisting steps of the Pt(111) surface become increasingly important. Due to the increased binding energy the platinum step edges act as sinks for Ag-adatoms moving on the Pt-terraces. Thus, if the average diffusion length of Ag-adatoms  $\Lambda_a$  is sufficiently large for the adatoms to reach a substrate step, Ag-islands nucleate preferentially at Pt-step-edges and subsequently propagate onto the lower terrace. This becomes evident from the submonolayer morphologies shown in figs. 1b–1d, 2b and 2c, covering the temperature range from 110 to 170 K. While at

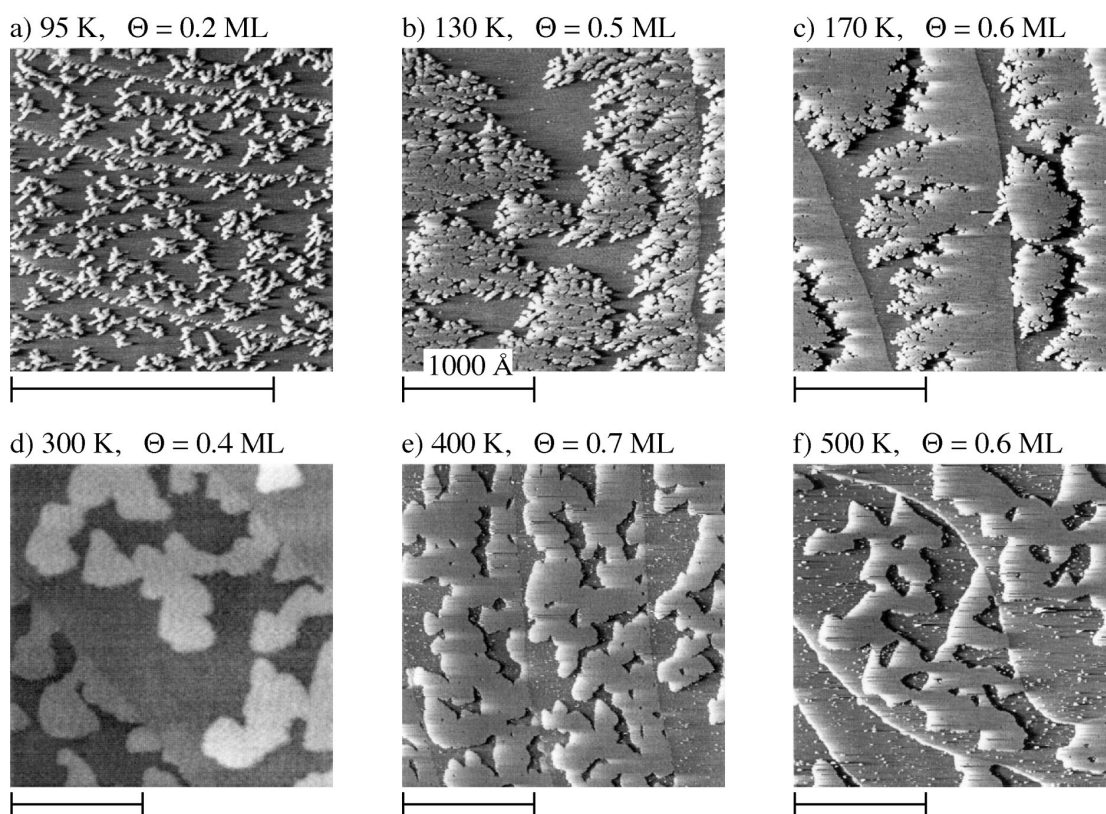


Fig. 2. STM topographs of higher-coverage Ag submonolayer films ( $0.2 \leq \theta \leq 0.7$  ML) on a Pt(111) surface, grown and imaged at the temperature indicated. The lateral scale is given by the bar, representing a length of 1000 Å.

110 and 130 K steps are only partially wetted and the majority of nucleation still takes place on terraces, at 170 K  $\Lambda_a$  is already larger than the average distance between neighbouring steps ( $\Lambda_s \approx 1000 \text{ \AA}$ ) and nucleation takes place almost exclusively at platinum step edges.

The Ag-islands nucleating and growing on terraces in the temperature range from 100–150 K have a highly dendritic form. Hwang et al. [9] and Bott et al. [11] have recently observed similar dendritic island shapes in the growth of Au on Ru(0001) at 300 K and in the homoepitaxy of Pt on Pt(111) at 205 K, respectively. The dendritic form is believed to be caused by the hindered atom diffusion along the step edges bordering the islands. For Au on Ru(0001) the fractal dimension of the islands has been deduced to 1.72 [9], in quantitative agreement with the 2D diffusion-limited-aggregation (DLA) growth mechanism [12]. We are currently underway to analyse the dendritic nature of the Ag-islands in detail as a function of the deposition temperature [10].

Above  $\sim 160 \text{ K}$  very large and dense Ag-islands grow away from the substrate steps, as shown in figs. 1d, 1e, 2c and 2d. These islands have a surprisingly low density of defects, even at  $T = 170 \text{ K}$  in fig. 2c. From the fact that these monoatomic islands are imaged as flat areas, whereas subsequent Ag-layers show a domain-wall network with vertical corrugation (not shown here) we conclude that the monoatomic thick islands are  $(1 \times 1)$  structured. This is in accordance with sharp  $(1 \times 1)$  LEED patterns observed for submonolayer coverages. In the absolute STM image fig. 2d the Ag-islands are imaged by about  $0.6 \text{ \AA}$  higher than the platinum steps and appear therefore brighter than the adjacent platinum terraces. The slightly larger Ag lattice constant would only result in a height difference of  $0.1 \text{ \AA}$ , most of the increased imaging of Ag-islands must therefore be due to electronic effects, probably due to the lowered workfunction by Ag adsorption [13]. While the island boundaries at room temperature are rather smooth, the boundaries of the islands grown at 170 K are rather irregular, reminiscent of the hindered step edge diffusion in the formation of dendritic islands discussed above.

The film morphologies grown below 270 K are indeed metastable and have kinetic origin. After brief annealing to 300–600 K all low temperature structures convert into much more compact forms. Only the film structure grown around 300 K is unaltered by annealing up to 600 K [14]. A detailed report of these annealing experiments will be given elsewhere [10]. The generic growth forms observed in the kinetic regime can be understood in the framework of a simple qualitative argument. The evaporation of adatoms onto a substrate drives the system into nonequilibrium, which tries to restore equilibrium by forming islands. The adatoms migrate on the surface and when meeting each other they can form critical nuclei, which subsequently can grow to islands by attachment of further adatoms. Nucleation and growth are competing processes and the migration barrier of adatoms together with the deposition rate determine the outcome of this competition. The diffusion of a Ag-adatom is terminated when it hits a critical nucleus or an island and condenses there. With increasing coverage the density of stable nuclei increases until a saturation density is reached. From there on impinging Ag-atoms condense solely at existing islands. At this state they are migrating the average distance  $\Lambda_a$ .

At low temperatures ( $\leq 50 \text{ K}$ ) migration is slow with respect to deposition resulting in small values for  $\Lambda_a$  and a high density of stable nuclei (dimers at these temperatures). With increasing temperature  $\Lambda_a$  increases and already at low coverages island growth sets in (see fig. 1a). With further increasing  $\Lambda_a$ , the saturation island density decreases and larger clusters (islands containing several tens to thousands of atoms) can grow, the shape of which is now determined by the average diffusion length of atoms adsorbed at the perimeter of the island  $\Lambda_1$ . For small values of  $\Lambda_1$  the islands grow ramified while for higher values of  $\Lambda_1$  the islands condense in compact shapes. At even higher temperatures, the average adatom diffusion length becomes of the order of the average length between two neighbouring substrate steps  $\Lambda_s$ . More and more nucleation can take place at substrate steps and eventually for  $\Lambda_a \gg \Lambda_s$  all islands grow from step edges, a

phenomenon which is called “step flow”. The perimeter shape of these islands is still determined by the magnitude of  $A_1$ , and can be irregular or smooth.

This simple argument strictly holds of course only for the case of homoepitaxy with no structural competition between adlayer and substrate. In heteroepitaxy the structural mismatch adds as additional variable to the problem. In the case of Ag on Pt(111) however, as mentioned above, the first Ag-monolayer is nicely accommodated at the Pt(111) surface forming a perfect ( $1 \times 1$ ) adlayer. The lateral corrugation of the Ag–Pt(111) interaction potential seems to be sufficient to stabilize the 4% compression with respect to a Ag(111) bulk plane. The magnitude of this compression is, indeed, equal to the compression observed on the reconstructed (111) surfaces of Au and Pt, which thereby minimize their surface free energy [15,16].

The submonolayer film morphology grown at 300 K was already attributed to a quasi-equilibrium state because it was found to be unchanged by annealing. The local 2D thermodynamic equilibrium of Ag submonolayer films grown above 300 K becomes even more evident by inspection of figs. 1f, 2e and 2f showing STM images of the 400 and 500 K monolayer. These images reveal a two-phase coexistence of a 2D solid phase (large condensed Ag-islands) in equilibrium with a 2D gas phase which is composed of small Ag-clusters and probably Ag-adatoms (“real” 2D gas). At these elevated temperatures atoms from the perimeter of the condensed islands evaporate continuously onto the substrate terraces (and readsorb from the terraces) establishing a 2D gas phase, the density of which corresponds to its respective 2D vapour pressure. Further proof of this “2D equilibrium” interpretation is given by two experimental observations: (1) At constant coverage the density of the 2D gas phase increases with increasing temperature (compare the images 2e and 2f) and (2) at constant temperature first a “real” 2D gas phase is formed at very low coverages ( $\theta_{\text{Ag}} \leq 0.03$  ML) before large Ag-islands (2D condensate) are formed which remain in coexistence with the 2D gas phase. Two recent He-scattering experiments of the submonolayer Ag epitaxy on Pt(111) are

also clearly in favour of a 2D gas condensate phase transition in the temperature range between 320 and 600 K [17].

The observation of a 2D thermodynamic equilibrium state and the 2D gas condensate phase transition of the Ag-monolayer at elevated temperatures is in perfect accordance with earlier experimental results of Kolaczkiwicz and Bauer [18], who observed the 2D gas condensate phase transition for Cu, Ag and Au submonolayers on the W(110) surface. Our STM results show, however, that the deluted phase is a non-ideal 2D gas, mainly composed of small clusters, requiring substantial corrections to the model used to extract quantitative thermodynamic parameters.

The STM measurements at elevated temperatures might also be of relevance to another observation made by Kolaczkiwicz and Bauer [19]. From a detailed analysis of the 2D heat of evaporation versus temperature of submonolayer gold and silver films on W(110) they concluded that a two-dimensional roughening transition of the island edges should take place at  $T_{\text{R}}^{2\text{D}} = 500$  K (Ag). An enhanced ruggedness of the island perimeter (of the condensed phase) is indeed observed at temperatures above 400 K in our experiment (see fig. 2f) and is probably due to 2D edge roughening of the Ag-islands.

The STM measurements in the temperature regime from 50 to 140 K have also been used to determine the diffusion barrier of single Ag-adatoms on the Pt(111) surface. The analysis of the measured saturation density of stable islands yields an activation energy of  $E_{\text{d}} = 140 \pm 10$  meV. Detailed results will be presented elsewhere [10]. This value is higher than the diffusion barrier of  $E_{\text{d}} = 58 \pm 3$  meV recently calculated by Blandin and Massobrio [20] for the Ag/Pt(111) system but is very close to the migration barrier of 150 meV determined for Ag adatom diffusion on the Ag(111) surface [21].

This work was generously supported by the Swiss National Science Foundation. The authors thank Udo Linke of KFA Jülich for his expert cutting and polishing of the Pt-crystal-surface. We gratefully acknowledge stimulating discussions with R. David, C. Massobrio, Th. Michely and B. Poelsema.

**References**

- [1] R. Kern, G. Le Lay and J.J. Metois, in: *Current Topics in Materials Science*, Vol. 3, Ed. E. Kaldis (North-Holland, Amsterdam, 1979) p. 131.
- [2] M.G. Lagally, Ed., *Kinetics of ordering and growth at surfaces* (Plenum, New York, 1990).
- [3] S.C. Wang and C. Ehrlich, *Phys. Rev. Lett.* 67 (1991) 2509.
- [4] Y.W. Mo, J. Kleiner, M.B. Webb and M.G. Lagally, *Phys. Rev. Lett.* 66 (1991) 1998.
- [5] E. Bauer, *Z. Krist.* 110 (1958) 372.
- [6] J.A. Venables, G.D.T. Spiller and M. Hanbücken, *Rep. Prog. Phys.* 47 (1984) 399.
- [7] R. Kunkel, B. Poelsema, L.K. Verheij and G. Comsa, *Phys. Rev. Lett.* 65 (1990) 733.
- [8] D.D. Chambliss, R.J. Wilson and S. Chiang, *Phys. Rev. Lett.* 66 (1991) 1721.
- [9] R.Q. Hwang, J. Schröder, C. Günther and R.J. Behm, *Phys. Rev. Lett.* 67 (1991) 3279.
- [10] H. Röder, H. Brune, J.P. Bucher and K. Kern, to be published.
- [11] M. Bott, Th. Michely and G. Comsa, *Surf. Sci.* 272 (1992) 261.
- [12] P. Meakin, in: *Phase Transitions and Critical Phenomena*, Vol. 12, Eds. C. Domb and J.L. Lebowitz (Academic, Press, New York, 1988) p. 335.
- [13] T. Härtel, U. Strüber and J. Küppers, *Thin Solid Films* 229 (1993) 163.
- [14] Annealing above 620 K results in an irreversible alloying transition. H. Röder, R. Schuster, H. Brune and K. Kern, *Phys. Rev. Lett.* 77 (1993), in press.
- [15] J.V. Barth, H. Brune, G. Ertl and R.J. Behm, *Phys. Rev. B* 42 (1990) 9307.
- [16] A.R. Sandy, S.G.J. Mochrie, D.M. Zehner, G. Grübel, K.G. Huang and D. Gibbs, *Phys. Rev. Lett.* 68 (1992) 2192.
- [17] G. Vandoni, Ch. Félix, W. Harbich, R. Monot and J. Buttet, to be published; G. Rosenfeld, A. Becker, B. Poelsema, L.K. Verheij and G. Comsa, to be published.
- [18] J. Kolaczkiwicz and E. Bauer, *Surf. Sci.* 155 (1985) 700.
- [19] J. Kolaczkiwicz and E. Bauer, *Phys. Rev. Lett.* 54 (1985) 574.
- [20] P. Blandin and C. Massobrio, *Surf. Sci.* 279 (1992) L219.
- [21] G.W. Jones, J.M. Marcano, J.K. Nørskov and J.A. Venables, *Phys. Rev. Lett.* 65 (1990) 3317.