Microscopic View of thin film growth

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The technology of thin film growth with the ability to create artificial structures on a submicrometer scale has led to many new applications as well as to the discovery of new physical phenomena. Despite the considerable progress in this field, the knowledge of the nonequilibrium growth techniques involved in the building of artificially structured materials is far from being sufficient. Our understanding of the processes which control growth at a fundamental, atomic level is still limited [1].

Even simplest methods of producing thin films like the vapor phase epitaxy (VPE), i.e., the deposition of thermal energy atoms onto a crystalline substrate, has a high complexity in a microscopic view. The arrangement of the film atoms is determined by basic atomic processes (surface diffusion, nucleation, etc.) as well as by the energetic of the interface created, i.e., the structural and electronic competition between film and substrate material. The initial random distribution of adatoms onto the substrate surface will condense to clusters with a certain size and shape monitoring the chemical and electronic properties of the adlayer. The optimization of growth techniques towards smoother interfaces and lower defect densities requires the knowledge of what happens on an atomic scale during the thin film formation process.

It will be demonstrated here, that with nanometer scale microscopy the dynamic processes controlling growth are quantitatively measurable. The used observation method with subnanometer resolution is variable temperature scanning tunneling microscopy (STM). This home built instrument measures the topography of a surface at temperatures between 25K and 800K [2]. The model-system chosen is silver layer growth onto a platinum substrate with (111) orientation. The films are deposited by thermal evaporation in an ultrahigh vacuum environment. Afterwards they are imaged by STM under isothermal conditions, i.e., growth and imaging temperature are identical. The amount of deposited silver (the coverage Θ) is measured in monolayers (ML) of the Pt(111) substrate (= 1.5×10^{15} atoms per cm^2).

In the following, two examples are given to illustrate the power of this approach. In a first step we will look to the nucleation at the solid film phase. Condensation and thermalisation of the Ag atoms takes place at the point of impact onto the substrate. The Ag adatoms are then able to make a random walk visiting different adsorption sites. For a jump to a next neighbor binding site they have to overcome an energetic diffusion barrier. For $T \leq 45K$ the thermal energy is too small for surface diffusion and the Ag adatoms stick in their initial random positions. Higher temperature increases mobility and a nucleation event becomes possible, i.e., the encounter of two diffusing atoms. Once such a dimer has been formed, Ag atoms arriving in the neighborhood will more probably attach to this nucleus than form new islands. Finally, at a critical Ag coverage the entire substrate will be saturated with nuclei and further deposition leads only to the growth of existing islands.

The experimental observation of this nucleation to growth transition presented in Fig.1 showing the film morphology as a function of Ag coverage grown at T = 75K with a deposition flux R of 1ML in 900s. In the STM image a) silver islands appear as bright dots. Their density ρ has been also
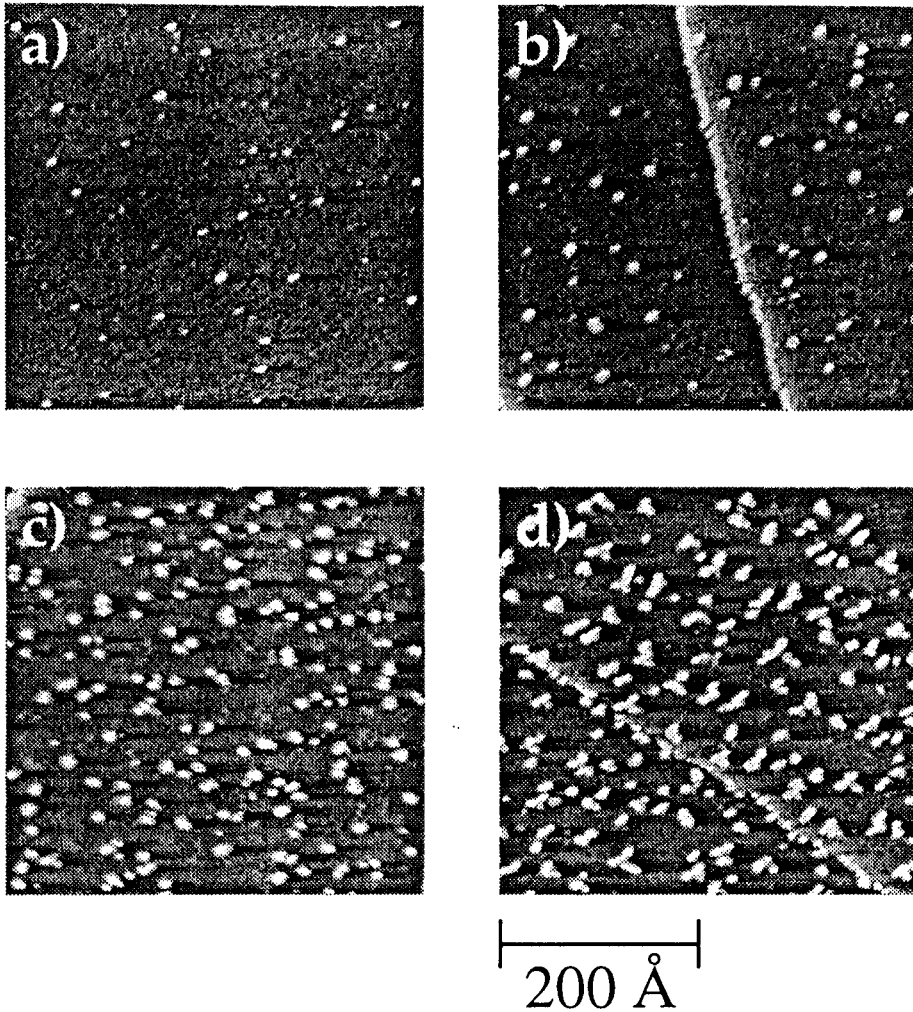
200 Å

Fig.1: Nucleation of Ag on Pt(111): Four STM images showing the evolution of the Ag island shape and density as function of coverage at 75K: a) $\Theta = 0.24\%$ of 1ML, $\rho = 0.10\%$ of 1ML, $n = 2.4\pm0.4$; b) $\Theta = 0.60\%$, $\rho = 0.23\%$, $n = 2.6\pm0.5$; c) $\Theta = 3.0\%$, $\rho = 0.46\%$, $n = 6.4\pm1.1$; d) $\Theta = 6.0\%$, $\rho = 0.50\%$, $n = 11.9\pm2.0$

evaluated in ML, i.e., the number of islands per surface site. Dividing the coverage Θ by the island density ρ gives the average island size n. In a) the majority of islands are dimers (n = 2.4). Increasing the coverage Θ by a factor 2.5 in b) leaves the mean size practically unchanged (n=2.6). This means that from a) to b) arriving Ag atoms form solely new dimers and only nucleation takes place. In c) the coverage increase by a factor of 5 is only compensated by a two times higher island density and consequently the mean size of the islands goes up to 6.4, i. e., the growth of existing islands starts. Doubling again the coverage, the island density stays practically constant and reaches its saturation value $\rho_{sat.}$ in d). The growth of two times larger islands is now visible supported by the change in island shape. While in c) they appear rather symmetric, in d) they start to branch into three directions with an angle separation of 120°. This branching process will be discussed below by analyzing larger ramified islands. From the above coverage series we can conclude that the ramification of island starts at a critical size of n ≈ 7.

The nucleation process contains direct information about the diffusion, since the mobility of the Ag adatom determines the competition between the creation of new and the growth of existing islands. Increasing the average diffusion length with increasing temperature the saturation island density ρ_{sat}
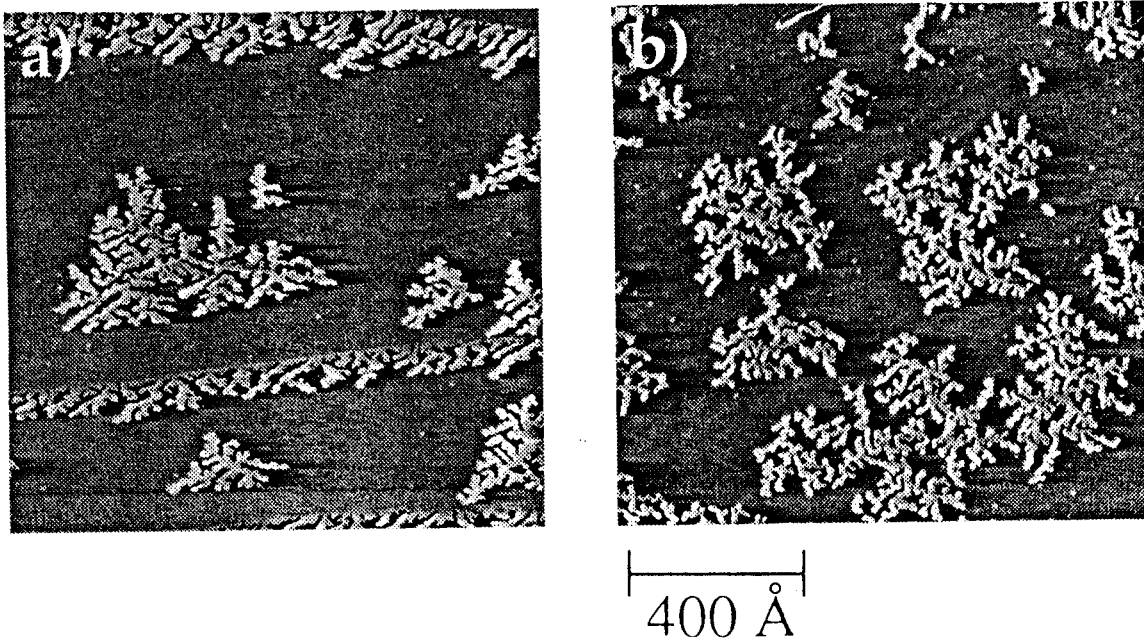
400 Å	

Fig.2: Shape variation: Two STM images showing the shape of large Ag islands grown with different deposition flux: a) $\Theta = 12\%, T = 130K, R = 1ML$ in 900s, dendritic shape; b) $\Theta = 12\%, T = 110K, R = 1ML$ in 64000s, randomly ramified shape

will decrease. Fitting the ρ_{sat} (T) data to rate equations of nucleation theories a precise value of the diffusion barrier and the frequency of atomic motions can be determined.

The second example deals with the ramified island shape and its modification by the deposition flux. The large islands in Fig.2 a) and b) have been grown at T =130K and 110K, respectively. The fractal structure of the randomly ramified aggregates in b) can be explained by a "hit and stick" model. Each Ag atom sticks irreversibly at the point of first contact with the growing aggregate. Theoretical simulations of this growth condition predict island forms with a fractal dimension of 1.70, which had been experimentally verified for the Ag aggregates on the Pt(111) surface. Consequently, at the temperatures used in Fig.2 the diffusion of atoms along the island border is limited. Only upon heating up to $\approx$ 200K the ramified shapes convert to compact shapes. Triggered by the higher flux used in a) the global island shape is distinctly different from the fractal shape of b). While the aggregates in a) show three preferential growth directions (dendritic form), the branches in b) are randomly oriented. The explanation of this phenomenon is related to the atomic symmetry of the surface causing an anisotropy of the growth directions. In b) roughly one atom per second is attached to an island. Therefore successive sticking events are independent from each other and the branching is random. At the higher (factor 70) deposition rate in a) coupling of sticking events preferentially takes place in three growth directions and the islands grow in an oriented shape.

In conclusion, it has been shown that characteristic parameters of elementary growth steps in vapor phase epitaxy like diffusion barriers, binding energies and frequency factors can be determined by variable temperature STM. Once this information has been obtained, artificially formed film aggregates can be built, i. g., cluster with a well-defined size. This becomes possible by changing the diffusion conditions of the condensing atoms, i.e., with an appropriate choice of the substrate temperature and the deposition flux[3].

[1]   E. Bauer, et al., Journal of Material Research 5 (1990) 852.

[2]   H. Röder, H. Brune, J.-P. Bucher and K. Kern, Surface Science 298 (1993) 121.

[3]   H. Röder, E. Hahn, H. Brune, J.-P. Bucher and K. Kern, Nature 366 (1993) 141.