Spontaneous formation of nanostructures at metal-surfaces

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Abstract

Two rather different adsorbate systems are studied in-situ with STM which lead to the spontaneous formation of nanostructures within the adsorption layer. Firstly, in ultrahigh vacuum bilayers of Ag on Pt(111) are shown to form a periodic network of dislocation lines between patches of fcc- and hcp-stacking of the two Ag layers. Secondly, the electroadsorption of SO_4^{2-} anions is demonstrated to cause the formation of a highly periodic Moiré-structure at a Cu(111) electrode surface in contact with sulphuric acid. Despite the totally different ambients both systems undergo similar structural changes as a function of coverage and temperature in UHV, and electrode potential and time in solution. Both surfaces might well serve as templates for the design of more complex architectures of periodic nanostructures.

Introduction

Nanostructures will play a key role in future technologies. Due to their strongly reduced dimensions their properties can not be predicted by simple extrapolation from the macroscopic properties of the same material. Instead, their properties are directly governed by quantum mechanics (quantum size effects) and may thus be tuned by varying the size, in order to serve technological applications, as for example in the development of new materials, in information technology and sensorics, in heterogeneous catalysis etc. Surface science holds a key position in providing the experimental methods and theoretical models for a basic understanding of both the mechanisms of nanostructure formation and the resultant properties.

Systems based on nanostructures may either simply consist of a large number of disordered nanometer particles (as e.g. on supported catalysts) or should additionally exhibit a periodic arrangement of the particles (as e.g. for high density data storage devices). Both kinds of nano-systems can either form spontaneously ("god made") or be artificially fabricated by nano-machining ("man made"). In this work emphasis will be placed on the presentation and discussion of nanostructures which form by spontaneous self-organization into more or less periodic two-dimensional "nano-grids". These nano-grids could be used as templates for more complex architectures of periodic nanostructures. Two examples will be given, namely the formation of a dislocation-network in Ag-layers on Pt(111) as prepared by vapor deposition in ultrahigh vacuum, and the growth of SO_4^{2-}-stabilized nanometer structures at a Cu(111)/electrolyte interface. Both systems have been studied in the group of the authors with in-situ Scanning-Tunneling-Microscopy (STM), that is in ultrahigh vacuum or in an electrochemical cell, in combination with other surface sensitive methods (XPS, LEED, HREELS etc.) or electrochemical cyclovoltammetry (CV).

Results and discussion

Dislocation network in Ag-layers on Pt(111)

The growth structure of heteroepitaxial films of one metal on the surface of an unlike metal substrate is not only determined by interatomic bond energies and kinetic parameters (activation barriers) but also by the difference in atomic radii of both constituents, that is by their lattice mismatch. Due to the 4,1% larger lattice constant of Ag (4,0856Å) compared to Pt (3,9237Å) a monolayer of Ag on Pt(111) (one monolayer defined as 1 Ag atom per Pt surface atom) is under high compressive stress. For one monolayer of silver on Pt(111) this additional elastic energy term is obviously compensated by the energy gain due to the formation of Ag-Pt bonds; the first Ag layer on Pt(111) is pseudomorphic [e.g. 1]. This is no longer true for the second and higher Ag layers because the Ag-Ag interaction energy (E_{Ag-Ag} = 254 kJ/mol) is substantially lower than the Ag-Pt interaction energy (E_{Ag-Pt} = 283 kJ/mol) [2-3]. As a consequence the second and higher layers require an additional mechanism to release their strain energy, namely the

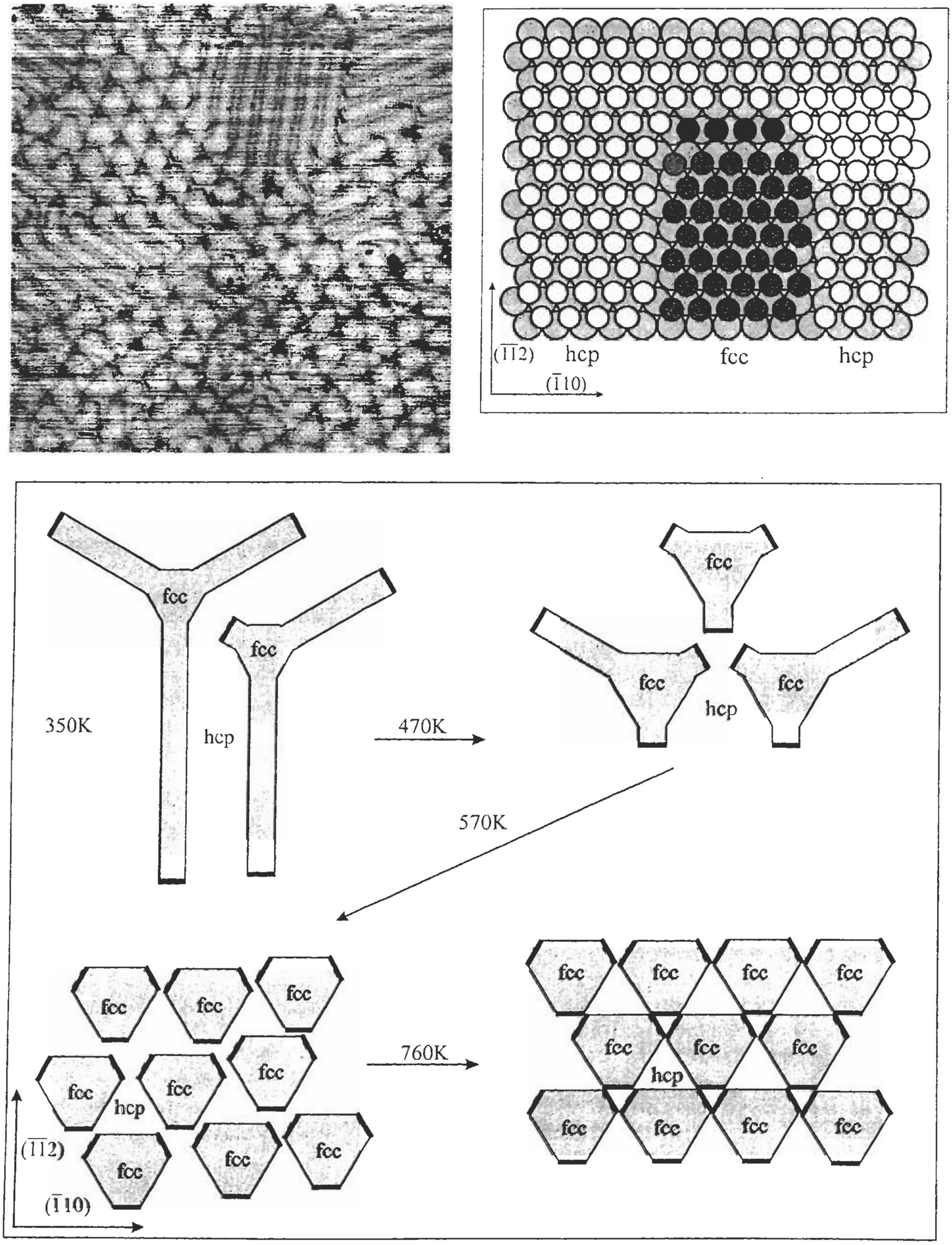

Fig.1 a) Dislocation network within a Ag double-layer deposited at 470K on Pt(111) and annealed at 570K. Two kinds of dark lines (short and deep dark, and long and less dark) are identified with short rows of Ag atoms in bridge-positions and dislocation lines between fcc- and hcp-regions (see model in 1b which shows one of three possible orientations). c) Illustration of the evolution of the dislocation network as a function of annealing temperature.

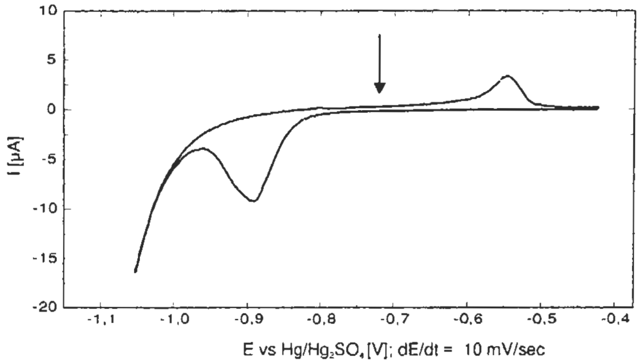

Fig. 2a

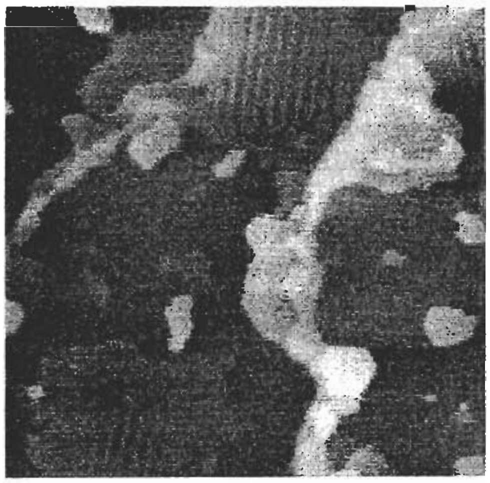

Fig. 2b

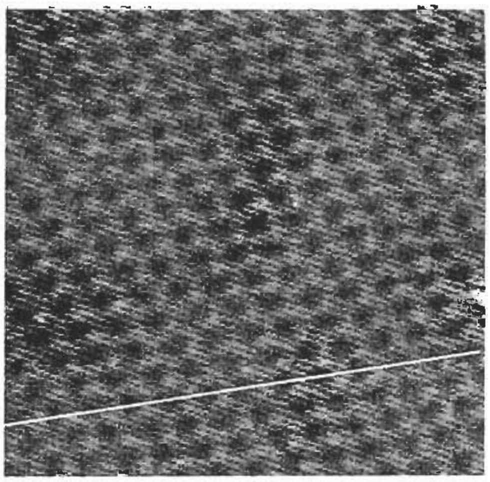

Fig. 2c

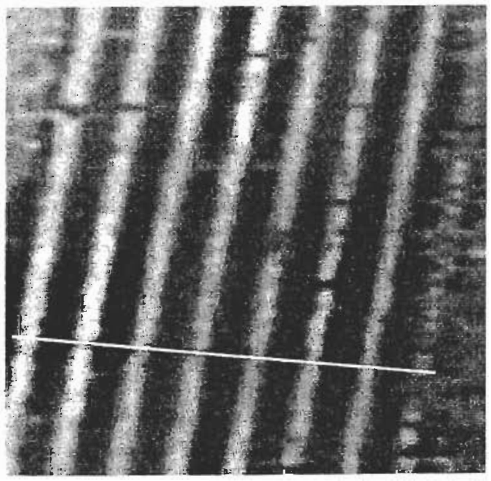

Fig. 2d

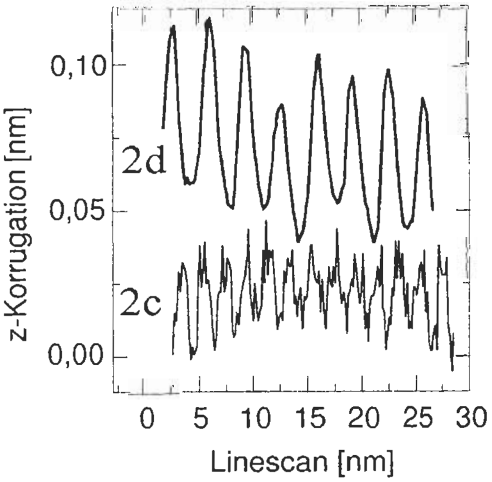

Fig. 2e

Fig.2 a) Cyclic voltammogram of Cu(111) in 10 mN H_2SO_4 with the SO_4^{2-}-adsorption and SO_4^{2-}-desorption peak at -550 mV and -880 mV vs. Hg/Hg_2SO_4, respectively. b) STM-image of the Cu(111) surface registered in-situ at an electrode potential of -720 mV (arrow in Fig. 2a). Close-ups of the coexisting Moiré- and stripe-structure are displayed in Fig. 2c and d, respectively. e) Line scans along the white lines in Figs. 2cand d showing periodicity and amplitude of both structures on the nanometer scale.

incorporation of dislocations.

Fig. 1a shows a Ag double-layer region of 100 nm x 100 nm on Pt(111) which was detected by STM after the deposition of 1,8 ML of silver at 470 K followed by annealing at 570 K for 100 s. Two kinds of dark lines separate brighter areas. The long dark lines correspond to direct transitions between regions with Ag atoms occupying fcc- and hcp-sites, respectively (see Fig. 1b). Their three (equivalent) directions are due to the threefold symmetry of the substrate. The short darker lines terminate the long fcc-regions (upper right corner of Fig. 1a) or form increasingly regular triangles (lower right corner of Fig. 1a), and are tentatively assigned to a short row of Ag atoms in bridge positions (darkest atoms in Fig. 1b) [5]. Both types of dark lines thus correspond to dislocation lines of reduced Ag atom density (light domain boundaries) which lead to strain relaxation (compared to a pseudomorphic Ag-layer), and which due to a reduced local charge density are imaged dark. Fig. 1c finally illustrates the evolution of the dislocation network as a function of deposition or annealing temperature. With increasing temperature long "arms" of fcc-structure, which provide only uniaxial strain relaxation perpendicular to the long dark lines, shrink ultimately leading to a fine-meshed dislocation network between alternating regions of fcc- and hcp-stacking. The growth of this highly periodic structure is driven by the expansion of the Ag-typical fcc-structure and a more isotropic strain-relaxation.

Structure formation at the Cu(111)/SO$_4^{2-}$ electrolyte interface

Fig. 2a displays the cyclic voltammogram of Cu(111) in 10 mN aqueous H_2SO_4 solution measured with a scan rate of 10 mV/s versus a Hg/Hg_2SO_4 reference electrode. The anodic peak at -550 mV and the cathodic peak at -880 mV correspond to adsorption and desorption of SO$_4^{2-}$-anions, respectively, as verified by XPS after sample transfer into a UHV-chamber [6]. The large separation of both peaks on the voltage scale suggests a strong kinetic hindrance of the SO$_4^{2-}$-adlayer formation/ dissolution. This in turn provides the basis for studying the SO$_4^{2-}$ anion adsorption at different potentials (as a function of time).

As an example Fig. 2b shows an in-situ STM image of 52 nm x 52 nm registered with an STM bias voltage of 160 mV at an electrode potential of -720 mV (marked by an arrow in Fig. 2a). Overall, different terraces and islands of copper are displayed in different grey tones. In addition, however, two distinct fine structures are clearly visible on the Cu surface, namely (here larger) regions of a hexagonal Moiré-structure [7] as well as regions of long parallel bright lines. Both highly periodic structures are enlarged in Figs. 2c and 2d (both 30 nm x 30 nm). Line scans along the white lines are shown in Fig. 2e and result in wave lengths of 23,3Å (Moiré) and 37,8Å and amplitudes of 0,3Å and 0,7Å , respectively. Both structures are assigned to an SO$_4^{2-}$-stabilized restructuring of the Cu(111) electrode in contact with the electrolyte, with the Moirébeing the final, more stable structure. Note the similarity to the above described Ag/Pt(111): The Moiré-structure is more isotropic than the line-structure. The influence of the SO$_4^{2-}$-adlayer becomes also apparent from the size and shape of the small Cu-islands in Fig. 2b; the island boundaries always encompass multiples of one Moiré unit [8].

Summary and conclusion

Both examples, Ag/Pt(111) prepared by vapor deposition in UHV and SO$_4^{2-}$/Cu(111) at the Cu (111)/electrolyte interface, show spontaneous structure formation on the nanometer scale. Depending on the preparation conditions, namely coverage and temperature or electrode potential and time the evolution from uniaxial to more isotropic periodic structures is observed on the threefold symmetric substrates in both ambients. These or similar systems and the careful control of their growth conditions may provide a fruitful route to arrive at highly periodic and technologically relevant nanostructures.

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