Growth-mode-specific intrinsic stress of thin silver films

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The growth and morphology of thin films are directly related to their intrinsic stress. In the system silver on mica (001) *three different Vollmer-Weber-type growth modes* were clearly distinguished by *in situ* intrinsic-stress measurements, using a very sensitive cantilever beam device. For epitaxial silver films, a stress contribution due to the formation of single crystalline domain walls is observed.

The growth of thin films has been the subject of numerous investigations in the past.[1,2] In order to correlate theoretical models of film growth with experimental results, however, there is still a lack of experimental techniques, which allow the *in situ* observation of film morphology at the respective preparation conditions (UHV, elevated substrate temperatures, etc.). The relation between the mechanical stress and the film microstructure offers an additional approach to solve this problem. It is well known that thin films develop large intrinsic stress during their preparation.[3] Structural elements such as grain boundaries,[4] dislocations,[5] voids,[3] impurities,[6,7] and other defects have been located as regions of strain in the films. In addition, strain at the film-substrate interface due to surface tension effects,[8,9] different thermal expansion coefficients or lattice mismatch,[10] as well as dynamical processes such as film recrystallization,[11,12] contribute to the total intrinsic stress. Since the size of most of these stress contributions is directly correlated with film morphology as well as film growth, important structural information can be extracted from the intrinsic stress. Measurements of the intrinsic film stress therefore are a sensitive tool to study nucleation and growth as well as time development of thin films *in situ* and in a nondestructive manner.

Here we used intrinsic-stress measurements to study the growth of silver on single-crystalline mica. Generally, the growth mode of silver is determined by (i) its mobility, which in the present case has been controlled by the substrate temperature and (ii) its wetting behavior. Since silver does not wet mica, and depending on its respective self-diffusion and surface diffusion three different island or Vollmer-Weber (VW) growth modes have been clearly distinguished by their intrinsic stress. We can thus present here a unique picture of different possible VW-type growth modes: (i) in the temperature range between 220 and 470 K well-known polycrystalline VW-type film growth [Fig. 1(b)], (ii) at 110 K VW-type nucleation and columnar grain growth [Fig. 1(a)] as expected from comparison with the high melting point (which denotes low mobility) metals, and (iii) at temperatures above 470 K epitaxial VW-type film growth [Fig. 1(c)], where a stress mechanism due to the formation of single crystalline domain walls is detected.

The experiments were performed in an UHV chamber with a base pressure better than 1×10^{-10} mbar. Silver was deposited from resistively heated Knudsen-type evaporation sources at pressures better than 2×10^{-9} mbar. The deposition rate was 0.1 ± 0.01 nm/s and has been controlled by a quartz-crystal microbalance. The mica (001) substrates were cleaved in air and have been dehydroxylated[13] before each experiment by heating in UHV to 770 K in order to establish reproducible substrate conditions. The stress measuring device is based on the cantilever beam principle and includes facilities for heating and cooling the substrate. The substrate deflection is determined with a resolution better than 10 nm by a sensitive differential capacitance method. The respective film forces F—normalized to the substrate width w—were calculated from the substrate deflection δ using Stoney's formula[14]

$$\frac{F}{w}=\frac{Et^2}{3l^2(1-\nu)}\delta$$

adapted to the proper experimental geometry. E, γ, l, and t are Young's modulus, Poisson's ratio, length, and thickness of the substrate, respectively. For the structural investigation of the epitaxial silver films a second mica substrate was coated together with the cantilever beam substrate and transferred *in situ* to a four-grid low-energy electron diffraction (LEED) optics. Details of the experimental setup will be described elsewhere.[15]

Figure 2 shows the force per unit width versus thickness and time curves of silver films that have been deposited up to thicknesses of 100 nm onto mica (001) at various substrate temperatures. All film forces have been measured *in situ* and continuously during as well as after

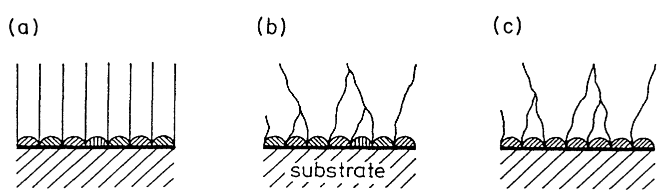

FIG. 1. Schematic illustration of the three modes of Vollmer-Weber-type film growth: (a) columnar, (b) polycrystalline, and (c) epitaxial VW growth.

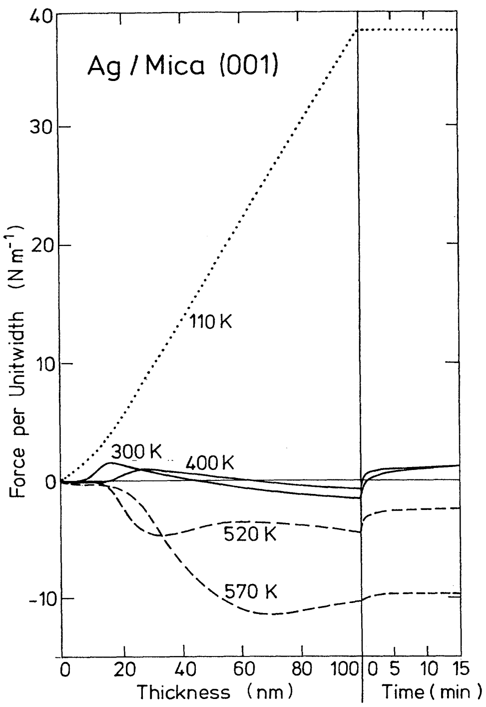

FIG. 2. Film forces per unit width vs thickness (left side) and time (right side) of silver films deposited onto mica (001) at various temperatures. By convention positive and negative values denote tensile and compressive forces, respectively.

film deposition. In the temperature range under investigation three types of curves have been observed. At a substrate temperature of 110 K the film force is tensile only and increases from the very beginning of film growth (dotted line in Fig. 2). In the medium temperature range (220–470 K) small tensile forces are measured at low and small compressive forces at higher film thicknesses (solid lines in Fig. 2). At temperatures above 470 K large compressive forces were detected already in the early stages of film growth (dashed lines, Fig. 2).

In the following we attempt to summarize the present understanding on stress mechanisms and correlated microstructure and base our discussion on the film forces of the medium temperature films (solid lines in Fig. 2). Film forces with similar line shapes have been reported previously for silver films deposited onto amorphous substrates such as glass[16] and MgF_2 (Ref. 17) as well as for other low melting point materials.[17] The shape of these curves was found to be characteristic of *polycrystalline VW-type film growth,* which comprises island, network, and channel stages until the film becomes continuous. Silver on single-crystalline mica (001) exhibits the same growth mode: VW mode is confirmed by *in situ* measurements of the electrical film conductance; x-ray diffraction shows that film growth occurs exclusively with (111) planes parallel to the substrate, while LEED reveals random in-plane orientation. These findings are also in agreement with previous transmission electron microscopy (TEM) investigations.[18] Due to the analogy in stress and microstructure we interpret the present force curves using the stress model for amorphous substrates.[8,9] The maxima of the film forces have been found to correspond to those mean film thicknesses, at which the films become completely continuous,[16,8] and therefore reflect the number and size of the islands at percolation (end of network state). Notice that the maximum is shifted from 17 to 28 nm, when the substrate temperature is raised from 300 to 400 K. This indicates that due to the increased surface diffusivity of silver at higher temperatures the number of islands at percolation decreases, while the island size increases. The film forces of the discontinuous films are tensile and governed mainly by two mechanisms: (i) recrystallization,[11] which is accompanied by a densification of the films, and (ii) relaxation of polycrystalline film grain boundaries[4] (see below), where the atoms in average are more widely spaced than in equilibrium grain boundaries, which were used in theoretical models up to now.[19] The compressive stress of the continuous films has its origin in the compressive strain built up in the precoalescence film region during the island-growth stage. Due to the surface tension the equilibrium lattice constant of individual islands is smaller than in the bulk. It increases with island growth (lattice expansion mechanism[8]), but since the film adheres to the substrate, a compressive strain develops within each island (capillarity strain). When the film is continuous, this capillarity strain is transmitted layer by layer into the thick film.[8,9] The larger the mean island size the smaller the respective stress contribution (capillarity stress) at the percolation point. The tensile force measured after having finished the film deposition indicates continuing recrystallization of the films.[12]

The stress contributions of grain-boundary relaxation and capillarity stress mechanisms can be calculated using a simple model to estimate the island size at percolation from the force maxima (solid curves in Fig. 2). The model is based on the following assumptions: (i) individual islands are hemispherical and of equal size, (ii) after percolation first all of the channels are filled; then the island radius R at percolation is equal to the mean film thickness at the end of coalescence. With these assumptions the capillarity stress σ_C can be calculated from Thomson's equation[20]

$$\sigma_C = 2\varepsilon / R$$

with ε being the surface tension ($\varepsilon_{Ag} = 1.4 \pm 0.3$ N m^{-1}).[21] The calculated capillarity stress contributions of -16×10^7 and -10×10^7 N m^{-2} are in good agreement with the incremental film stress of -6.6×10^7 N m^{-2} and -4.5×10^7 N m^{-2} observed experimentally at 300 and 400 K, respectively (Fig. 2). From the difference between the calculated and experimental data we obtain a first estimate for the grain-boundary relaxation stress of the order of 5×10^7 N m^{-2}.

When the silver film is deposited at a substrate temperature of 110 K (dotted curve in Fig. 2) a different stress behavior is observed. The film stress is tensile only and increases from 2×10^8 N/m^2 at about 10-nm average film thickness. Due to the low self-diffusion of silver at this temperature recrystallization processes are inhibited and

VW-type columnar grain growth is the prevailing growth mode. This interpretation is further confirmed by the observation of a constant film force at the end of the film deposition indicating that no recrystallization takes place. In an analogy to the behavior of high melting point materials deposited at room temperature[22] the film stress is dominated by grain-boundary relaxation. Its value even exceeds the tensile strength of silver ($\approx 1.5\times10^8$ N m^{-2}),[23] which can be understood by accounting for the decreasing number of dislocations in small grains. Due to the large number of grain boundaries and the low mobility the information of the capillarity strain is lost at about 10 nm mean film thickness. Using the model from above an average grain size of about 3 nm is estimated from the change of incremental stress.

When the substrate temperature is raised above 470 K (dashed curves in Fig. 2), a huge compressive stress contribution is determined in the early stages of film growth that never has been found in previous investigations of thin metal films on amorphous substrates. On the single-crystalline mica (001) surface, silver is well known to grow epitaxially at substrate temperatures of about 570 K.[18] This is confirmed by our LEED results (Fig. 3). They show that silver grows with (111) planes parallel to the mica (001) surface and Ag[$11\bar{2}$] oriented parallel to mica [100]. The lattice constants of Ag(111) and quasihexagonal mica (001) are 0.289 and 0.52 nm, respectively, leading to a giant lattice mismatch. It is still about 4% even with four silver atoms in the two-dimensional quasihexagonal unit cell of mica, corresponding to a lattice mismatch stress of 0.75 N/m per monolayer. But no respective stress contribution has been detected here. This indicates that the film-substrate interaction is sufficient to impose the epitaxial orientation on the growing silver films, but it is too weak to transmit the lattice constant of mica to the silver film. These findings seem to be typical of epitaxial VW systems[15] and are in contrast to Stranski-Krastanov systems, e.g., Ge/Si (001),[10] where the large lattice mismatch stress of 0.8 N/m per monolayer has been detected in the monolayer range. At mean film thicknesses of about 15 nm a compressive stress contribution appears that increases gradually with substrate temperature up to 570 K. It dominates until the onset of percolation as has been determined from simultaneous conductance measurements. This stress contribution seems to be characteristic of *epitaxial VW-type film growth,* which becomes the predominant growth mode at 570 K. We attribute this contribution to the coalescence of individual islands, which is the prevailing growth process near percolation, at which many instant grain boundaries are formed at the same time. Although the majority of islands is epitaxially aligned, they still may be displaced from each other by a nonintegral number of lattice spacings due to the misfit between the lattices of silver and mica. Therefore, when two islands

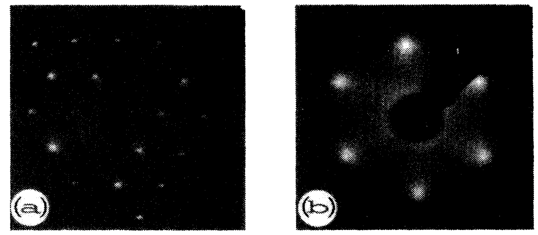

FIG. 3. *In situ* LEED patterns of (a) mica (001) before Ag deposition and (b) 100-nm Ag grown epitaxially on mica (001) at 570 K; primary energy $E_p = 125$ eV.

grow together, they may have to strain at the grain boundary in order to get into perfect register. Matthews,[24] who investigated defects in epitaxial silver films on mica with transmission electron microscopy, reported about 10^{10} dislocations per cm^2 as major imperfections. The majority of dislocations forms during the network stage of film growth to accommodate the displacement misfit strain of coalescing islands; a detailed discussion can be found in Ref. 25. The appearance of compressive stresses in the present case is contrary to the coalescence of randomly oriented islands of polycrystalline films, where "large angle grain boundaries" always give rise to net tensile stresses. Similar results have been observed with Au and Cu films deposited onto mica (001) and will be published elsewhere.[15] At higher film thicknesses a tensile stress contribution is detected, which peaks at 60 nm for a substrate temperature of 520 K. From comparison with the polycrystalline films (solid lines in Fig. 2) we conclude that the maxima again indicate the film thicknesses at which the films become completely continuous.

In conclusion it has been shown that intrinsic-stress measurements are powerful tools for *in situ* investigations of film growth. Due to the correlation between intrinsic stress and film morphology the film force developing during film deposition directly reveals the growth mode of the films. In the experiments presented here it was even possible to distinguish between three different VW-type growth modes. In addition, microstructural information, e.g., on grain size, island density, etc. is provided as well as valuable stress data useful for theoretical modeling on, e.g., grain boundaries. It should be emphasized that due to the absence of *lattice mismatch stress,* mica proved an ideal substrate to investigate the stress contribution of the network stage of epitaxial thin films in an unconcealed manner.

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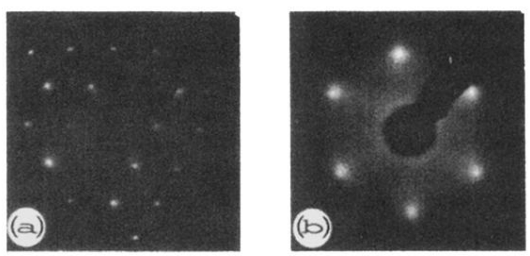

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