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Surface structure of thin metallic films on mica as seen by scanning tunneling microscopy, scanning electron microscopy, and low-energy electron diffraction

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Silver, gold, palladium, and chromium films have been evaporated onto mica at substrate temperatures ranging from $-150\,°C$ to $+400\,°C$. Scanning tunneling microscopy (STM) images were obtained under ambient conditions. Silver and gold films exhibit an increasing grain size together with a grain flattening as the substrate temperature increases. At 275 and 400 °C for silver and gold, respectively, terraces with dimensions of the order of more than 100 nm are formed. However, also characteristic holes on the scale of a few 10 nm were always present. In addition, the gold films exhibit characteristic holes on the nanometer scale. While the larger holes are also visible on scanning electron microscopy micrographs, the smaller are not. Low-energy electron diffraction patterns prove the (111) orientation of both, silver and gold films; however, the quality of the silver patterns is better, consistent with the more perfect terraces as seen by STM. Palladium, evaporated at temperatures up to 350 °C did not exhibit similarly large and flat terraces. An improvement is achieved if prior to the palladium, silver is evaporated at elevated temperatures. Chromium, contrary to the fcc metals Ag, Au, and Pd crystallizes bcc, and forms a stable surface oxide under ambient conditions. The reproducibility of its STM images under ambient conditions depends on the applied bias and can be attributed to the surface oxide. Films evaporated at 50 °C exhibit a grainy structure. For the 350 °C films areas with a columnar morphology have been observed. In conclusion, epitaxially grown Ag(111) films evaporated at 275 °C onto mica have been shown to exhibit large flat terraces suitable for nanoscale modifications and chemisorption studies with the STM.

I. INTRODUCTION

The surface structure of thin metallic films plays an important role for various interfacial phenomena, e.g., in electrochemistry and the chemical physics of thin film superstructures. Evidently, the interfacial structure is of interest, both on the microscopic and on the more macroscopic length scales. For example, Langmuir–Blodgett (LB) monolayers are typically 2 nm thick and are intended to coat a solid substrate with a monomolecular film over macroscopic dimensions. Therefore, the flatness and perfection of the substrate on these scales is of major importance. The goal of the present study is the determination of the surface structure of thin evaporated metal films on mica. It is also motivated by the need for well characterized alternative substrates for nanolithography with the scanning tunneling microscopy (STM),[1] LB films and STM studies of organic adsorbates.[2]

STM is a formidable tool to determine the structure of metallic surfaces in various ambients over the whole range from the optical scale (i.e., μm) to the atomic scale (i.e., 0.1 nm). One of the first metallic systems STM has been applied to were polycrystalline silver and gold films as well as epitaxially grown Au(111) films on mica, revealing the grain structure of the polycrystalline films as well as atomically flat terraces with a $23 \times \sqrt{3}$ reconstruction of the epitaxial

gold.[3-7] In the present study the surface structure of thin films made from four different metals on mica have been investigated under ambient conditions by STM and, for comparison, by SEM and LEED. Silver has been chosen since it can be grown epitaxially on mica.[8] It is similar to gold, however its richer surface chemistry makes it an interesting candidate for chemisorption studies. Also palladium is of particular interest in surface chemistry due to its catalytic activity. It crystallizes, like silver and gold, in a fcc lattice; its melting point, however, is considerably higher, causing a different epitaxial growth behavior. Chromium is a completely different case since it crystallizes bcc; noteworthy, it is harder than the other metals and forms a stable thin surface oxide under ambient conditions.

II. EXPERIMENT

Green mica substrates have been obtained from Mica Supplies (UK). They were cleaved freshly in air and metallic films of 100 nm tickness were evaporated thermally onto them at an evaporation rate of 0.06 nm/s. The base pressures during evaporation were varied between 10^{-5} and 10^{-9} mbar. The STM instruments employed in this study have been described before.[9,10] They were operated under high vacuum and ambient conditions with electrochemically
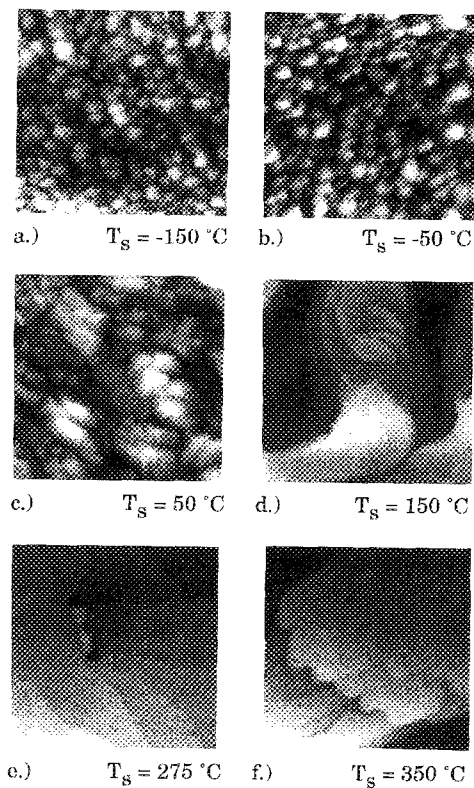
FIG. 1. STM images of Ag(111) on mica, evaporated at different substrate temperatures. (a) $-150\,°C$; (b) $-50\,°C$; (c) $+50\,°C$; (d) $+150\,°C$; (e) $+275\,°C$; (f) $+350\,°C$. Image size: 250 nm×250 nm.

etched Pt/Ir tips and a tunneling current between 200 pA and 2 nA. SEM micrographs were made with a JEOL 848IC microscope.[10] Low-energy electron diffraction (LEED) patterns were obtained *in situ* with a four grid reverse LEED optics (Omicron).

III. RESULTS AND DISCUSSION

The structure of thin evaporated metal films depends on a number of parameters, including the substrate material, its temperature during evaporation, evaporation rate, vacuum quality, and film thickness. The substrate temperature during evaporation plays a particularly important role.[8] Therefore, a temperature series for both silver and gold was taken. Figures 1 and 3 demonstrate that at low substrate temperatures Ag and Au films are grainy, with both grain size and peak-to-valley roughness around 5 nm for the $-150\,°C$ sample. With increasing temperature the grain size grows, and flat terraces appear. In the case of silver, small terraces are already present on the $50\,°C$ sample [Fig. 1(c)], and larger ones at $150\,°C$. In passing, note the screw dislocation in Fig. 1(d). Beyond a temperature of about $300\,°C$ the silver surface roughens again on a lateral scale of a few 100 nm [Fig. 1(f)]. This is in good agreement with earlier reports;[11] it may be due to enhanced outgassing of the mica substrate at elevated temperatures. The peak-to-valley roughness in Fig. 1(f) amounts to 40 nm. The roughness is also indicated by a loss of metallic reflectivity. At a given temperature, the grains are generally larger for silver than for gold, consistent
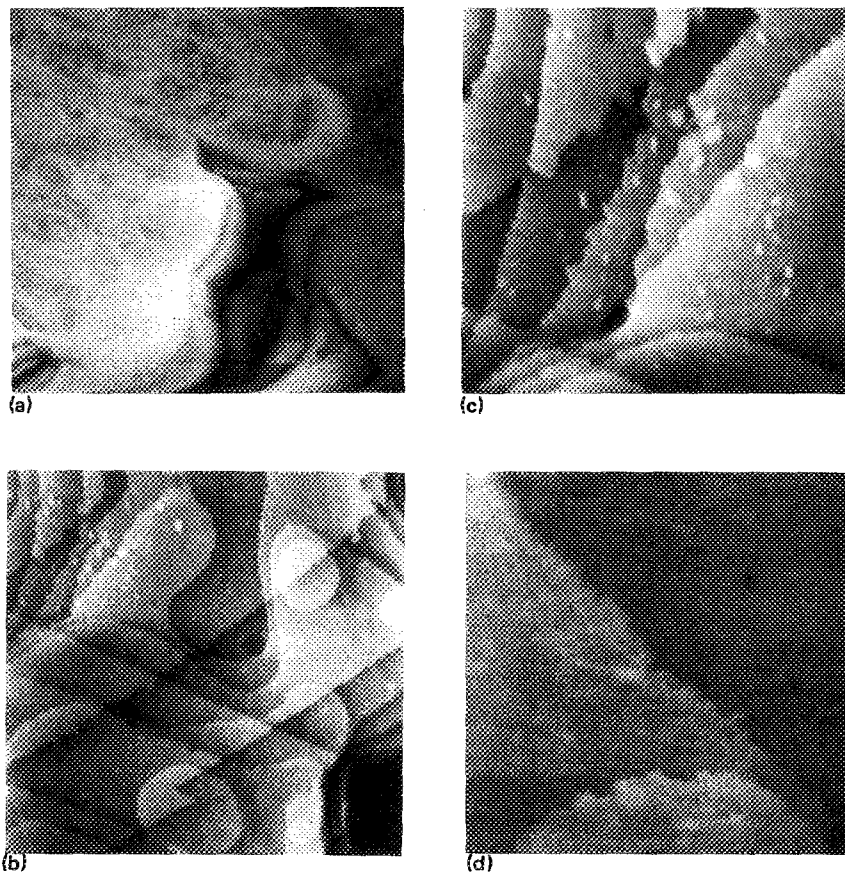

FIG. 2. STM images of Ag(111) on mica, evaporated at 275 °C. Image size: (a) 1.2 μm×1.2 μm; (b) 850 nm×850 nm; (c) 380 nm×380 nm; (d) 140 nm×140 nm.

a.) $T_S = -150\ °C$ b.) $T_S = -50\ °C$

c.) $T_S = 50\ °C$ d.) $T_S = 150\ °C$
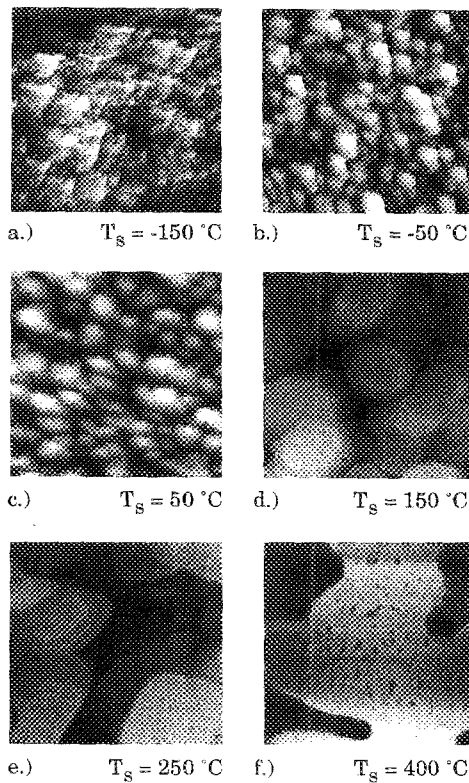
e.) $T_S = 250\ °C$ f.) $T_S = 400\ °C$

FIG. 3. STM images of Au(111) on mica, evaporated at different substrate temperatures. (a) $-150\ °C$; (b) $-50\ °C$; (c) $+50\ °C$; (d) $+150\ °C$; (e) $+250\ °C$; (f) $+400\ °C$. Image size: 250 nm×250 nm.

with the lower melting point of silver. The largest terraces have been found around 275 and 400 °C for silver and gold, respectively. However, it must be noted that even the largest terraces are not bigger than a few 100 nm in diameter. Figures 2 and 4 demonstrate that the films exhibit holes and ridges on the scale of a few 10 nm. In addition, particularly the gold films exhibit characteristic holes, which are about 1 nm deep and a few nanometers in diameter [Figs. 3(f) and 4(e)]. It should be noted that the room-temperature mobility at the surface is obviously not sufficient to allow the holes to be filled. This may be attributable to some impurities segregated to the surface. While the larger holes are also detectable by scanning electron microscopy (SEM) (Fig. 5), the smaller ones are not. The LEED patterns (Fig. 5) of both silver and gold films prove the (111) orientation of their surfaces. However, the silver patterns are more pronounced than the gold patterns. This can be understood on the basis of the STM images, which show a large number of nanometer size holes in the gold terraces, resulting in a relatively small coherence length for the diffracted electrons.

Silver and gold films have been prepared at both 10^{-5} and 10^{-9} mbar. They were imaged by STM in both air and vacuum in a bias range of ± 500 mV with currents between 2 pA and 2 nA. In all cases basically the same features were observed. It should be noted that while no atomic resolution was obtained for the fresh silver samples in air, a well-defined adsorbate layer does give images with atomic resolution;[12] however, this is not subject of the present study.
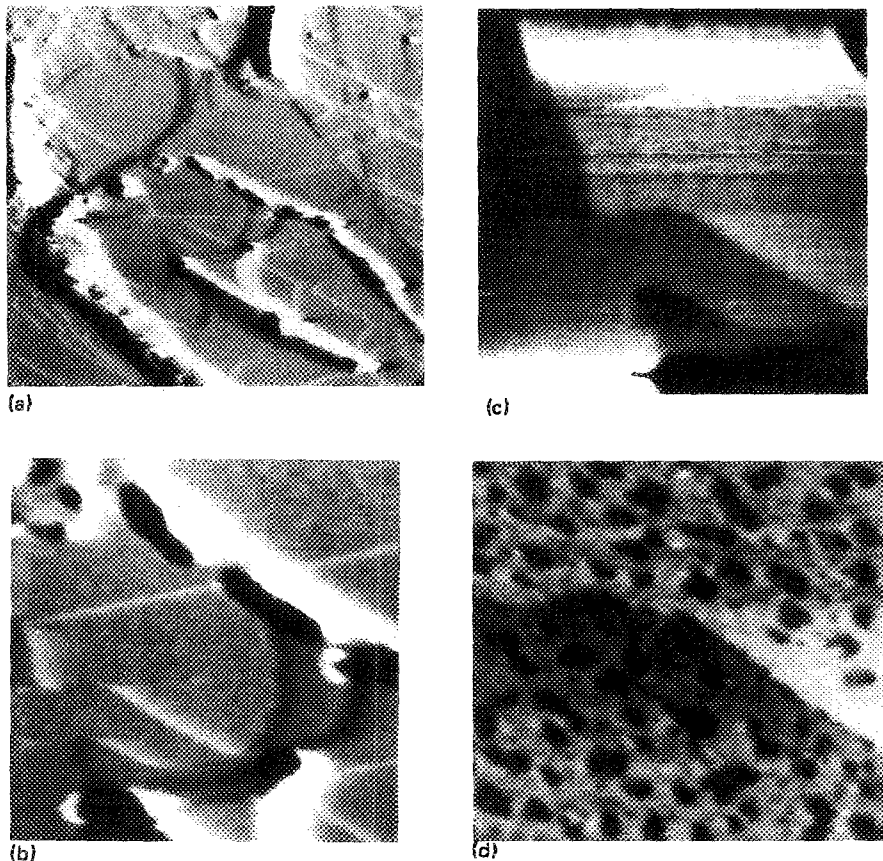

(a)

(c)

FIG. 4. STM images of Au(111) on mica, evaporated at 400 °C. Image size: (a) 1.2 μm×1.2 μm; (b) 350 nm×350 nm; (c) 240 nm×240 nm; (d) 60 nm×60 nm.

(b)
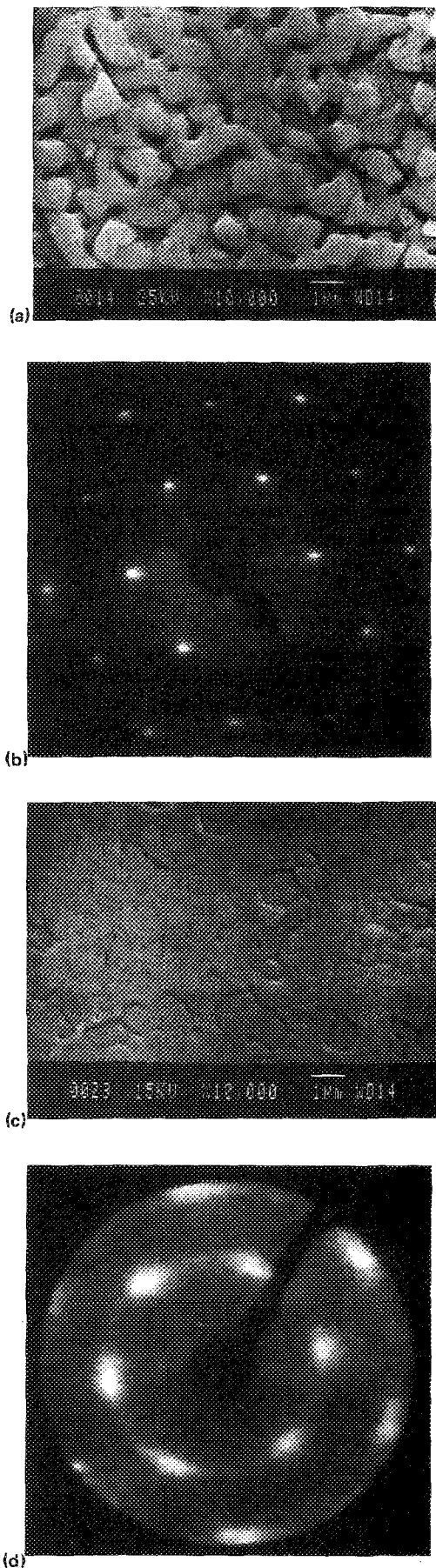

(d)

(a)

(b)

(c)

(d)

FIG. 5. SEM micrographs and LEED patterns of (a) Ag and (b) Au films on mica, evaporated at 275 and 400 °C, respectively.

Palladium, like gold and silver, is a fcc noble metal. It melts at 1552 °C, which is about 600 and 500 °C higher than the melting points of silver and gold, respectively. As a consequence, it can be expected that the optimum temperature for epitaxial film growth is also higher for palladium. Indeed, Fig. 6 demonstrates that the films evaporated at 10^{-5} mbar at temperatures of 50 and 350 °C are grainy with grain sizes considerably smaller than for the corresponding silver or gold films. An improvement is achieved by evaporating palladium onto Ag(111) films, which had been evaporated before onto mica at the optimum temperature for epitaxial growth, i.e., 275 °C. Figure 6(c) indicates that the silver substrate reduces the necessary temperature for epitaxy if compared to mica. Similarly it had been observed that the epitaxial temperatures for Ag(100) and Pd(100) on Ag(100) are much lower than on mica.[13] A reason for this may be the fairly good match of lattice constants between the two metals. For the palladium film evaporated at 175 °C flat grains of about 20 nm diameter are imaged on top of the typical silver terraces. Palladium evaporation at higher substrate temperatures (275 °C) leads to considerable interdiffusion between the metallic layers, as determined by x-ray diffraction, and also to increased surface roughness [Fig. 6(d)]. A further improvement in grain size may be achieved by evaporation under ultrahigh instead of only high vacuum conditions, since due to the high reactivity of palladium towards residual gases one may expect a significant amount of defects for evaporation under the vacuum conditions employed so far.

Chromium crystallizes in a bcc lattice and is therefore not expected to form the same flat (111) terraces on mica like the fcc metals. Indeed, a film evaporated at 10^{-5} mbar and 50 °C exhibits a grainy structure with grain sizes comparable to the palladium case [Fig. 7(a)]. It should be noted that

a.) $T_S = 50$ °C   b.) $T_S = 350$ °C

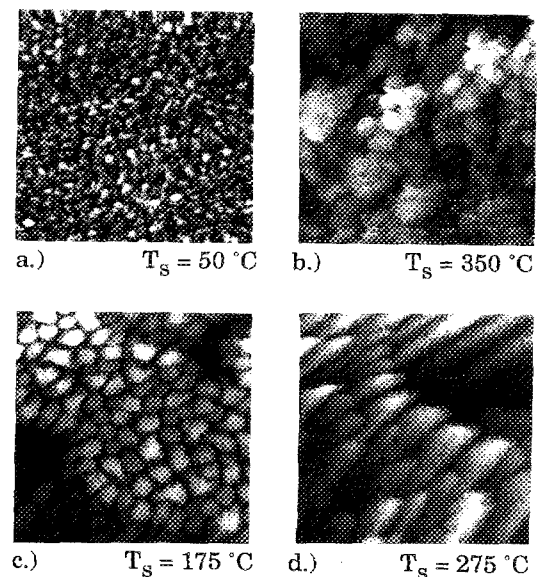c.) $T_S = 175$ °C   d.) $T_S = 275$ °C

FIG. 6. STM images of palladium. (a) Pd on mica, evaporated at 50 °C substrate temperature; (b) Pd on mica, evaporated at 350 °C substrate temperature; (c) and (d): Pd on Ag on mica; the substrate temperature during the evaporation of Ag was 275 °C and for the subsequent evaporation of Pd it was (a) 175 °C and (b) 275 °C. Image size: 250 nm × 250 nm.

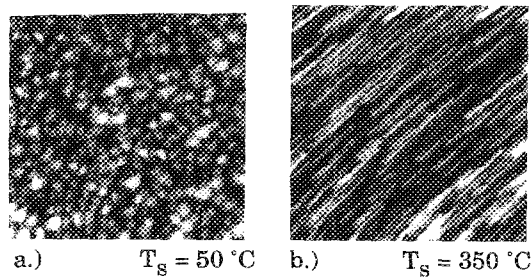a.) $T_S = 50\ °C$ b.) $T_S = 350\ °C$

FIG. 7. STM image of chromium on mica, evaporated at different substrate temperatures. (a) 50 °C; (b) 350 °C. Sample bias: − 1 V. Image size: 250 nm × 250 nm.

reproducible images in air could only be obtained in a certain bias range, a fact which can be attributed to the surface oxide. It appears that the conductivity of the oxide is not large enough for stable imaging at very low sample bias, and at too high bias further redox reactions may occur. Figure 7(b) shows an STM image of a film evaporated at 350 °C, exhibiting a columnar structure. While this is in good agreement with transmission electron microscopy (TEM) results obtained on thin epitaxial Cr films on Cu(111),[14] it must be noted that also less well ordered regions were observed. In any case, no flat terraces suitable for more detailed adsorbate studies have been detected.

IV. CONCLUSIONS

Thin films of silver, gold, palladium, and chromium deposited on mica can be imaged reproducibly by STM under ambient and high vacuum conditions. However, particularly for chromium, the bias range for reproducible imaging is limited due to surface oxides, which may even be formed or reduced during the operation of the STM. The investigation of the influence of the substrate temperature on the surface structure of the films allowed us to optimize the conditions for the formation of flat terraces, suitable, e.g., for STM studies of adsorbates or nanoscale modifications. A most suitable substrate in this respect turned out to be Ag(111)

evaporated at 275 °C. A disadvantage of this material for use as a substrate may be the fact that it is not very hard. In order to obtain flat substrates from materials with a higher melting point it would be desirable to go to even higher substrate temperatures during evaporation; however, this is limited by the thermal stability of the substrate employed. As an alternative, it was demonstrated that the grain size at a given substrate temperature could be improved if prior to the film of interest a lower melting fcc metal film was evaporated onto mica.

ACKNOWLEDGMENTS

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