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A comparative study of platinum nanodeposits on HOPG (0001), MnO(100) and MnO_x/MnO(100) surfaces by STM and AFM after heat treatment in UHV, O₂, CO and H₂

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Citation

Tsybukh, R. (2010, September 22). *A comparative study of platinum nanodeposits on HOPG (0001), MnO(100) and MnO_x/MnO(100) surfaces by STM and AFM after heat treatment in UHV, O₂, CO and H₂*. Retrieved from <https://hdl.handle.net/1887/15973>

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CHAPTER 6

Platinum deposition on the MnO(100) surface

In this chapter we report preliminary studies of the deposition of platinum on the as-received MnO(100) surface as well as on the MnO(100) surface altered by annealing in UHV, hydrogen and oxygen. The characterization of the samples was performed by using AFM, STM, XPS and RBS techniques.

6.1 Platinum deposition on an as-received MnO(100) single-crystal

A series of experiments presented in this section were performed with a new as-received MnO(100) single-crystal. AFM images of this sample showed similar surface morphology as was registered previously (see chapter 5, Fig. 5.3). The R_{rms} roughness, measured at several locations of the surface was about 0.6 nm. The sample was not processed in any way to clean it from contaminations before metal deposition. AFM imaging after deposition of 4.8 ML Pt [Fig. 6.1 (A)] registered a surface morphology similar to the as-received sample with 0.5-4 nm deep crisscrossed relics of the abrasive sample polishing process. AFM analysis did not register any discernible metal deposits on the surface and R_{rms} roughness was of a similar value as on the as-received sample. Any attempt to image the surface after Pt deposition by STM failed. The reason for this could be a bad electrical contact of the sample with the sample plate combined with the insulating nature of MnO. XPS analysis of the sample after Pt deposition revealed all peaks characteristic of Pt and substantially attenuated oxygen peak in comparison with the as-received sample [Fig. 6.2 (B)]. The peak of carbon contamination was seen as well. Peaks characteristic of manganese could not be observed, except barely discernible peaks in the 2p and 3p core excitation regions. Thus, the XP spectra clearly indicate that the surface is covered with a rather thick Pt layer. It may consist of either a homogeneous Pt film or, possibly, a close packed arrangement of Pt clusters. Subsequent annealing in UHV at first for 2 h at 650 °C and again for 2.5 h (4.5 h total) resulted in the surface topography, as shown in Fig. 6.1 (B). The surface became “bumpy” and still exhibited scratches due to the polishing procedure. The height of the “bumpy” structures was in the range of 0.5-2 nm. After annealing the sample, the Mn 2p and 3p peaks appeared again, albeit their intensity is lower than registered for the as-received sample. Almost all peaks characteristic of platinum are well resolved, but they are smaller than after the metal deposition. At the same time the Pt 5s and 4p_{1/2} peaks vanished. Table 6.1 lists the peak

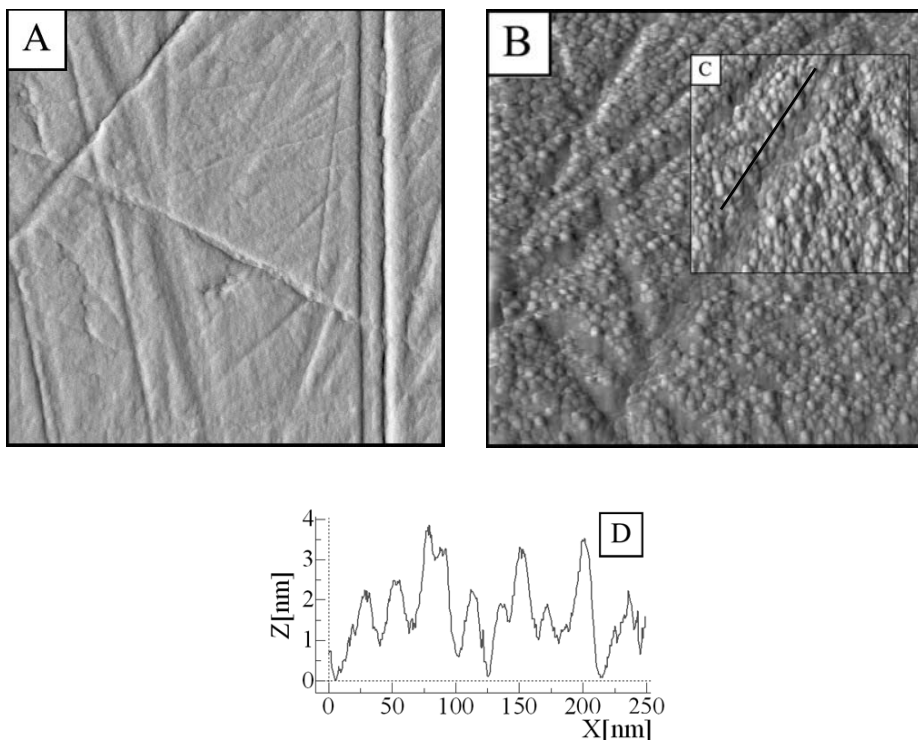


Figure 6.1: (A) AFM image ($400 \times 400 \text{ nm}^2$) of the as-received MnO(100) single-crystal after deposition of Pt (4.8 ML). (B) AFM image ($500 \times 500 \text{ nm}^2$) of the same sample after annealing in UHV for 4.5 h (total) at 650°C . (C) Inset ($300 \times 300 \text{ nm}^2$) shows the surface in more detail. (D) The line profile across a portion of the surface, marked by the black line in (C).

positions for manganese and oxygen as registered by XPS before and after the metal deposition and the annealing procedures.

The RBS spectrum of an as-received MnO(100) single-crystal after Pt deposition is presented in Fig. 6.3. According to RBS the surface is covered with a 4.8 ML of Pt.

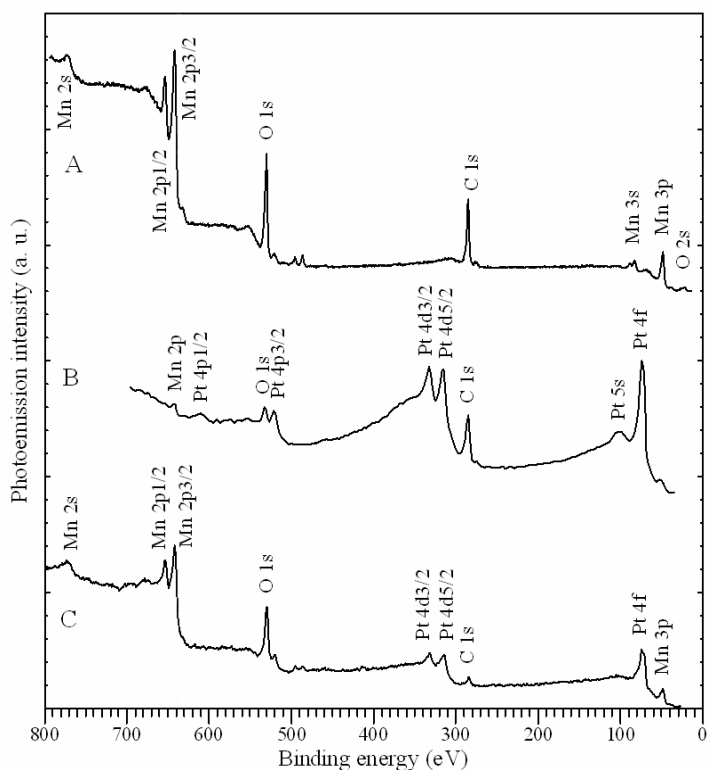


Figure 6.2: Survey of XP spectra: **(A)** As-received MnO(100). **(B)** As-received MnO(100) with 4.8 ML of Pt. **(C)** As-received MnO(100) with 4.8 ML of Pt annealed in UHV for 4.5 h at 650 °C.

Table 6.1: Binding energies (eV) measured on an as-received MnO(100) single-crystal and Pt (4.8 ML)/MnO(100) sample after annealing in UHV at 650 °C for 4.5 h.

Sample	O1s	Mn2p _{3/2}	Mn2p _{1/2}	Mn3s (1)	Mn3s (2)
An as-received MnO(100)	529.2	641.0	652.8	82.0	88.0
Pt (4.8 ML) /MnO(100) annealed in UHV at 650 °C for 4.5 h	#	639.6	651.0	#	#

Note: # - not measured.

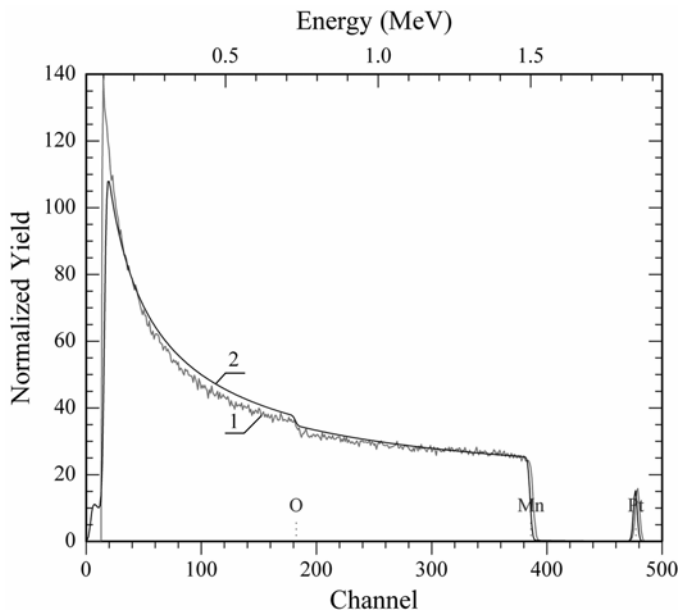


Figure 6.3: (1) RBS spectrum of the as-received MnO(100) covered with 4.8 ML of Pt. (2) Fit to the spectrum made by using the RUMP program.

6.2 Deposition of Pt on the MnO(100) surface previously modified by annealing in UHV, hydrogen and oxygen

The next set of the experiments were conducted using samples which were pretreated as described in § 5.2.1 (A) (Fig. 5.9). After the last treatment described in § 5.2.1 (A) the sample was subjected to annealing in hydrogen $p(\text{H}_2)=3.0 \times 10^{-4}$ mbar at 700 °C for 1 h. AFM imaging performed right after this procedure revealed a bumpy-like structure on the surface with a height of 20-40 nm (Fig. 6.4). Subsequent annealing of the crystal in oxygen $p(\text{O}_2)=3.0 \times 10^{-4}$ at 700°C for 3 h resulted in the formation of the TLPs (Fig. 6.5). The height of these structures is about 20 nm. A line-profile made approximately along the median line of the TLPs results in a width of about 250 nm. On the top of the pillars vaguely protruding rectangular plate-like structures resembling terraces were observed (see, e.g., the location marked with the black rectangular in Fig. 6.5 (A). At the same time, while many of the TLPs had a very rough surface [Fig. 6.5 (B)], the top side of some of them appeared to be quite smooth [Fig. 6.5 (C)]. Left for 2 days in UHV during a bake out of the setup, the surface exhibited many TLPs, topped with a multitude of vaguely protruding rectangular plate-like structures [Fig. 6.6 (A)]. These structures are better discernible in the small scale image Fig. 6.6 (B).

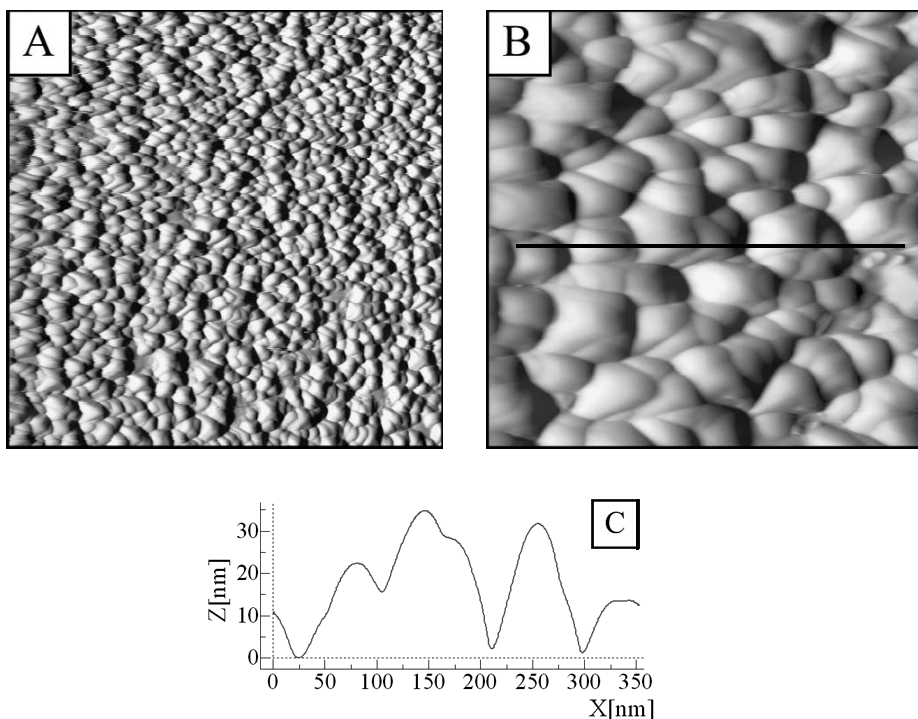


Figure 6.4: AFM images of MnO(100) after annealing in hydrogen $p(H_2)=3.0 \times 10^{-4}$ mbar at 700 °C for 1 h. Image size: (A) 1500×1500 nm². (B) 400×400 nm². (C) A cross-section along the line indicated in (B).

After exposing the crystal to ambient conditions for several days, the top surface of the TLPs was found to be covered with a multitude of even better defined flat rectangular terrace-like structures (Fig. 6.7). Some of them displayed an almost perfect square shape and on the other ones very distinct kinks can be seen. For the sake of clarity several AFM images recorded at different scales and at different locations of the surface are shown in Fig. 6.8. Unfortunately, atomic resolution on the top of the flat regions could not be obtained. After performing deposition of 10 ML Pt on this surface, AFM imaging registered the appearance of only a minute corrugation on the terrace-like structures. All other structures on the images were practically identical to those before deposition. STM imaging of the surface was not possible. Again the reason for this could be because of a bad electrical contact of the sample and the sample plate.

Annealing of this sample in UHV at 300 °C for 1 h and subsequently for 3 h at 320 °C did not result in observable changes of the surface topography. The rectangular terrace-like structures appeared to be very smooth with minute corrugations. STM imaging after these heating cycles was again not successful.

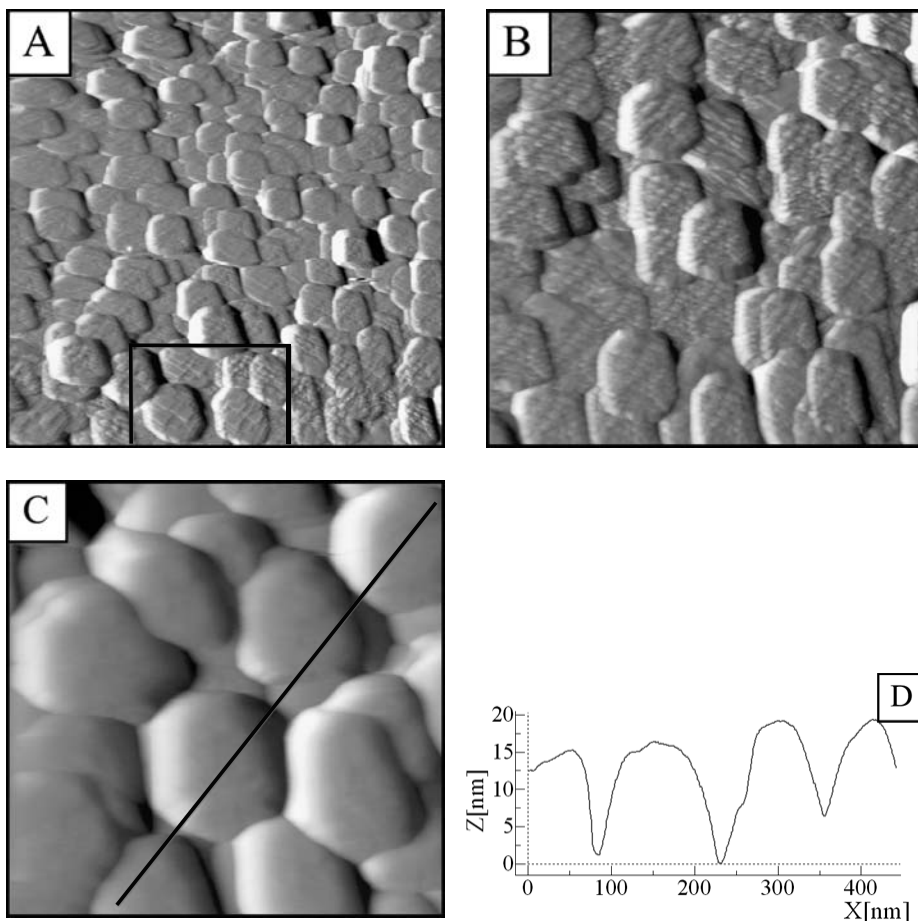


Figure 6.5: Collection of AFM images of MnO(100) after annealing at 700 °C in oxygen $p(\text{O}_2)=3.0 \times 10^{-4}$ mbar for 3 h. Image size: (A) $1500 \times 1500 \text{ nm}^2$. (B) $1000 \times 1000 \text{ nm}^2$. (C) $400 \times 400 \text{ nm}^2$. (D) A line-profile across the portion of the surface marked with the black line.

Further, the sample was annealed for an extended period of time (16 h) in UHV at 320 °C. After this procedure the surface topography has changed in the following way. The terrace-like structures became rough and covered with particle-like structures which occupied their whole surface as detected by AFM (Fig. 6.9). Interestingly, this time it was possible to perform STM measurements. It was done at a sample bias voltage of 5.6, 3.2, 2.0, -2.0 V. Except for imaging at a bias of 5.6 V, which led to the deterioration of the image contrast, the appearance of the surface morphology did not change considerably when imaging was carried out at other bias voltages as given above. The STM images of the surface taken at different tunneling conditions are displayed in Fig. 6.10 and Fig. 6.11. All the images are constant-current topographies and represent raw data without

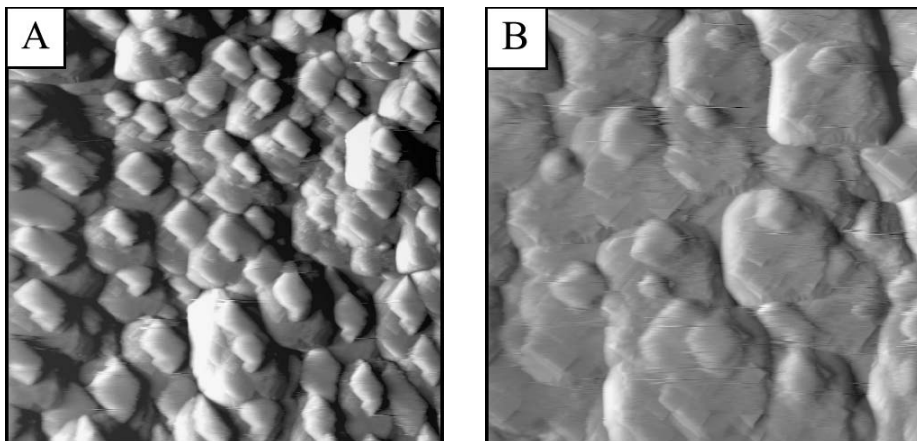


Figure 6.6: *AFM image of MnO(100) after being in the set-up during a bake out for 2 days. Image size: (A) $1000 \times 1000 \text{ nm}^2$. (B) $700 \times 700 \text{ nm}^2$.*

application of any filtering procedure. The surface shows rectangular terrace-like structures which are comparable in size to those observed by AFM. The terrace-like structures are entirely covered by a densely packed layer of three-dimensional particle-like structures. Interestingly, at some locations of the surface freed from the terraces-like structures the TLPs became visible again. After subsequent annealing of the surface at the same temperature for several hours, the surface morphology did not exhibit a well-defined topography due to the appearance of a very large roughness which precluded stable AFM imaging. With increasing annealing temperature the deteriorated parts of the surface expanded until the entire surface became disordered. Interestingly, the large TLPs observed by AFM, such as shown in Fig. 6.8 (B) could not be imaged by STM. Thus, it is concluded that only states within the surface overlayer contribute to the STM image contrast at the applied tunneling conditions. The possibility of STM imaging may indicate that long annealing of the sample favors the spreading of Pt over the surface. This result also illustrates that Pt is mobile on the altered MnO(100) surface well below its melting temperature. Due to diffusion it can provide a better contact of the sample with the sample plate that makes STM imaging possible. Another possibility is that the near-surface region of the MnO crystal can acquire half-metallic state that allows STM imaging due to the formation of other manganese oxides or the formation of vacancies. The latter possibility was pointed out in [1]. Finally, it may also be a combination of the described effects. At present it is difficult to judge whether the contrast in the images is only due to the formation of Pt layer alone. One can also imagine the intermixing of Pt with manganese oxide(s) within a thin surface overlayer. This may also reduce the band gap in the

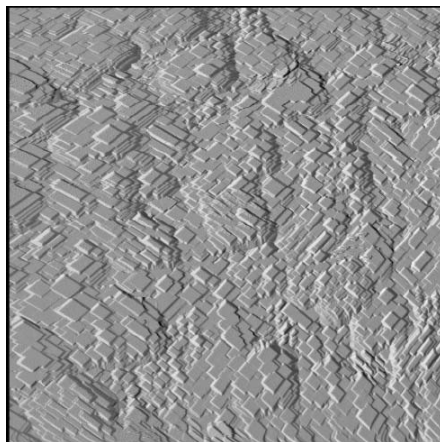


Figure 6.7: *AFM image ($1300 \times 1300 \text{ nm}^2$) of MnO(100) after being in the set-up during a bake out for 2 days and exposure to ambient conditions for several days.*

near-surface region which would make STM imaging possible. It is known that the capability of STM to image, for example, thick insulating films on a conductive substrate does not depend primarily on the width of the band gap, but rather on the relative positions of the valence and conduction band edges of the insulating film with respect to the corresponding band edges of the substrate [2]. Note that for all cases a conductive contact with the base plate is required. Inspection of the STM images also reveals that platinum decorate the entire surface of the rectangular terrace-like structures maintaining by this way their integrity, so to say “frosting” them. This is demonstrated by successive annealing of the sample in UHV at higher temperature (420°C) for 3 h. Such sample treatment caused the 3-D particle-like structures to become more distinctly visible. But at this point imaging of the surface by STM was already not possible anymore. As can be seen in the AFM images in Fig. 6.12, the pattern of rectangular terrace-like structures on the surface began to disintegrate as a result of the annealing and the distance between the structures began to widen. At the same time the particle-like overlayer still covers the entire terrace-like structures and preserving the shape of some of them. Additional annealing of the sample at 420°C for 3 h led to further deterioration and breaking up of the terraces-like structures, as shown in Fig. 6.13.

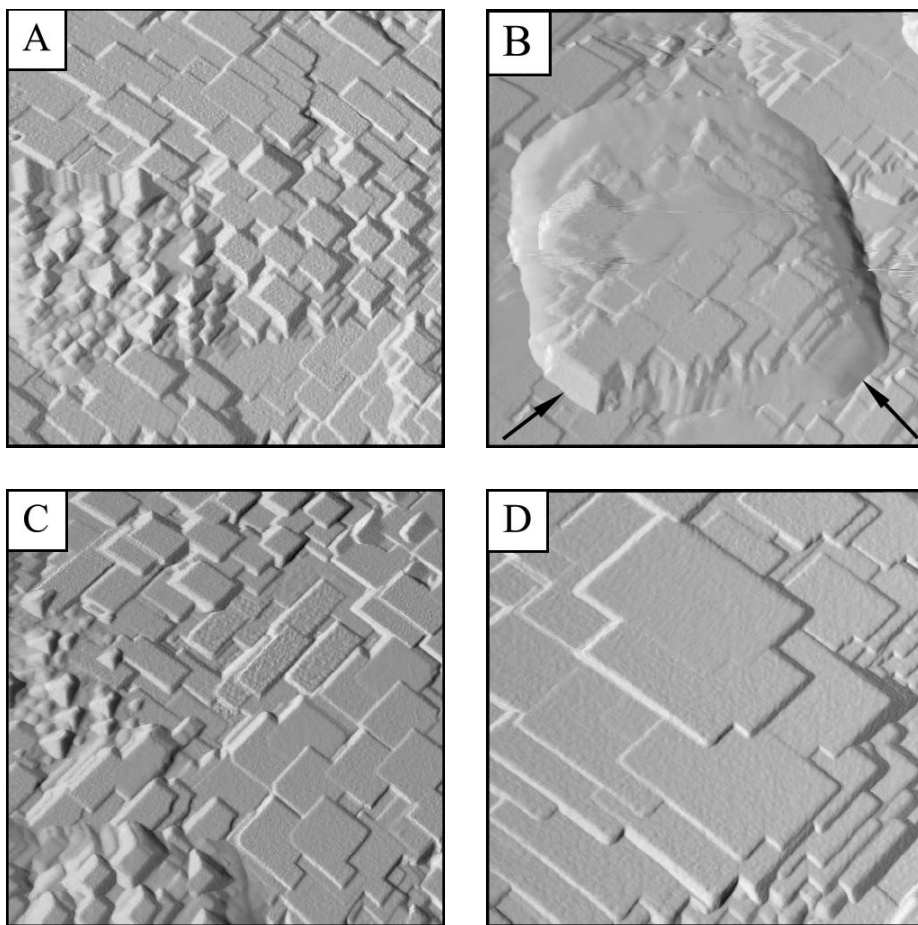


Figure 6.8: Series of AFM images of MnO(100) recorded after being in the set-up during a bake out for 2 days and exposure to ambient conditions for several days. Image size: (A) $460 \times 460 \text{ nm}^2$. (B) $400 \times 400 \text{ nm}^2$. (C) $400 \times 400 \text{ nm}^2$. (D) $280 \times 280 \text{ nm}^2$.

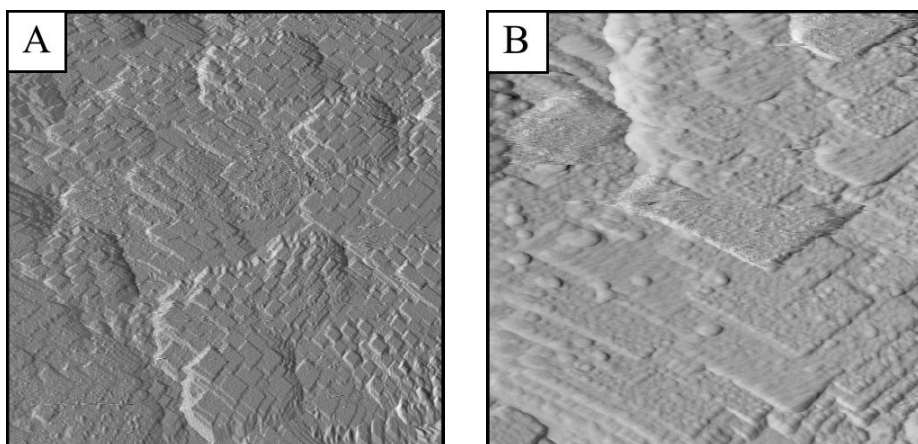


Figure 6.9: AFM images of MnO(100) after deposition of 10 ML Pt and annealed for 16 h in UHV at 320 °C. Image size: (A) $1000 \times 1000 \text{ nm}^2$. (B) $300 \times 300 \text{ nm}^2$.

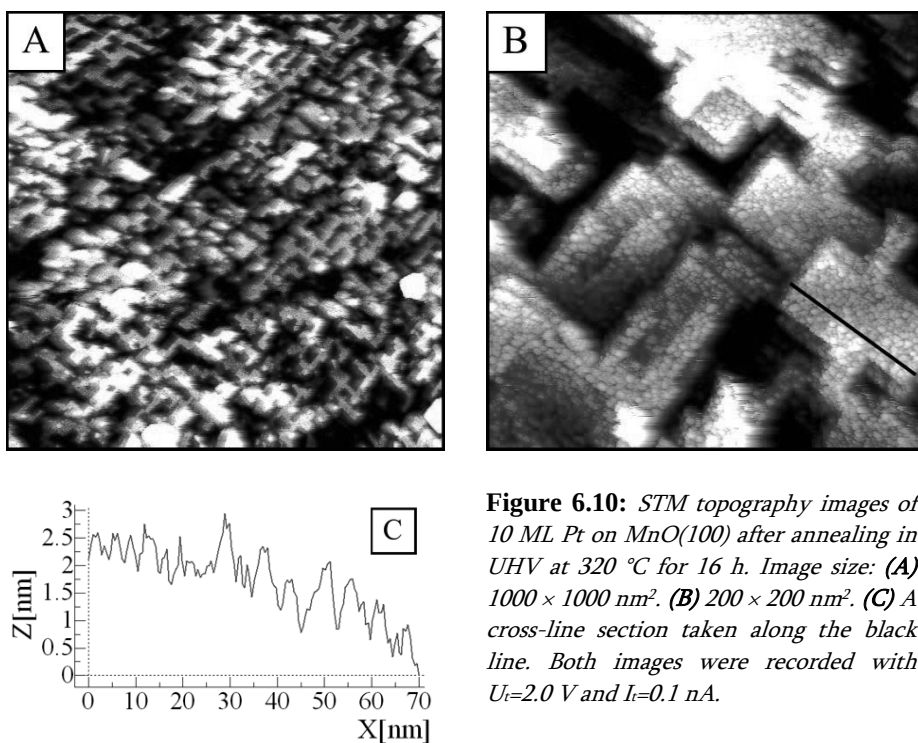


Figure 6.10: STM topography images of 10 ML Pt on MnO(100) after annealing in UHV at 320 °C for 16 h. Image size: (A) $1000 \times 1000 \text{ nm}^2$. (B) $200 \times 200 \text{ nm}^2$. (C) A cross-line section taken along the black line. Both images were recorded with $U_t=2.0 \text{ V}$ and $I_t=0.1 \text{ nA}$.

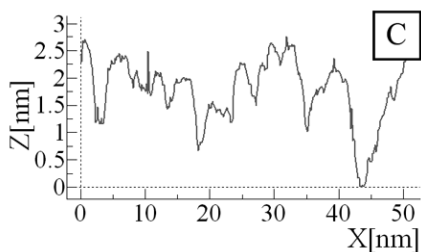
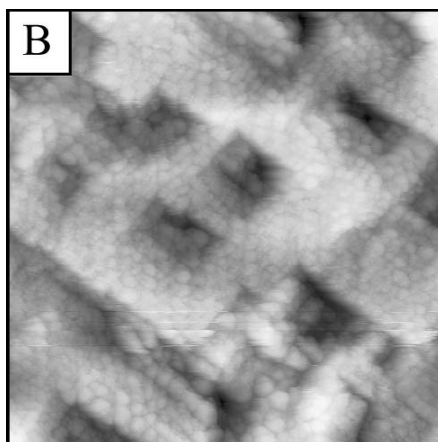
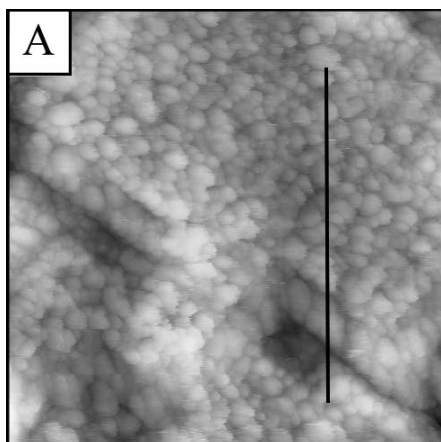


Figure 6.11: STM topography images of 10 ML Pt on MnO(100) after annealing in UHV at 320 °C for 16 h. Image size and tunneling conditions: (A) $70 \times 70 \text{ nm}^2$, $U_t=2 \text{ V}$, $I_t=0.1 \text{ nA}$. (B) $150 \times 150 \text{ nm}^2$, $U_t=-2.0 \text{ V}$, $I_t=0.1 \text{ nA}$. (C) A cross-line section taken along the black line.

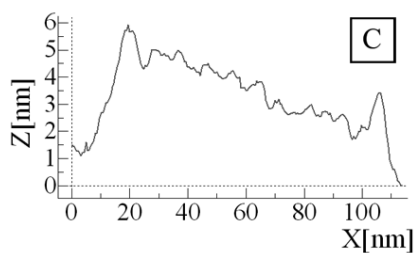
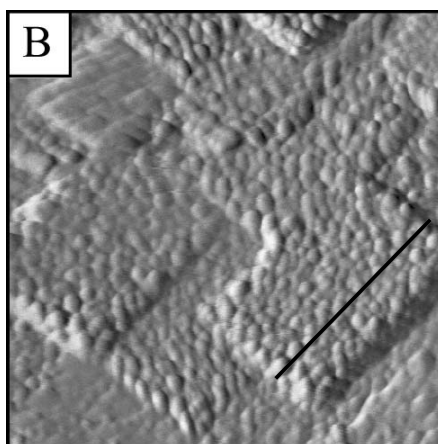
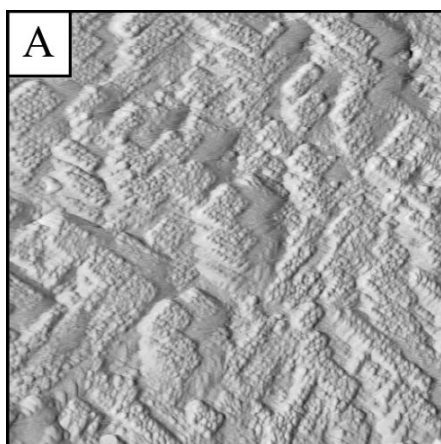


Figure 6.12: AFM images of MnO(100) with 10 ML Pt annealed in UHV at 420°C for 3 h. Image size: (A) $500 \times 500 \text{ nm}^2$. (B) $200 \times 200 \text{ nm}^2$. (C) A cross-line section taken along the black line.

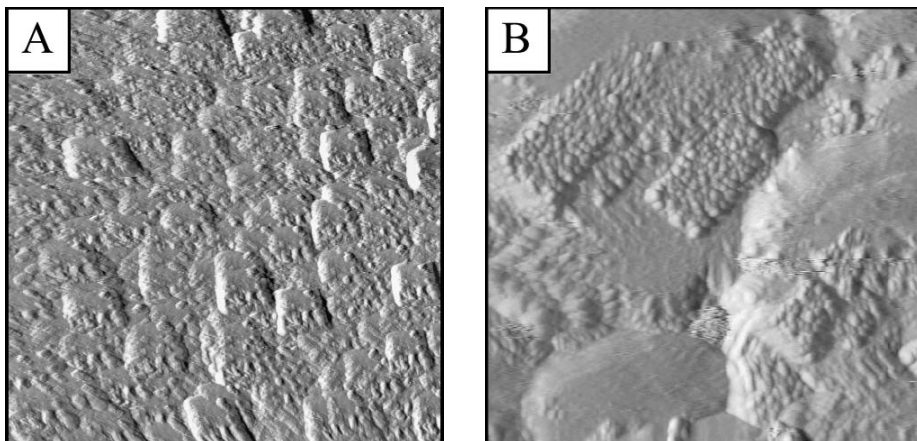


Figure 6.13: AFM images of *MnO*(100) with 10 ML Pt further annealed in UHV at 420 °C for additional 3 h (total time 6 h). Image size: **(A)** 1500 × 1500 nm². **(B)** 300 × 300 nm².

6.3 Discussion

In the context of the present study it is worth noting that so far the growth of only two metals, namely Fe [3] and Cu [4], on MnO has been investigated. In both cases the deposits were analyzed by XPS. The growth of Fe (1-9 Å) was studied on a polycrystalline MnO film grown over a stainless steel substrate at room temperature. A layer-by-layer growth mode of iron film was established. Successive study [5] revealed that in this coverage range initially strong interaction between Fe and the substrate takes place that leads to Fe oxides formation. At increased coverage indications were found that the diffusion of Fe(O) at the interface took place simultaneously with the growth of an upper metallic Fe layer. In the case of Cu some indications were found of a strong intermixing between Cu and MnO for low Cu coverage (1-2 Å). At higher coverages (3-12 Å), a copper overlayer showed a Cu 3d peak close to the bulk value. The experiments indicated initial Cu diffusion into the MnO layer followed by the growth of a bulk-like copper layer.

The AFM imaging performed in the present study showed that 4.8 ML of Pt deposited on the as-received MnO(100) sample did not cause an observable change of the topography of the surface. However, since platinum was shown to be present on the MnO(100) surface by RBS as well as XPS, this points to the following possibilities: (a) a closed Pt layer covering all surface structures is formed; (b) the metal is distributed on the surface in the form of tiny clusters and AFM cannot resolve these structures (to some extent this may be caused by the

surface roughness). At present, it is difficult to discriminate between these alternatives. XP spectra clearly indicate that the surface is covered with a rather thick Pt layer, as the manganese and oxygen peaks are almost completely vanished. This fact points to the possibility of the formation of a closed Pt film on the surface. After annealing the system in UHV at 650 °C for 4.5 h, XPS shows the recovering of manganese and oxygen peaks, although they are smaller than on the spectrum of the fresh sample. The peaks characteristic of Pt are also smaller in comparison with the sample analyzed after Pt deposition (see Fig. 6.2). This implies that the area of the surface covered with Pt must be reduced. Since the temperature is too low for Pt desorption one may envisage two possibilities for this effect: either Pt deposits sinter making free some part of the surface or Pt diffuses into/intermixes with the oxide. The AFM measurements provide no evidence for the formation of large Pt particles or agglomerates although as can be seen in Fig. 6.1, the surface after the annealing procedure became “bumpy”. Probably this surface morphology is the result of Pt agglomeration or its intermixing with the material of the support. The latter possibility cannot be excluded since indications of an intermixing of Mn and Pt within the first layers of the surface were registered at 400 K [6]. Furthermore, at 500-650 °C the formation of Pt₃Mn compound is possible [7]. The formation of Mn-Pt oxide like species and decoration of Pt by MnO_x was also suggested by Grbic *et al.* [8], who studied the promotion of Pt/Al₂O₃ catalyst with MnO_x. It should be noted that, unfortunately, XP spectra in high resolution mode that could clear up the issue of platinum and manganese interaction have not been recorded for the MnO(100) sample after the metal deposition and after the annealing.

AFM and STM imaging of the MnO(100) surface altered by annealing in UHV, hydrogen and oxygen just after deposition of Pt (10 ML) indicates the formation of the closed metal film. Annealing the sample in UHV at 320 °C for 16 h led to the formation of the 3-D particle-like morphology distinctly observed by AFM and STM (Fig. 6.9-6.11). As shown by AFM (Fig. 6.12 and Fig. 6.13), subsequent annealing at higher temperature (420 °C) led to the disintegration of these structures. Apparently, in this way the Pt layer was partly destroyed and the contact with the sample plate was lost that prevented further STM imaging. It should be noted that the TLPs that were observed on these samples before Pt deposition resemble very much those observed after annealing of the as-received MnO(100) surface in oxygen, $p(\text{O}_2)=5\times 10^{-5}$ mbar (§ 5.3.2). As was discussed, this surface structure may be composed of the Mn₃O₄ and/or γ -Mn₂O₃ phase(s). Consequently, the observed particle-like morphology may represent Pt on the Mn₃O₄ and/or γ -Mn₂O₃ phase(s).

Concluding this chapter it is instructive to compare the morphology of Pt deposits on MnO(100) (– active surface) and HOPG (– “inert” surface). As was

found in chapter 4, Pt forms upon deposition 3-D particles on HOPG which interact weakly with the atomically smooth surface due to the absence of dangling bonds. The formation of Pt 3-D particles on a HOPG surface is in agreement with the predictions of the growth mode based on the positive value of the differences of the surface energies of these materials, their weak interaction (thus, small interface energy) as well as high value of the lattice mismatch. Similarly as for an HOPG surface, the growth mechanism of Pt on the MnO(100) can be considered using two different approaches. From the viewpoint of the surface free energy, $\Delta\gamma = \gamma_{Pt} - \gamma_{MnO} + \gamma_{int}$, where γ_{int} is the interface energy. A 3-D island growth is favored when $\Delta\gamma > 0$, while layer-by-layer growth is favored for $\Delta\gamma \leq 0$. Since the difference in surface energy (γ) of platinum (for the Pt(111) surface $\gamma = 2.30 \text{ J/m}^2$ [9]) and MnO (for the (100) surface: $\gamma = 0.71\text{--}0.86 \text{ J/m}^2$ [10]), $\gamma_{Pt(111)} - \gamma_{MnO(100)}$, is equal $1.44 - 1.59 \text{ J/m}^2$, it favors a 3-D growth. However, $\gamma_{MnO(100)}$ was calculated theoretically and the accuracy of the performed calculations is unknown at the moment. The γ_{int} depends on the strain and the strength of chemical interactions between metal and oxide at the interface. Despite that metal-oxide interfaces are very actively studied [11–18] at present due to structural complexity they are not understood well enough. Hence, the value of the γ_{int} for metal-oxide interface is difficult to calculate and, in general, it is unknown [16–18]. But it is known that noble metals do not generally wet oxide surfaces. At low-enough coverage and temperature they can sometimes form 2-D particles, but above a critical coverage, the metals form 3-D particles [15].

The other viewpoint is based on the lattice mismatch. The difference of the lattice constants is about 13 % in this system. Hence, the non-uniform strain in the system may favor a 3-D island growth. In general, in order to predict the growth mode these two factors together should be considered. Yet another factor which can steer the growth of metallic deposits is the oxide surface stoichiometry [15]. It should be noted that the growth mode can be influenced by the presence of adsorbates on the surface. Also for the unambiguous establishment of the metal growth mode well-defined surfaces are necessary. Taking into account these facts it seems that the 3-D growth mode is preferred in the Pt/MnO system. However, since Pt particles were not registered upon Pt deposition, it is difficult at present to assert definitely which growth mode is realized in the system and further experiments are necessary to solve this issue.

6.4 Conclusions

In summary, the deposition of Pt on the surface of an as-received MnO(100) single-crystal and a MnO(100) surface altered by annealing in UHV, hydrogen and oxygen was examined. The main results are as follows:

1. AFM imaging showed that 4.8 ML of Pt deposited on the surface of an as-received MnO(100) single-crystal appears to form a closed film on the surface. Annealing of the sample in UHV at 650 °C for 4.5 h made its surface “bumpy” and the height of the “bumpy” structures was in the range of 0.5-2 nm. This may indicate Pt aggregation or its intermixing with the manganese oxide phase(s) in the near-surface region.
2. Deposition of 10 ML of Pt on the MnO(100) surface which was previously altered by a series of annealings under UHV, hydrogen or oxygen, exhibited TLPs, topped with rectangular terrace-like structures and resulted in a slight increase of the corrugations on the top of these structures. Subsequent annealing of this sample for 16 h in UHV at 320 °C resulted in a large increase of the roughness of the rectangular terrace-like structures due to the formation of the particle-like structures over their entire surface. Successive annealing of the sample in UHV at higher temperature (420 °C) for 3 h: the 3-D particle-like structures on the terrace-like structures became more pronounced. However, this procedure also led to the disintegration of the terrace-like structures at some locations of the surface. Additional annealing cycles of the sample at 420 °C for 3 h caused further deterioration and disordering of the surface.

6.5 References

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