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Generation and nucleation of adatoms during ion bombardment of Pt(111)

Thomas Michely and George Comsa
Institut für Grenzflächenforschung und Vakuumphysik, Forschungszeutrum Jülich, Postfach 1913, D5170 Jülich, Germany
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The morphology of a Pt(111) surface has been investigated by scanning tunneling microscopy after low-energy Ar^+-ion bombardment as a function of the target temperature during sputtering. On the surfaces sputtered below 550 K, Pt-adatom islands located *on* the initial surface layer are observed. Their existence is related to a substantial generation of adatoms during the ion bombardment, which has been predicted theoretically. The absence of the Pt-adatom islands on samples sputtered at temperatures above 550 K is correlated with the disappearance of the three-dimensional-growth mode in the homoepitaxy of Pt on Pt(111) above 500 K.

Surface morphological effects due to ion bombardment are a long-standing matter of interest. They are of great technological importance for ion-beam machining, depth profiling, ion-beam-assisted deposition, and surface texturing. The investigation of these effects by real-space methods has been limited so far by instrumental capabilities to a resolution of specific features of a few nanometers,[1] or by the particular sample geometry used in field ion microscopy (FIM) and field electron microscopy (FEM). With the advent of scanning tunneling microscopy[2] (STM) this situation changed greatly and the investigation of the surface morphology generated by ion bombardment became accessible on an atomic scale. Because of the observation of the atomic-scale topography it is now possible to gain additional insights into the defect production and annealing mechanisms. Examples are the observations of the effects of single-collision cascades on semiconductors,[3] the investigation of the morphological effects of low-energy He^+ implantation,[4] and the analysis of the temperature dependence of ion-bombardment removal regimes and vacancy island formation.[5]

The production of adatoms during ion bombardment is one of the elementary processes contributing to the surface morphology. The existence of this process has been predicted theoretically by Harrison and co-workers.[6,7] In the *simulation* of 5-keV Ar^+-ion bombardment of Cu(100), Webb and Harrison[7] observed that, due to bombardment-induced atom-replacement sequences in the surface layer, a large number of atoms is pushed *onto* the surface layer, typically on regular lattice sites. This mechanism of adatom formation should be operative at any temperature, i.e., even at 0 K. There is, in addition, another mechanism that might be operative in adatom formation, but only at finite temperatures. During ion bombardment, vacancy-interstitial pairs (Frenkel pairs) can be formed *below* the surface. The interstitials are highly mobile in Pt already at temperatures above 50 K.[8] They can migrate with a certain probability to the surface and form adatoms *on* the surface layer. The atoms that eventually become adatoms on the surface via one of the two mechanisms have never left the crystal. We will call this kind of adatoms produced during ion bombardment "target adatoms," following the terminology of Harrison *et al.* Adatoms can be formed during sputtering also by redeposition.[9] This mechanism has to be clearly distinguished from target-adatom formation. *Redeposited* atoms are sputtered atoms which, after having left the surface, hit it again on features located in their line of flight. Thus redeposited atoms can only be formed on surfaces that are at least microscopically rough, containing surface features like pits or cones; in contrast, target adatoms also are generated on atomically flat surfaces. This allows one to distinguish experimentally between the two types of processes.

There are only a few experimental observations that can be brought into connection with target-adatom formation. One is the observation by FIM and FEM of microprotrusions on tungsten field emitters exposed to He^+- or H^+-ion bombardment after fluences of the order of 10^{19} ions/m^2 or larger.[10-12] The nucleation and growth of these microprotrusions has been ascribed to an enhanced migration of surface atoms during ion bombardment. However, the FIM observation of voids and dislocation loops after field evaporation of several monolayers, from field emitter tips exposed to a similar He^+-ion fluence, indicates a gas-implantation-induced mechanism of formation.[10,13] It has been recently demonstrated that microprotrusions are easily formed also on the flat Pt(111) surface by the surface annealing of dislocation loops, resulting from the loop punching of overpressurized He bubbles below the surface,[4] created during He^+-ion bombardment. Another experimental fact relevant to target-adatom formation is the observation of bright spots in the field electron pattern after ion impacts.[11] Each of these bright spots is supposed to be the consequence of a single-ion impact and has been interpreted as an indication of displaced surface atoms. The observation seems to suggest displaced surface atoms, although the image contrast in FEM, essentially due to work-function changes, may have various causes and consequently cannot be unambiguously attributed to a specific surface configuration. To the authors' knowledge, there is thus no definitive experimental proof for the formation of target adatoms on metals. Here we report the observation of adatom-island formation during ion bombardment of an atomically flat surface. This is a direct proof of target-adatom generation on metals.

The experiments described in the following were per-

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formed in a UHV chamber specially designed for STM investigations of ion-bombarded surfaces. The apparatus allows full sample temperature control down to 100 K in each step of sample preparation and sample analysis, in particular also during STM operation. The sample is mounted thermally insulated on a solid metal block, which is damped against vibrations. The block is fixed on a rigid manipulator tube of 70-mm outside diameter with two degrees of freedom: rotation and translation. This allows the sample to be moved in front of the preparation and measuring stages: LEED and Auger spectroscopy, ion gun and STM. The average ion flux of the differentially pumped ion gun can be measured by a Faraday cup mounted in the manipulator tube. The STM is a modified "Beetle-type"[14] microscope turned upside down. All topographs presented in this paper were obtained in the constant-current mode. Typically the tunneling current was 1 nA with a tunneling voltage of +300 mV applied to the tungsten tip. Variations of tunneling voltage and current did not influence the morphology observed on the STM topographs. The base pressure of the chamber is below 2×10^{-10} mbar without the cold wall operative.

The platinum crystal has been cut with high precision parallel to the (111) plane, leading to an average terrace width of 1000–2000 Å. The clean sample is prepared by cycles of oxygen exposure ($p_{\text{oxygen}}=2\times10^{-6}$ mbar) and 1-keV Ar^+ bombardment both at 850 K and subsequent annealing at 1200 K. The sputtered sample is prepared by exposing it to the ion beam for a given time while keeping the crystal at constant temperature. This temperature is referred to in the following as the sputtering temperature. The results presented here were obtained with a 600-eV Ar^+-ion beam at normal incidence and the sample kept at temperatures between 350 and 625 K. The beam is scanned to ensure a homogeneous fluence over the entire sample. When the desired ion fluence is reached, the ion bombardment and the sample heating are switched off simultaneously and the sample cools down. The morphology is frozen in. The sample is then transferred to the STM position, the STM is lowered onto the sample holder, and the tip approached. The STM topographs are taken from various locations on the Pt(111) surface. The sputtering yield for normal incidence 600-eV Ar^+ ions onto Pt(111) was determined to be 2.2 atoms/ion at sputtering temperatures around 750 K by a method based on STM analysis of topographs.[5] All the topographs presented here were measured on samples sputtered with an average ion flux of 2.6×10^{16} ions/m^{2}s and a fluence of 3.1×10^{18} ions/m^2, which corresponds to the removal of 0.45 ± 0.05 monolayers (ML).

In Fig. 1, four topographs prepared at different sputtering temperatures—(a) 350 K, (b) 450 K, (c) 550 K, and (d) 625 K—are compared. All other conditions of sputtering and the scales of the images are identical. On all images vacancy islands of various shapes and sizes one atomic layer deep are visible (dark). These are formed by the nucleation of monovacancies produced by sputtering and the further growth of these nuclei. At sputtering temperatures below 550 K [i.e., in Figs. 1(a) and 1(b)] small adatom islands with diameters up to 30 Å are observed on the topographs as bright spots. Since only 0.45 ML have been sputtered away, it is evident that the adatom islands are situated *on* the initial surface layer. The adatom islands disappear at temperatures around 550 K under the given conditions of flux. Topographs taken from samples with sputtering temperatures around 540 K typically show a few adatom islands, whereas on topographs taken from samples with 550 K sputtering temperature there are no more adatom islands. The line scan in Fig. 2 demonstrates that the height of the adatom islands is just the height of a Pt monolayer of the Pt(111) surface. Adatom islands produced at sputtering temperatures above 500 K exhibit step edges that follow preferentially the close-

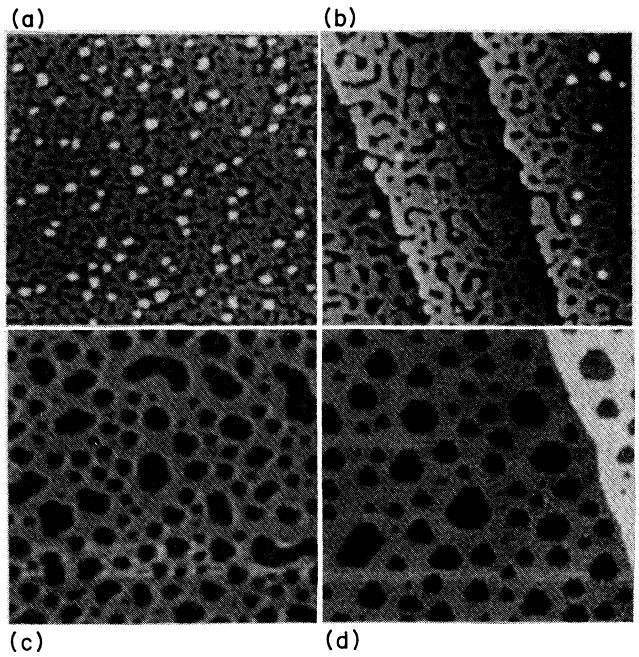

FIG. 1. Topographs of Pt(111) after removal of 0.45 ML at (a) 350 K, (b) 450 K, (c) 550 K, and (d) 625 K, respectively. The scan width in each topograph is 700×700 Å^2 with all other conditions of preparation and sputtering identical (see text).

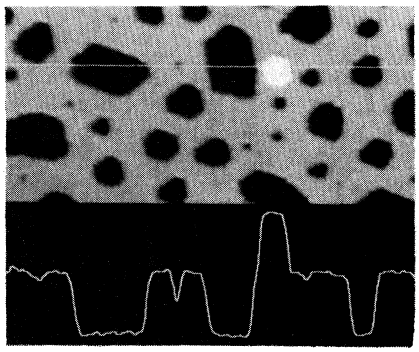

FIG. 2. Topograph as in Fig. 1, except for the sputtering temperature of 540 K and the scan width of 400×200 Å^2. The line scan demonstrates that the adatom island is 1 monolayer high.

packed ⟨110⟩ directions, as obvious, e.g., in Fig. 2. According to the described properties of the adatom islands, the reproducibility of their formation and the sample cleanness, there can be no doubt that the adatom islands are Pt adatom islands. Annealing experiments discussed below are also in agreement with this conclusion.

Before we leave the description of the topographs we want to point out that also the vacancy islands undergo a transition, namely, a shape transition in the same temperature range. Whereas in Figs. 1(a) and 1(b) the vacancy islands have elongated and mostly branched shapes with their step edges rather arbitrarily oriented, in Figs. 1(c) and 1(d) the vacancy islands have a convex shape with step edges following the close-packed ⟨110⟩ directions.[15]

In summary, (i) platinum-adatom islands of monatomic height are formed on the initial surface layer during ion bombardment at temperatures below 550 K; this demonstrates unequivocally that *target adatoms* are generated with substantial efficiency during the sputtering process. (ii) At sputtering temperatures above 550 K no Pt-adatom islands are formed during ion bombardment. This observation does not imply an inhibition of the adatom generation mechanism at higher temperatures, but rather of the adatom-island formation (see below).

In the following, first a description of the adatom-island formation process will be given and then the absence of adatom islands at higher temperatures will be discussed.

Pt-adatoms on Pt(111) are highly mobile at the temperatures of interest: They can be assumed to be mobile even at temperatures below 100 K.[16] During sputtering the density of target adatoms increases continuously and may reach a degree of supersaturation high enough to form stable adatom clusters, i.e., adatom clusters for which the probability to grow by another adatom arriving at its step edge is greater than the probability to lose an adatom by dissociation or sputtering. These stable adatom clusters will continue to grow during the sputtering time until the source of adatoms, i.e., the ion bombardment, is cut off. Upon cooling the adatom islands are frozen and can be observed in the STM topographs.

The absence of adatom islands above 550 K can hardly be explained by changes in the sputtering process itself. Indeed, in view of the relatively high energies involved, the sputtering process is known to be largely temperature independent. This is particularly true at temperatures well below the melting point (for Pt, $T_m = 2045$ K). Therefore, the explanation has to be found in a process which becomes active above about 550 K and which impedes the build up of an atom density high enough to lead to stable adatom clusters. Such a process has been uncovered recently during the study of the homoepitaxial growth of Pt on Pt(111). It has been found that when increasing the substrate temperature, around 500 K there is a transition from three-dimensional growth (often called island growth) to 2D layer-by-layer growth.[17] This transition results from the fact that the interlayer mass transport which is hampered below 500 K becomes possible at higher temperatures. More precisely, the potential barrier present at the edge of monoatomic high Pt-islands (present down to substrate temperatures ~300 K, see Ref. 17) which hinders at $T < 500$ K the Pt adatoms to jump down onto the lower level terrace can be overcome above 500 K due probably to the higher kinetic energy of the Pt adatoms.[18]

The onset of this interlayer mass transport above 500 K also explains straightforwardly the absence of adatom islands in the topograph figures 1(c) and 1(d) at sputtering temperatures of 550 K and above. Indeed, it is obvious from Fig. 1 and also from preceding experiments[5,19] that the monovacancies created by ion bombardment above 180 K are mobile and cluster into vacancy islands. These islands which represent lower level (111) terraces are separated from the initial (111) surface by monoatomic steps, along which the mentioned potential barrier is present, in general. Below 500 K the barrier keeps the target adatoms from jumping down into the vacancy islands so that their density on the initial outermost layer can grow, leading eventually to their nucleation into stable adatom clusters which after further growth are seen in Fig. 1. Above 500 K the target adatoms become able to overcome the barrier, and jump down into the vacancy islands where they are caught at the lower part of the step edge. This leakage of the barrier, which increases with temperature, hampers increasingly the buildup of a high density of target adatoms on the initial Pt layer so that around 550 K nucleation into stable adatom clusters is no longer possible. As a consequence, no target-adatom islands are observed above this temperature.

The remarkable correspondence between the growth mode transition monitored by thermal He scattering[17] and the disappearance of target-adatom islands as observed by STM (Fig. 1) and the fact that both are straightforwardly explained by the same process—the change in the ability of the potential barrier to withhold adatoms from leaving the upper terrace—is strong additional support for the existence of the process itself and for the fact that the adatom islands seen in Fig. 1 are formed by the nucleation of target adatoms.

In addition, annealing experiments were performed to investigate further the properties of the adatom islands. For this purpose samples sputtered at 350 K were annealed to higher temperatures after the end of sputtering. The most significant result of the experiments is that the adatom islands disappear only after annealing at a temperature of about 600 K. Thus the maximum temperature of island formation during sputtering (550 K) and the temperature of their disappearance by annealing (600 K) are significantly different. This indicates that the origin of the absence of adatom islands after sputtering above 550 K and that of the disappearance of already existing islands upon annealing above 600 K are different. As discussed above, the maximum temperature of island formation during sputtering is determined by the onset of interlayer mass transport; on the other hand, the temperature at which they disappear during annealing is determined by the onset of the thermal dissociation of the islands. The onset of the interlayer mass transport of adatoms is due to the increased thermal energy of the adatoms at higher temperatures, allowing them to overcome a potential barrier associated with step edges.[17] In contrast, the onset of thermal dissociation of adatom islands is due to the thermal 2D evaporation of Pt atoms from the island

step edge.[20] This adds another element of consistency to the discussion above.

In summary, it was demonstrated that even at low-energy ion bombardment, target adatoms are produced in large numbers, confirming theoretical predictions of their existence.[6,7] These target adatoms nucleate into adatom islands, up to such temperatures at which the condition of three-dimensional growth in the homoepitaxy of Pt on Pt(111) is fulfilled.

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[1]G. Carter, B. Navinsek, and J. L. Whitton, in *Sputtering by Particle Bombardment,* edited by R. Behrisch (Springer, Berlin, 1983), Vol. 2, p. 231.

[2]G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).

[3]I. H. Wilson, N. J. Zheng, U. Knipping, and I. S. T. Tsong, J. Vac. Sci. Technol. A **7**, 2840 (1989).

[4]Th. Michely and G. Comsa, J. Vac. Sci. Technol. B **9**, 862 (1991).

[5]Th. Michely and G. Comsa, Surf. Sci. (to be published).

[6]D. E. Harrison, Jr., P. W. Kelly, B. J. Garrison, and N. Winograd, Surf. Sci. **76**, 311 (1978).

[7]R. P. Webb and D. E. Harrison, Jr., Radiat. Eff. Lett. **86**, 15 (1983).

[8]W. Schilling, P. Ehrhardt, and K. Sonnenberg, in *Fundamental Aspects of Radiation Damage in Metals,* edited by M. T. Robinson and F. W. Young, Conference No. 751006, Pt. 1 (Energy Research and Development Administration, Washington, D. C., 1975), p. 470.

[9]I. H. Wilson, J. Belson, and O. Auciello, in *Ion Beam Modification of Surfaces,* edited by O. Auciello and R. Kelly (Elsevier, New York, 1984), p. 225.

[10]Zh. I. Dranova and I. M. Mikhailovskii, Fiz. Tverd. Tela (Leningrad) **12**, 132 (1970) [Sov. Phys. Solid State **12**, 104 (1970)].

[11]J. Y. Cavaille and M. Drechsler, Surf. Sci. **75**, 342 (1978).

[12]P. R. Schwobel, J. Appl. Phys. **64**, 2359 (1988).

[13]J. M. Walls, R. M. Boothby, and H. N. Southworth, Surf. Sci. **61**, 419 (1976).

[14]K. H. Besocke, Surf. Sci. **181**, 145 (1987).

[15]Th. Michely and G. Comsa (unpublished).

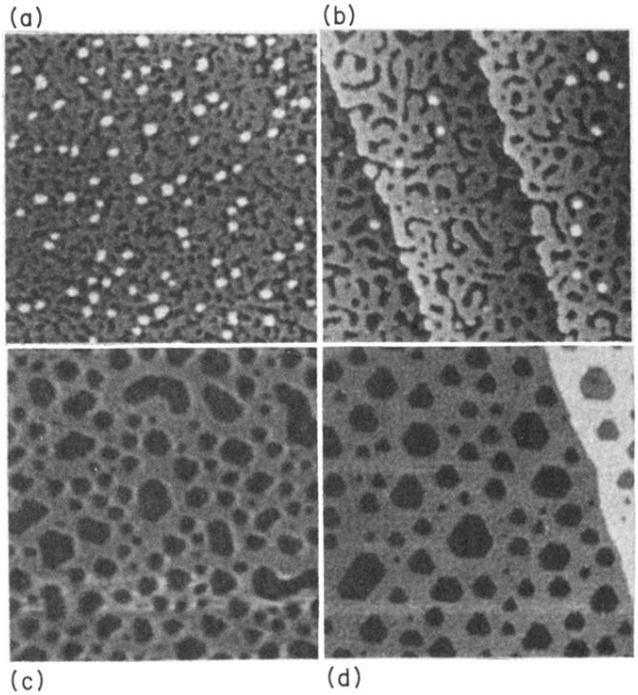
[16]D. W. Basset and P. R. Webber, Surf. Sci. **70**, 520 (1978).

[17]R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **65**, 733 (1990).

[18]When interlayer mass transport takes place, it proceeds by adatom diffusion across a down step. The inverse up-step process is highly improbable. This is known from FIM investigations, where the former has been observed often, while the latter never. This is to be expected even in a simple nearest-neighbor model in which the down-step jump implies the breaking of one bond, while the up-step one of three bonds.

[19]B. Poelsema and G. Comsa, *Scattering of Thermal Energy Atoms* (Springer, Berlin, 1989).

[20]More detailed information about the 2D vaporization and condensation of islands are expected to be obtained in vapor-deposition experiments in which the size and shape of the islands can be manipulated more easily. Such experiments, investigating the effects of temperature and deposition rate, are in progress.



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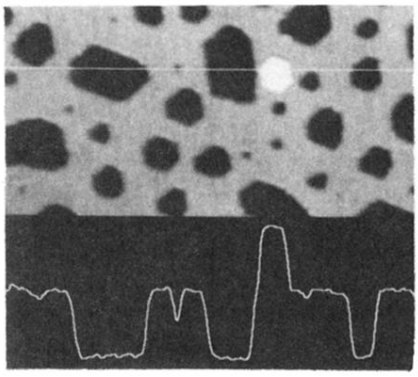

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