# "Two-Layer" Behavior of the Pt(111) Surface during Low-Energy Ar$^+$-Ion Sputtering at High Temperatures

Bene Poelsema, Laurens K. Verheij, and George Comsa
*Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich GmbH, D-5170 Jülich, West Germany*

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The discovery of a "two-layer" behavior of the surface resulting from the concomitant action of sputtering and annealing at high temperatures is reported. As a result the intensity of thermal He beams scattered from a surface under ion bombardment exhibits pronounced oscillations. The use of this new feature for the measurement of sputtering yields of virgin surfaces is proposed.

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Little attention has been paid so far to the influence of processes in the outermost surface layers on the dynamics and morphology of radiation damaged surfaces. There is, however, some evidence that such an influence exists.[1-3]. Thermal-He scattering is extremely sensitive with respect to any kind of surface disorder (adsorbates,[4] steps,[5,6] ion-induced damage[7]), it is nondestructive, and it can be performed during ion sputtering (no mutual influence). Accordingly, we used He scattering to study the Pt(111) surface during ion bombardment as a function of surface temperature $T_s$. The most exciting result, the discovery of the "two-layer" behavior during bombardment at high $T_s$, will be presented here. Its practical implication is a unique method for the measurement of sputtering yields on virgin surfaces.

The measurements to be reported were performed in a system described previously.[8] The He beam energy was 16 meV. For an incident angle $\theta_i = 52°$ the transfer width originating in the instrumental geometry is $w \simeq 350$ Å. A differentially pumped ion gun was used to produce the radiation damage. The intensity and homogeneity of the ion beam were measured *in situ* with a Faraday cup. All results reported were obtained with 600-eV Ar$^+$-ion flux of $4.7 \times 10^{12}$ ions cm$^{-2}$ s$^{-1}$, incident at 50° from the surface normal. The sputtering yield of 600-eV Ar$^+$ ions on poly-Pt at 0° is reported to be 1.2–1.4 atoms per ion.[9]

Two specific features of thermal-He scattering are used in the present study: the defect-induced attenuation of the coherently scattered He beam[6,7] and the interference between He waves scattered from terraces separated by monatomic steps.[5,6] Let us summarize the pertinent aspects of these features in the most simple case of Pt(111). The He-scattering pattern of an ideal close-packed surface consists in a good approximation only of a strong specular beam (mirrorlike scattering). At a real surface (i.e., with steps) a limited disturbed region near the steps does not scatter specularly.[6] Adjacent terraces can be made to scatter in phase, or in antiphase, by an appropriate choice of the angle of incidence $\theta_i^{\text{in}}$ and $\theta_i^{\text{anti}}$, respectively.[5,6] The corresponding specular intensities $I^{\text{in}}$ and $I^{\text{anti}}$ contain information on different aspects of the surface morphology.

The specular intensity $I^{\text{in}}$ results from the constructive interference of the scattering from the undisturbed areas of the terraces. Accordingly, the ratio $I^{\text{in}}/I_0^{\text{in}}$ is a measure for the undisturbed terrace area; $I_0^{\text{in}}$ is the specular intensity measured from an ideal, disturbance-free surface.[6]

Under antiphase conditions, destructive interference from the undisturbed areas of adjacent terraces causes a decrease of the specular intensity, i.e., $I(\theta_i)$ has a relative minimum at $\theta_i^{\text{anti}}$.[5,6] However, destructive interference can be observed only over a distance comparable to or smaller than the transfer width $w$ of the instrument. Accordingly, $I^{\text{anti}}/I^{\text{in}}$ is a measure for the average terrace size $\Delta$ relative to the transfer width $w$.[5,10] Note that for very large terraces ($\Delta >> w$) $I^{\text{anti}} = I^{\text{in}}$, whereas for an ideal instrument ($w = \infty$) and a real surface $I^{\text{anti}} = 0$.

The slightly different Debye-Waller factors for $\theta_i^{\text{anti}}$ (52°) and $\theta_i^{\text{in}}$ (43°) are taken into account by use of the ratio of the normalized intensities $R = (I^{\text{anti}}/I_0^{\text{anti}}) \times (I^{\text{in}}/I_0^{\text{in}})^{-1}$ rather than $I^{\text{anti}}/I^{\text{in}}$ as a measure for $\Delta/w$.[11]

The Pt(111) surface was practically defect free: The average terrace width was larger than 3500 Å.[6] This situation was reestablished at the start of each experimental run. $I^{\text{in}}$ (or $I^{\text{anti}}$) was monitored continuously during ion bombardment.

The plots in Fig. 1 show $I^{\text{in}}/I_0^{\text{in}}$ vs Ar$^+$-ion fluence at various constant surface temperatures $T_s$. All curves show a decrease of the specular He intensity with increasing Ar$^+$ fluence due to the damage created by ion impact. The temperature-induced defect annealing is also obvious: The

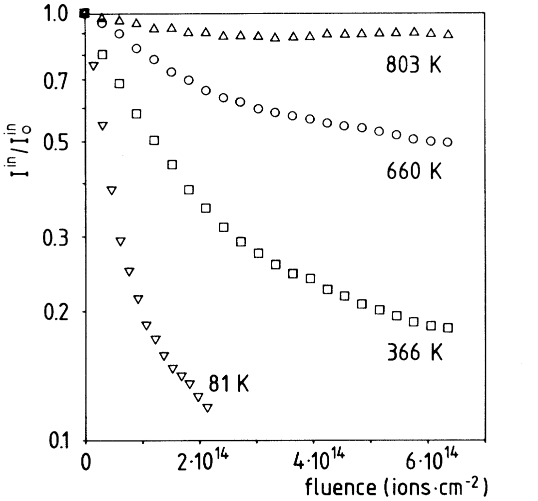

FIG. 1. Normalized specular He intensity $I^{\mathrm{in}}/I_0^{\mathrm{in}}$ vs 600-eV $\mathrm{Ar}^+$-ion fluence at various Pt(111) surface temperatures; He scattering under in-phase conditions ($\theta_i = \theta_f = 43°$).

higher the temperature, the lower the reduction in reflectivity. The various shapes of the curves are the result of the different mechanisms of defect annealing.[1–3, 12]

Note from Fig. 1 that at temperatures around 800 K the decrease in reflectivity is very low ($< 10\%$) even after sputtering away several monolayers and that it saturates. At these temperatures the simultaneous damaging and annealing leads to new, highly reflecting Pt(111) terraces with a low concentration of defect sites. As shown above, information on the size of the terraces can be obtained by monitoring of the intensity $I^{\mathrm{anti}}$.

At 89 K, the curve of $I^{\mathrm{anti}}/I_0^{\mathrm{anti}}$ vs fluence is identical to the corresponding $I^{\mathrm{in}}/I_0^{\mathrm{in}}$ curve in Fig. 1 in the whole fluence range. No new specularly reflecting terraces are created. Apparently, the vacancy clusters, which are created after a certain defect density is exceeded,[12] remain so small that their reflecting area is completely covered by the disturbance induced by the bordering step atoms. At $T_s > 300$ K the plots of $I^{\mathrm{anti}}/I_0^{\mathrm{anti}}$ vs fluence start to deviate from the corresponding plots in Fig. 1. The deviations set in at lower fluences and become larger, the higher the surface temperature. This demonstrates that the size of the vacancy clusters and newly formed (111) terraces increases with increasing temperature.[1–3] These terraces are sufficiently large to lead to a substantial mutual extinction of the specular He beam under antiphase conditions. The analysis of curves of $I^{\mathrm{anti}}/I_0^{\mathrm{anti}}$ leads, in conjunction with the corresponding $I^{\mathrm{in}}/I_0^{\mathrm{in}}$ curves, to valuable information on the simultaneous damaging and annealing mechanisms. This will be presented elsewhere.[12] Here we show and analyze the high-temperature (750 K $< T_s <$ 850 K) results. These results exhibit an unexpected behavior and allow a quite simple interpretation. In addition they lead to an elegant and efficient method for measuring sputtering yields on virgin surfaces.

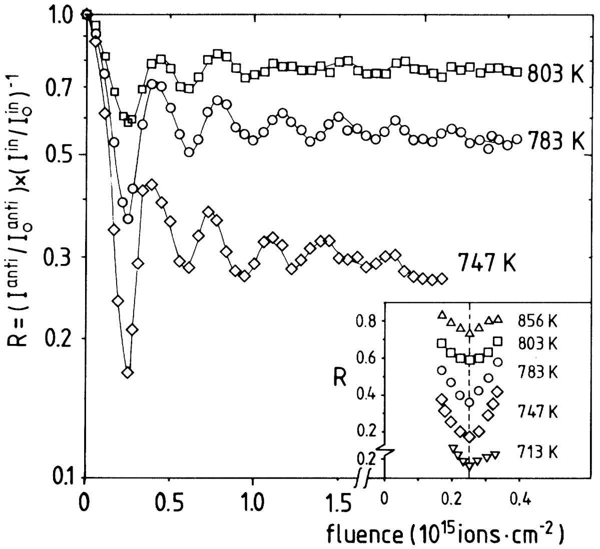

FIG. 2. Ratio of the normalized specular He intensities $(I^{\mathrm{anti}}/I_0^{\mathrm{anti}})(I^{\mathrm{in}}/I_0^{\mathrm{in}})^{-1}$ vs 600-eV $\mathrm{Ar}^+$-ion fluence at various Pt(111) surface temperatures; He scattering under antiphase ($\theta_i = \theta_f = 52°$) and in-phase ($\theta_i = \theta_f = 43°$) conditions, respectively. The thin solid lines are drawn just to guide the eye. The inset shows the first minima for five runs on an expanded abscissa and a linear ordinate.

In Fig. 2, curves of $R = (I^{\mathrm{anti}}/I_0^{\mathrm{anti}}) \times (I^{\mathrm{in}}/I_0^{\mathrm{in}})^{-1}$ vs fluence are plotted at the indicated temperatures. All three curves exhibit a pronounced oscillatory behavior. The oscillations are damped, $R$ reaching a steady-state value which increases with $T_s$. Estimates of the average terrace widths corresponding to these steady-state values are $\Delta_{747\mathrm{K}} \simeq 320$ Å, $\Delta_{783\ \mathrm{K}} \simeq 500$ Å, and $\Delta_{803\ \mathrm{K}} \simeq 1000$ Å, respectively. The increase of the average terrace width with $T_s$ can be rationalized by introducing a characteristic distance for vacancy annihilation, $d$. Let us consider a second-layer terrace, with linear dimensions smaller than $2d$, bordered by a ledge on an otherwise flat surface (first layer). By definition any vacancy created within a distance $d$ from the ledge will be annihilated. The annihilation is due to both the migration of the vacancy to the ledge and the filling up of the vacancy with migrating Pt atoms.[1–3] The vacancy annihilation proceeds by consumption of ledge atoms belonging to the first layer, i.e., the terrace grows at the expense of the rest of the surface. When the linear dimensions of the terrace become larger than $2d$, the vacancies created in its central region are no long annihilated; they cluster and a second terrace (third layer) is growing. Outside the terrace border, the evolution is similar. Of course terrraces in one layer may coalesce, but their size is ultimately limited to dimensions of the order of $d$ by the appearance of new terraces. This dynamical process eventually covers the whole surface with terraces of an average width $\Delta$ of the order of $d$. Both the mobility of vacancies and the density of Pt adatoms increase strongly with $T_s$. Thus, the critical distance $d$ and thus also $\Delta$ increase with $T_s$ as demonstrated by the data.

The existence of a characteristic distance for vacancy annihilation, $d$, explains also the oscillations in Fig. 2. Let us first consider an idealized situation: The crystal is initially perfect consisting of a single (111) terrace and the temperature is so high that $d$ is larger than the crystal dimensions. During sputtering the second layer will be gradually uncovered. Any vacancy created either in the first or in the freshly uncovered second layer is filled up with Pt atoms originating from the ledge separating the two layers, i.e., at the expense of the first layer. The third layer starts to be uncovered only after the first layer is completely removed. This is thus an ideal "two-layer" process. Let us now assume that the whole surface is imaged by an ideal He-scattering instrument ($w=\infty$). Starting with the initial value ($R=1$), the ratio $R$ decreases due to the destructive interference between the waves scattered from the growing second layer and shrinking first layer. When the areas of the two layers become equal, $R=0$. Upon further bombardment the area of the second layer becomes larger than that of the first one and thus $R$ increases. The initial value is recovered when the first layer is completely removed and only the second layer is exposed. If we continue the ion bombardment, the process repeats itself and the oscillatory behavior results.

A real He-scattering instrument (finite $w$) will not show any oscillations when directed on this ideal two-layer process because $\Delta/w >> 1$ and thus $R$ is always $=1$. However, the oscillations can be made visible by reduction of the surface temperature, i.e., by reduction of $d$ and thus $\Delta$ to dimensions comparable to $w$. The idealized situation assumed above is now partially met: Initially the crystal is still almost perfect ($\Delta > 3500$ Å) but $d$ is relatively small; note that, for the curves in Fig. 2, $d$ is still equal to or larger than $w$ ($d \approx \Delta \gtrsim w$). From the point of view of the whole crystal, which is initially almost perfect, a gradual degradation from the ideal two-layer behavior just described is to be expected. The signs for this degradation are obvious in Fig. 2: damping of the oscillation amplitudes and shortening of the periods. Both are more evident at lower $T_s$, i.e., for smaller $d$. However, during at least the first half oscillation period the behavior over the whole crystal [more precisely over the areas of the initial perfect (111) terraces—$\Delta > 3500$ Å] is almost an ideal two-layer behavior. This is evident, in particular, from the inset in Fig. 2, where the minima of five curves are shown on an expanded scale: In all five runs the first minimum is reached at the same fluence ($2.5\times10^{14}$ ions cm$^{-2}$) in spite of the fact that the $d$ values differ substantially (up to a factor of 9). The corresponding minimum $R$ values are not zero simply because $\Delta/w$ is not zero ($0.7 \lesssim \Delta/w \lesssim 6.4$). The reason for the appearance of the first minimum at always the same fluence is straightforward: As long as enough first-layer atoms are present (up to the half period they prevail) any new vacancy in the second-layer terraces is annihilated and the third layer cannot be uncovered. It is only towards the end of the first period, i.e., when most of the first layer is removed, that new vacancies in the second layer are no longer annihilated and third-layer terraces gradually appear (before the first layer is completely removed). This is the reason why at the end of the first period, $R$ does not recover its initial value $R=1$.

The degree of the deviation from the ideal two-layer behavior depends, of course, on the size of the area considered. On areas with linear dimensions of the order of $d$, i.e., of the order of the average terrace width $\Delta$, the two-layer behavior is maintained indefinitely. Accordingly, the gradual degradation of the pure two-layer behavior to a more than two-layer behavior on a large area ( > 3500 Å in size) can be understood by consideration of areas with linear dimensions of the order of $d$ ($d$ areas). The two-layer behavior of the $d$ areas is initially in phase and grows only gradually out of phase as a consequence of the uncovering of third-layer areas before the first layer is completely removed; less and less $d$ areas reach simultaneously the single-layer or the half-layer situation. The He-scattering instrument averages the momentary situation over the area of the He-beam spot size (about 0.2 mm in diameter). The gradual out-of-phase growth of the $d$ areas lead to the gradual degradation of the oscillations in Fig. 2 and eventually to the stationary situation, when the behavior of the various $d$ areas is completely out of phase.

The fact that, at least in the first half period, the two-layer behavior holds over large areas leads to a unique method for measuring sputter yields of virgin surfaces. Indeed, at the first minimum the first and second layer have equal areas, i.e., $2.5\times10^{14}$ ions $\mathrm{cm}^{-2}$ have sputtered away half of a Pt(111) layer ($7.5\times10^{14}$ Pt atoms).[13] The sputtering yield of the 600-eV $\mathrm{Ar}^+$ ions results to be $3.0\pm0.1$ atoms per ion in reasonable agreement with preceding data[9]: the corresponding poly-Pt value would be 1.9–2.2 (assuming a cosine dependence). Measurements with $\mathrm{Ar}^+$-ion energies in the range 400–1000 eV show the same kind of oscillations and the plot of sputtering yield versus ion energy has a trend similar to the poly-Pt case.[9] The proposed method avoids tedious weighing procedures of the sputtered material and requires only a careful calibration of the ion flux.

The discovery of the two-layer behavior has two remarkable implications: (1) a unique opportunity to measure sputtering yields at virgin surfaces and (2) the finding that the sequential layer-removal model, frequently used in secondary ion mass spectroscopy, is applicable only at high temperatures and low fluences. The outstanding sensitivity of He-scattering with respect to surface morphology, its nondamaging character, and its compatibility with running damaging and annealing processes make it a promising tool for the investigation of these processes.

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[13] In first approximation, the *net* transport between the first and deeper layers, due to cascade mixing, is zero (U. Littmark, private communication).