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# Mechanisms for annealing of ion-bombardment-induced defects on Pt(111)

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The morphology of a Pt(111) crystal during bombardment with 600-eV $Ar^+$ ions has been investigated at constant temperatures $T_s$ with thermal-energy atom scattering. Below $T_s \lesssim 600$ K the formation of three-dimensional (3D) structures is observed, while above $T_s \gtrsim 700$ K the removal proceeds layer by layer. From the quantitative modeling of the data, we infer that 3D structures develop when annealing proceeds only by *intra*layer diffusion of vacancies, while layer-by-layer removal is observed when *inter*layer mass transport also becomes effective. The latter process is believed to be related to the onset of meandering (roughening) of atomic steps.

In spite of the importance of surface damage, little attention has been paid so far to processes governing the morphology of surfaces during ion bombardment. Only a few *in situ* investigations of the evolution of the surface morphology *during* ion bombardment have been performed. These have been done using low-energy ion scattering[1,2] and also thermal-energy (He)-atom scattering (TEAS).[3,4]

The evolution of the surface morphology during ion bombardment depends on the interplay between sputtering and annealing, i.e., between damage creation and annihilation processes. Annealing, involving both the availability and the mobility of vacancies and/or adatoms depends strongly on surface temperature. It is the aim of this paper to shed light on the nature of the annealing processes going on during sputtering as a function of temperature.

The investigations have been carried out on almost defect free Pt(111). The results are believed to hold also for other metal surfaces. The measurements have been performed using TEAS which can be applied in the presence of the damaging ion beam. It supplies direct information on step densities and on the distribution of low index terraces *during* ion bombardment and annealing.

Previous TEAS investigations in our laboratory have shown that the vacancies created on Pt(111) by ion bombardment stay thermally immobile up to a surface temperature $T_s = 180$ K.[4] Above $T_s = 180$ K thermal annealing sets in, leading to a gradual decrease of the defect concentration with increasing temperature. In addition, layer-by-layer removal of platinum has been observed in the surface temperature range 700 K $\lesssim T_s \lesssim$ 850 K. The new results for 400 K $\lesssim T_s \lesssim$ 600 K can be rationalized in terms of the development of three-dimensional (3D) defect structures in which the exposed layers are Poisson distributed. The conclusion of general significance we infer concerns the physical origin of the difference between the annealing processes going on at different temperatures during sputtering, leading to the creation of three-dimensional defect structures at $T_s \lesssim 600$ K, and to layer-by-layer removal at $T_s \gtrsim 700$ K; while the creation of three-dimensional structures involves only *intra*layer diffusion, the layer-by-layer removal also requires *inter*layer mass transport.

The UHV-TEAS apparatus used in this investigation has been described in more detail elsewhere.[5] A 16-meV He beam is generated by expansion through a 30-$\mu$m nozzle cooled by liquid nitrogen (stagnation pressure 5 bars). The beam is collimated to a full width at half maximum of 0.2° and the solid angle of acceptance of the detector is 0.15°. The polar incidence angle of the probing He beam is adjusted mostly at $\theta_i = 51.5°$ (antiphase condition). Under these conditions the transfer width of the instrument[5] is ~400 Å and the spot area of the He beam on the surface is ~0.5 mm$^2$.

The ion beam is produced by a simple sputter gun. The 600-eV $Ar^+$ ion beam illuminates the entire 1-cm$^2$ Pt(111) surface at approximately 45°. The flux was about $1.5 \times 10^{13}$ $Ar^+$ ions/cm$^2$s with an inhomogeneity of less than 15% across the entire surface.

The crystal was cleaned using standard techniques: heating at about 700 K in an $O_2$ environment and, if necessary, $Ar^+$ sputtering. Before each experimental run the sample has been heated to above 1000 K. A step density of less than $10^{-3}$ of the surface prepared in this way has been determined by carefully measuring He rocking curves.[5]

The scattering of thermal He atoms from close-packed metal surfaces is dominated by an intense specular peak. The variation of the height of this peak with time, i.e., with ion fluence, serves as a probe of the evolving surface morphology during ion bombardment. Two types of information are available, depending on the scattering conditions. Appropriate adjustment of the incident He-beam angle leads to constructive (in-phase) or destructive (antiphase) interference between He scattering contributions from adjacent Pt(111) terraces.[5] The specular He beam is strongly attenuated by diffuse scattering at surface defects; it has been found, in particular, that monatomic step rows lead to diffuse scattering from a strip about 12 Å wide.[5] Therefore, starting with an almost defect free surface, the variation of the in-phase peak height directly reflects the evolution of the concentration of monatomic steps with ion fluence. The antiphase peak height yields, in addition, information on the area distribution of the exposed (111) terraces at different height levels.

Figure 1 shows antiphase "damage curves," i.e., the normalized height of the helium specular antiphase peak, measured during sputtering as a function of the ion fluence. The peak height $I$ is normalized to its defect free surface value $I_0$ at the same temperature so that the results for various temperatures can be compared directly: Debye-Waller effects are automatically canceled.[5] The data for the intermediate range $T_s = 428$, 499, and 598 K show an exponential decay and, most strikingly, are identical, irrespective of the temperature. This is in contrast to the data in the high-temperature range $T_s \gtrsim 700$ K ($T_s = 698$ and 800 K in Fig. 1 and those shown previously in Fig. 2 of Ref. 3); these show a clear minimum at a fluence of $3 \times 10^{14}$ ions/cm$^2$, where half of a Pt monolayer (ML) is sputtered away, and a strong temperature dependence. The lack of temperature dependence between 400 and 600 K of the antiphase data in Fig. 1 is surprising in view of the substantial change of the average terrace width in this temperature range: In-phase data similar to those shown in Fig. 1 of Ref. 3 demonstrate that at 600 K the step density is less than half that at 400 K, i.e., the terrace width has at least doubled. We will first explore the conditions which may generate a distribution of terraces compatible with these two types of experimental data: a temperature-independent exponential decay of the antiphase peak height versus fluence, in spite of substantial temperature dependence of the step density inferred from in-phase data.

The exponential decay of the antiphase peak height (Fig. 1) can be rationalized by the formation of three-dimensional defect structures. The formation of such structures has already been demonstrated during ion bombardment of Ni(110) in a similar temperature regime.[2] The damage curves in Fig. 1 can be described quantitatively by making two reasonable assumptions: (1) atoms are sputtered only from uncovered layers and (2) annealing involves only *intra*layer mass transport, i.e., the mobile monovacancies created by sputtering[3] are annealed only by merging with other vacancies or vacancy islands located in the same layer or more specifically, a vacancy can be annihilated when encountering a step-down edge but not a step-up edge.[6] (Vacancies belonging to the same layer, which have merged into a 2D cluster, are called vacancy islands; they are in fact terraces of the next lower layer.)

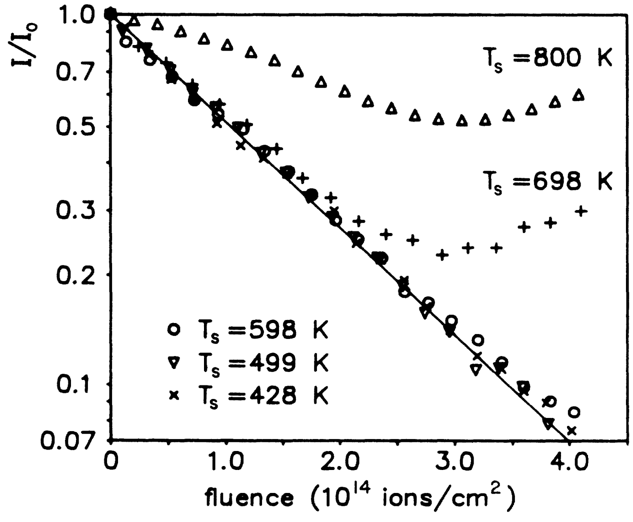

FIG. 1. Normalized antiphase specular He peak height during sputtering of the Pt(111) surface at the indicated temperatures with 600-eV Ar$^+$ ions vs fluence. The solid line corresponds to Eq. (4) for $Y = 2.5$ atoms/ion (see text).

Let us denote the sputtering yield by $Y$ and the exposed fraction of layer $n$ by $x_n$. The number of atoms sputtered from the $n$th layer by $dF$ ions impinging per unit area is given by $dN_n = x_n Y dF$. The corresponding removed area is $dN_n/n_s$, where $n_s$ is the number of Pt atoms per unit area in each layer. The differential change of the exposed fraction of layer $n$ amounts to

$$dx_n = Y n_s^{-1}(x_{n-1} - x_n) dF \, . \tag{1}$$

With the initial condition $x_0 = 1$ and $x_n = 0$ for all $n \neq 0$ at $F = 0$, the solution for the system of coupled differential equations (1) is given by

$$x_n = \frac{(Y n_s^{-1} F)^n}{n!} e^{-Y n_s^{-1} F} \, , \tag{2}$$

i.e., the exposed fractions of the layers $x_n$ are Poisson distributed. Assuming that the diffusely scattering strip along the steps is centered along the step edge, the normalized amplitude $A/A_0$ of the specular beam becomes under ideal antiphase conditions

$$\frac{A}{A_0} = \sum_{n=0}^{\infty} (-1)^n x_n = e^{-2Y n_s^{-1} F} \tag{3}$$

and thus, the normalized antiphase specular peak height is given by

$$\frac{I}{I_0} = e^{-4Y n_s^{-1} F} \, . \tag{4}$$

The validity of this equation is restricted to the low fluence regime, where up to about $\frac{2}{3}$ of a ML of Pt atoms have been removed. The reason for this is the relative instability of small layer entities left behind by sputtering and also effects related to methodological limitations. They will be discussed in a forthcoming paper.

Equation (4) accurately reproduces the experimental data in Fig. 1 for $T_s = 428$, 499, and 598 K; this holds for the exponential decay as well as for the independence from the step density, i.e., ultimately from temperature. (The sputtering yield $Y$ is not or hardly temperature dependent.[7]) In addition, the common temperature-independent slope of the antiphase damaging curves in Fig. 1 directly supplies a value of the sputtering yield $Y = 2.5$ atoms/ion for 600-eV Ar$^+$ ions incident on Pt(111).

Let us now briefly summarize the behavior during ion bombardment in the high-temperature range ($T_s \gtrsim 700$ K) which was uncovered some years ago by the same TEAS procedure and with a similar high-quality Pt(111) surface.[3,5] In this range, the height of the antiphase He peak versus ion fluence does not show an exponential decay, but damped oscillations with a period equal to the fluence needed to sputter one layer of Pt atoms. It has been concluded that this corresponds to an essentially layer-by-layer removal. Meanwhile, this has been confirmed by many measurements. A nice quantitative confirmation is also the fact that the value of the sputtering yield resulting from the position of the minima in the high-temperature curves ($T_s = 698$ and 800 K in Fig. 1) is identical in the limit of the experimental error, to the value from Eq. (4) in the intermediate temperature range. Quite different data (exponential versus oscillation) reflecting quite different processes (3D structures versus layer-by-layer removal) lead to the same sputtering yield value.

By definition, during ideal layer-by-layer removal, fractions of only two consecutive Pt-atom layers ($x_n$ and $x_{n+1}$ in the notation above) are exposed; i.e., $x_n + x_{n+1} = 1$. This implies that not only monovacancies created in the upper layer $n$, but also those created in the lower layer $n+1$ are annihilated by consuming Pt atoms belonging to layer $n$. Otherwise, if the monovacancies in layer $n+1$ were to anneal by merging with other vacancies in the same layer and form a vacancy island, this would represent an exposed $n+2$ layer fraction at variance with the definition of the layer-by-layer removal. On the other hand, the annihilation of vacancies in the $n+1$ layer by atoms of the $n$ layer implies *inter*layer mass transport. In other words the difference between the two temperature regimes is due to the fact that *inter*layer mass transport, which was forbidden in the intermediate, is allowed in the high-temperature regime.

The vacancy annealing involving *inter*layer mass transport, i.e., the annihilation of vacancies in the lower terrace by atoms originating in the surrounding "step-up" border, may proceed in either of the following ways: (1) migration of the vacancies to the steps and the jump of a step atom into the vacancy; and (2) the creation of adatoms by detachment of kink atoms from the step-up edge, migration of the adatoms on the lower terrace, where, after meeting a vacancy, they jump into it. Both ways involve a number of processes requiring thermal activation. While the activation energies for vacancy and adatom migration are low enough so that both vacancies and adatoms are known to be highly mobile well below 600 K, the activation energies for the other processes (jump of a step atom into an adjacent vacancy, creation of an adatom and jump of an adatom into a adjacent vacancy) are certainly larger. When the probability of one or of all of these processes becomes significant, *inter*layer mass transport occurs. So far, we do not know the magnitude of these activation energies and cannot tell whether the specific height of one or of all these activation barriers plays the determining role in the transition from the predominant *intra*layer to the *inter*layer annealing between 600–700 K.

However, the following observation might help to find the direct cause of the relative fast transition (within ~100 K) between these annealing modes: it appears that both ways mentioned above, which lead to vacancy annealing, are directly influenced by the number of kink atoms available. For (2) this is obvious, because the source of adatoms are precisely the kink atoms. But also in case (1) it is clear that the probability for a kink atom to jump into a vacancy is much higher than that of a "normal" more strongly bound step atom. On the other hand, a substantial increase of the kink density is associated with the roughening of stepped surfaces, which has been actively investigated recently.[8,9] The roughening of these particular surfaces is due to the strong meandering of the step rows, i.e., to the enhancement of the kink concentration. It is attractive to speculate that the onset of the *inter*layer annealing of vacancies and that of the step meandering are related. In the present case, the Pt(111) surface is initially nonstepped. However, during ion bombardment and annealing vacancy islands surrounded by step edges are continuously created; these step rows are expected to meander at the same temperature at which the step rows of a nominally stepped Pt surface would do so. There are so far no roughening measurements for stepped Pt surfaces. However, by scaling the roughening temperature of the Ni and Cu stepped surfaces measured so far[8,9] to the respective melting temperatures we get for the roughening temperature of a stepped Pt surface (with interstep distance > 6 step rows[10]) the right value around 600–700 K.

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