

Healing kinetics of a sputter-roughened surface

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The smoothening kinetics of a sputter-roughened Pt(110) surface has been investigated by in situ time-resolved X-ray diffraction. It is shown that the flattening of the surface due to surface diffusion proceeds with a power-law time dependence. The exponent n_α characterizing the decay of the average step density is found to depend on temperature, reaching the value $\sim 1/2$ at high temperatures (small roughness), close below the surface disordering temperature.

Recently there has been considerable interest in the dynamical evolution of order in condensed phases as they approach thermodynamic equilibrium from an initial non-equilibrium disordered state [1–7]. The background of this interest is the expectation that the kinetic behavior of different systems is only governed by a few fundamental properties like symmetry and dimensionality and thus could be classified according to different universality classes similar to equilibrium phase transitions. The now classic paper of Lifshitz and Slyozov [8] examined the growth kinetics of domains of one phase in a large matrix of a second phase. They found that the domain growth at long times is limited by diffusion through the matrix and that the growth of the average ordered domain size L , obeys a power law

$$L = A(T)t^n \quad (1)$$

with a universal exponent $n = \frac{1}{3}$. Here $A(T)$ is a temperature-dependent rate coefficient and t is the ordering time. In the Lifshitz–Slyozov model

the density of atoms and the order parameter is a conserved quantity. The kinetics of a two-phase system with non-conserved order parameter should obey the Lifshitz–Allen–Cahn (LAC) growth law with exponent $n = \frac{1}{2}$ [9]. Experimentally the asymptotic growth laws have been studied in the ordering kinetics of chemisorbed layers on single-crystal surfaces and in the kinetics of surface structural phase transitions [3–7,10,11]; $n = \frac{1}{3}$ has been observed in the ordering of $p(2 \times 1)$ oxygen adlayers on W(110) [3], while the LAC growth law has been observed in (2×1) oxygen on W(112) [4].

Closely related to the questions addressed above, and in addition of significant technological interest, is the smoothening kinetics of a crystal surface. A usual approach to prepare a well-ordered flat single-crystal surface is the initial “cleaning” damage of the surface by bombardment with low-energy ions (~ 500 – 5000 eV), a preparative process which is called sputtering, followed by extensive annealing at a high temperature T_A [12]. For temperatures T_A below the thermal roughening temperature T_R the anneal-

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ing will eventually lead to a microscopic smooth surface [13]. It has been shown by Villain [14] that the healing of a rough surface due to surface diffusion can be treated theoretically analogous to the Lifshitz–Slyozov theory and that the growth of the average flat terrace width should follow the same power law with exponent $\frac{1}{3}$.

Experimentally little attention has been paid so far to the annealing dynamics and morphology of radiation damaged surfaces. In this paper we report the first experimental study of the healing kinetics of a sputter roughened surface. The isothermal evolution of the morphology of a sputtered Pt(110) surface during annealing is followed by time-resolved X-ray diffraction. We find that the growth of the average terrace width between neighboring steps, i.e., the decay of the microscopic roughness of the crystal surface, follows a power-law with the exponent substantially varying with the annealing temperature and reaching value of $\sim \frac{1}{2}$ at high temperatures (~ 1000 K).

The measurements to be reported were made in the vacuum system described in detail in ref. [15] using the 5-circle diffractometer at beam line X16A of the National Synchrotron Light Source in Brookhaven. The Pt crystal was oriented ex situ to about 0.1° of the (110) orientation and polished before mounting to the sample holder. The sample temperature could be varied between 300 and 1600 K and was measured by a chromel–alumel thermocouple spot-welded to the crystal. The surface was cleaned by argon ion bombardment and subsequent annealing in an oxygen atmosphere in the usual way until no contamination could be detected by Auger spectroscopy. At low temperatures the surface is reconstructed with a (1×2) missing row structure, in which every second row of surface atoms along the $[1\bar{1}0]$ azimuth is absent [16]. A detailed analysis of the relative X-ray Bragg peak intensities and of the half-order rod profiles [17] revealed a substantial contraction of the first interlayer spacing and a modest lateral intralayer pairing on the second and fourth layer have been inferred.

In the following we will characterize the microscopic roughness by the density of surface steps rather than by the height–height correlation function (as is usual in studies of thermal rough-

ening). A surface with a high density of randomly distributed steps is rough, therefore roughness can be measured in a very direct way as step density. Steps affect the diffraction from a missing row reconstructed (110) surface in a particularly dramatic way. Because of the face-centering of the Pt-lattice, each step acts as a domain wall with quadrature phase difference, which leads to shifted superstructure (half-order) diffraction peaks at the in-plane diffraction position (momentum transfer perpendicular to the surface $l=0$) [18,19]. Shifted half-order diffraction peaks are indeed observed experimentally for Pt(110) [19] as well as for Au(110) [20].

The experimental diffraction profiles of Pt(110)(1×2) are quantitatively fitted in the framework of a simple model of surface disorder that contains besides randomly distributed monatomic steps (with total probability α) also conventional anti phase domain walls (with total probability β). In this model the (1.5, 0, 0) diffraction peak shifts by $\frac{1}{4}$ (in reciprocal lattice units) to larger wave-vectors solely due to the presence of the steps [19]. The peak broadening scales with $\frac{1}{2}\beta + \frac{1}{4}\alpha$ and is thus determined by the appearance of steps and anti phase defects. This unique behavior of the half-order diffraction peaks allowed us recently to demonstrate that the Pt(110)(1×2) surface undergoes at $T_c \approx 1080$ K = $0.53T_M$ a phase transition at which steps spontaneously appear [19]. Here we made use of the half-order peak shift to measure the evolution of the step density (i.e., the flatness) of a sputter roughened Pt(110) surface during the annealing process.

To study the isothermal smoothing kinetics, the clean and well-ordered Pt(110) surface was first bombarded with 1000 eV Ar^+ ions (dose of order 10^{16} Ar^+ ions per cm^2) at a target temperature of 300 K, in order to create a microscopically rough surface. Then the temperature of the sample was rapidly raised to a higher temperature T_{A1} and a sequence of X-ray diffraction profiles was recorded as a function of time during the anneal (the typical temperature stabilization time was ~ 1 min). When the smoothing began to slow down the sample temperature was again ramped up to a value $T_{A2} > T_{A1}$ and the diffrac-

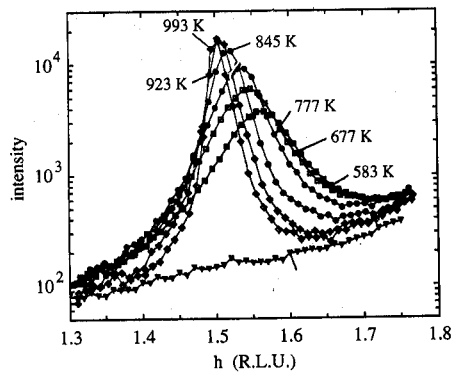


Fig. 1. The measured half-order diffraction peak lineshape ($h, 0.06, 0.06$) of a sputter-roughened Pt(110) surface after annealing at the temperature and time indicated. The direction of h is along the [001] surface azimuth.

tion profiles were again recorded versus annealing time, and so forth. Measurements were made from about 7 min after the initiation of the temperature step to 80 min thereafter, in the temperature interval between ~ 670 and ~ 990 K. Below ~ 650 K the smoothing of the surface was too slow to observe reliably. In fig. 1 we show a series of longitudinal X-ray diffraction profiles of the $(1.5, 0.06, 0.06)$ peak characterizing the healing of the rough surface. Each diffraction profile shown is the last spectrum of the isothermal time series at the temperature indicated. The series nicely demonstrates the healing of the sputter-roughened surface with increasing temperature. The freshly sputtered sample at 300 K gives almost no half-order signal at all. Annealing the sample at 677 K for 26 min generates a rather broad diffraction peak with the center significantly shifted by about 0.045 reciprocal lattice units (RLU) to higher wave vectors, characterizing a surface with a step density of $\alpha = 0.18$ (line defect density expressed in units of probability per lattice site). With increasing temperature the line continues to sharpen and the center shifts towards the half-order position. Eventually after a 38 min anneal at 993 K the diffraction line is very sharp and the wave-vector shift of the peak center is less than 0.001 RLU, characterizing a very flat surface with an average step spacing of about 500 Å.

Fig. 2 demonstrates the isothermal development of the $(1.5, 0.06, 0.06)$ diffraction peak profile with time for four different temperatures. Plotted versus annealing time are the peak shift, which is a direct measure of the step density, and the peak half width, which relates to the long-range coherence. Both quantities are extracted from fits of the diffraction line using the convolution of a simple Lorentzian with the distribution obtained for the fully annealed surface [19]. From fig. 2 we see that on a \ln - \ln scale peak shift and width decay linearly with time, i.e., both obey power-law behavior. However, while the peak width follows a power law with an almost temperature independent exponent, n_β , the exponent n_α of the peak shift substantially varies with temperature (see table 1). Its value starts close to the peak-width exponent $n_\alpha \approx n_\beta \approx 0.1$ at low temperatures and approaches $n_\alpha \approx \frac{1}{2}$ at 1000 K.

The more important of these two exponents is that of the peak shift which is a direct measure of

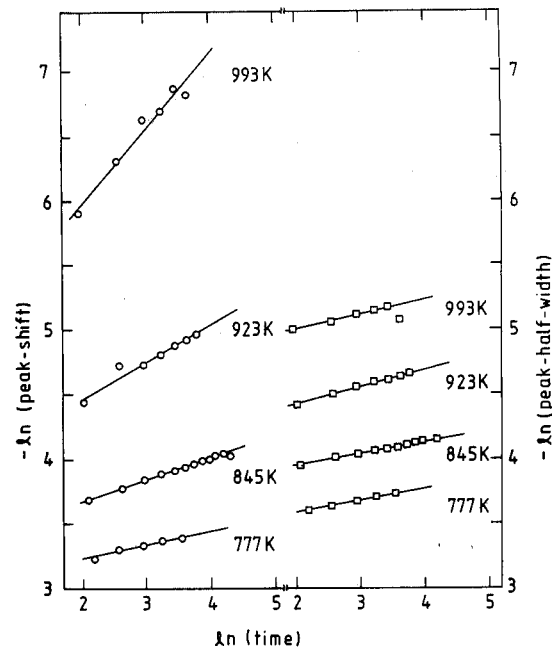


Fig. 2. The time dependent peak shift and peak width (HWHM) of the $(1.5, 0.06, 0.06)$ beam diffracted from Pt(110) is plotted for different annealing temperatures. Peak shift and width are measured in reciprocal lattice units and the time is measured in minutes. The solid lines represent power law fits to the data.

Table 1
The power law exponents n_α and n_β of the diffraction peak-shift and width, respectively, as a function of annealing temperature T_A

T_A (K)	n_α	n_β
777	0.099 ± 0.01	0.085 ± 0.01
845	0.164 ± 0.01	0.093 ± 0.01
923	0.302 ± 0.02	0.138 ± 0.016
993	0.581 ± 0.062	0.063 ± 0.034

the step density. The peak width although it is related to both RMS roughness and coherence length, is not a quantity that can be immediately compared with theory because predictions are not available. The step density is exactly equal to the theoretically predicted quantity which is the average flat domain size L . On Pt(110)(1×2) the steps are running preferentially along the $[1\bar{1}0]$ direction [21] reducing the problem to one dimension with $L \propto 1/\alpha$. According to the results in fig. 2 and table 1 the average step density increases with a power law $\alpha \sim t^{n_\alpha(T)}$ with $n_\alpha(T)$ being a function of temperature. Theories exist for thermal smoothening [14] and even theories that predict variable exponents [22]. In these theories the increase of the average flat terrace width with time, which is equivalent to the decay of microscopic roughness, is due to the diffusion of adatoms and vacancies on the surface. At temperatures high enough to overcome the barrier of diffusion, atoms migrate from the terrace edge of a small island (with chemical potential μ_1) to a neighboring larger terrace with a chemical potential $\mu_2 > \mu_1$, while vacancies follow the opposite way. Here the chemical potential of a terrace is defined by $\mu = \mu_0 + g/R$ with μ_0 being the chemical potential of the bulk, g the ledge free energy per unit length and R the radius of the island. As a net result terraces with higher chemical potential and valleys with lower chemical potential decay and the surface becomes smooth. However, this model is only valid in the limit of small thermal roughness with height fluctuations of a few atomic distances for lateral atomic distances of several hundred. Only in this limit of small roughness a power law behavior with a universal exponent $n_\alpha = \frac{1}{3}$ is expected.

This assumption is certainly unrealistic for a surface roughened by ion bombardment at low temperatures. Lancon and Villain [22] recently studied the smoothening kinetics of surfaces with larger roughness. Assuming that fluctuations of length L have a height proportional to L^γ , they derived a modified smoothening law with an exponent $n_\alpha = 1/(3 + \gamma)$ where γ is a measure of the initial roughness ($0 < \gamma < 1$). Only in the limit of small or negligible roughness $\gamma = 0$, the kinetics is described by the Lifshitz–Slyozov law. Initial state configurations can affect the smoothening exponent but are not sufficient to explain the variation of our experimental data.

The modified flattening theory of Lancon and Villain is also in disagreement with the experimental data at the high temperature end. While these authors predict the Lifshitz–Slyozov exponent $\frac{1}{3}$ for the limit of small initial roughness we measure a value of $n_\alpha \sim \frac{1}{2}$ in the experiment. The isothermal data set at 993 K has an initial distance of $\sim 200 \text{ \AA}$ between neighboring steps and thus should probe this limit.

Villain's smoothening mechanism does involve the assumption that mass transport of atoms and vacancies can equally well occur within a layer (intralayer mass transport) as between two consecutive layers (interlayer mass transport). A detailed study of the morphology of Pt(111) during Ar⁺-sputtering by Poelsema et al. [12,23], however, has revealed that below a critical temperature ($\sim 700 \text{ K}$ for the close packed Pt(111) surface) annealing involves mainly intralayer mass transport, i.e., the mobile atoms and vacancies are annealed only by merging with other vacancies or islands located in the same layer. Only above the critical temperature the annihilation of vacancies in the lower terrace by atoms from the surrounding step-up border, i.e., interlayer mass transport, becomes important. This process requires the creation of adatoms by detachment of kink atoms from the step-up edge, migration of the adatoms on the lower terrace and eventually the jump of the adatom into a vacancy. While we do not expect such a dramatic difference between intra and interlayer transport on the open, reconstructed (110) face of Pt, it might indeed be the complex competition between these which is re-

sponsible for the substantial temperature dependence of the annealing kinetics.

In addition the Lifshitz–Slyozov type of treatment of the surface smoothening process does ignore the microscopic anisotropy of the Pt(110) surface. Having a rectangular unit cell it has a doubly degenerated ground state with two equivalent (2×1) anti phase domains, and the order parameter which is defined as the difference in the area of the two domains is very unlikely to be conserved [24] which might give rise to Lifshitz–Allen–Cahn growth kinetics at high temperatures.

It is worth mentioning that the exponent $\frac{1}{2}$ is predicted by Martin and Perrailon [25] in a theoretical investigation of the flattening of a grooved anisotropic surface with parallel steps: a picture resembling to some extent the morphology of a Pt(110)(1×2) surface where steps are preferably running along the $[1\bar{1}0]$ direction [19,24].

In conclusion we have observed a temperature-dependent exponent in the ordering kinetics of a sputter-damaged surface. No single theory is available which describes our results for all temperatures. Theories that take our observations into account are therefore awaited with interest.

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References

- [1] A. Sadiq and K. Binder, *J. Stat. Phys.* 35 (1984) 517, and references therein.
- [2] J.D. Gunton, M. San Miguel and P.S. Sahni, in: *Phase Transitions and Critical Phenomena*, Vol. 8, Eds. C. Domb and J.L. Lebowitz (Academic Press, New York, 1983) p. 267, and references therein.
- [3] M.C. Tringides, P.K. Wu and M.D. Lagally, *Phys. Rev. Lett.* 59 (1987) 315.
- [4] J.K. Zuo, G.C. Wang and T.M. Lu, *Phys. Rev. Lett.* 60 (1988) 1053.
- [5] K. Heinz, A. Barthel, L. Hammer and K. Müller, *Surf. Sci.* 191 (1987) 174.
- [6] R.J. Behm, G. Ertl and J. Wintterlin, *Ber. Bunsenges. Phys. Chem.* 90 (1986) 294.
- [7] W. Witt and E. Bauer, *Ber. Bunsenges. Phys. Chem.* 90 (1986) 248.
- [8] I.M. Lifshitz and V.V. Slyozov, *J. Phys. Chem. Solids* 19 (1961) 35.
- [9] I.M. Lifshitz, *Sov. Phys. JETP* 15 (1962) 939; S.M. Allen and J.W. Cahn, *Acta Metall.* 27 (1979) 1085.
- [10] K. Heinz, G. Schmidt, L. Hammer and K. Müller, *Phys. Rev. B* 32 (1985) 6214.
- [11] P.A. Bennet and M.B. Webb, *Surf. Sci.* 104 (1981) 74; W. Telieps and E. Bauer, *Ber. Bunsenges. Phys. Chem.* 90 (1986) 197.
- [12] B. Poelsema, L.K. Verheij and G. Comsa, *Phys. Rev. Lett.* 53 (1984) 2500; L.K. Verheij, J.A. van den Berg and D.G. Armour, *Surf. Sci.* 122 (1982) 216.
- [13] J.D. Weeks and G.H. Gilmer, *Adv. Chem. Phys.* 40 (1979) 157.
- [14] J. Villain, *Europhys. Lett.* 2 (1986) 531; W. Selke, *J. Phys. C* 20 (1987) L455.
- [15] P.H. Fuoss and I.K. Robinson, *Nucl. Instrum. Methods* 222 (1984) 171.
- [16] E.C. Sowa, M.A. Van Hove and D.L. Adams, *Surf. Sci.* 199 (1988) 174; P. Fery, W. Moritz and D. Wolf, *Phys. Rev. B* 38 (1988) 7275.
- [17] E. Vlieg, I.K. Robinson and K. Kern, *Surf. Sci.* 233 (1990) 248.
- [18] P. Fenter and T.M. Lu, *Surf. Sci.* 154 (1985) 15.
- [19] I.K. Robinson, E. Vlieg and K. Kern, *Phys. Rev. Lett.* 63 (1989) 2578.
- [20] I.K. Robinson, Y. Kuk and L.C. Feldman, *Phys. Rev. B* 29 (1984) 4762.
- [21] G. Binnig, H. Rohrer, Ch. Gerber and E. Weibel, *Surf. Sci.* 131 (1983) L379; T. Gritsch, D. Coulman, R.J. Behm and G. Ertl, *Phys. Rev. Lett.* 63 (1989) 1068.
- [22] F. Lancon and J. Villain, NATO Advanced Research Workshop on Kinetics of Ordering and Growth at Surfaces, 1989, Maratea, Italy, and to be published.
- [23] B. Poelsema, R. Kunkel, L.K. Verheij and G. Comsa, *Phys. Rev. B* 41 (1990) 11609.
- [24] W. Schleier, G. Besold and K. Heinz, *Vacuum* 41 (1990) 412.
- [25] G. Martin and B. Perrailon, *Surf. Sci.* 68 (1977) 57.