

Evidence for a Relationship between the Anisotropy of Surface Energy and Surface Reconstruction: Comparison of Pt(110) and Cu(110)

H. P. Bonzel, N. Freyer, and E. Preuss

*Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich GmbH,
D-5170 Jülich, Federal Republic of Germany*

(Received 12 February 1986)

The amplitude decay of surface profiles in $[1\bar{1}0]$ and $[001]$ directions on (110) surfaces of Pt and Cu was compared and found to be purely exponential except for the Pt(100) $[001]$ case. The latter is also the direction of the (1×2) reconstruction typical for clean Pt(110). The nonexponential decay rate observed for Pt(110) $[001]$ was theoretically duplicated by incorporation of a large anisotropy in the surface energy of about 10% into the decay kinetics. Thus, a common cause for the (1×2) reconstruction and the nonexponential profile decay along the $[001]$ azimuth may be the large anisotropy in the surface energy of Pt.

PACS numbers: 68.35.Md, 66.30.Fq, 68.35.Bs

From an intuitive point of view, it is expected that a large anisotropy of the surface free energy of a metal may not only cause a rearrangement of a surface on a macroscopic scale, such as faceting,^{1,2} but also on a microscopic or atomic scale, such as surface reconstruction. For fcc surfaces of metals, for example, the close-packed (111) -oriented plane has the lowest surface energy³ and hence is the preferred orientation when faceting occurs. On the other hand, the same orientation appears preferentially when (110) or (100) surfaces of Ir, Pt, or Au reconstruct.^{4,5} The driving force for this process should be the difference between the surface energies of the nonreconstructed (110) or (100) and the (111) surfaces, i.e., the anisotropy of the surface energy along the $[0\bar{1}1]$ or the $[100]$ zone of the stereographic triangle.

The present experiments dealing with morphological changes of periodic surface profiles on Pt(110) and Cu(110) single crystals have produced evidence which supports, for the first time, this suspected connection between surface-energy anisotropy and surface reconstruction. The time dependence of the morphology of these profiles, in the general geometry of a planar diffraction grating, showed a perfectly normal behavior when the profile grooves were oriented parallel to $[001]$ on Cu(110) and Pt(110) or parallel to $[1\bar{1}0]$ on Cu(110), but an unusual behavior when they were aligned parallel to $[1\bar{1}0]$ on Pt(110). In the latter case, the orientational variation of the profile occurs along $[001]$, the direction in which the Pt(110) surface exhibits the well-known (1×2) reconstruction.⁴ This unusual time behavior can be readily explained by a high anisotropy of about 10% of the surface energy along the $[0\bar{1}1]$ zone.

Surface profiles of 4.0–7.0- μm periodicity and up to 0.45- μm amplitude were etched into smoothly polished Pt(110) or Cu(110) crystals by use of an Ar plasma and standard lithographic techniques. The grooves of the profiles were aligned with either the $[0\bar{1}1]$ or

$[001]$ directions. The crystals were mounted inside a UHV chamber equipped with LEED and Auger-electron spectroscopy for surface-cleanliness control. They were annealed at high temperature in order to induce surface self-diffusion which caused the profile to assume a quasi steady-state shape.⁶ During the high-temperature anneal the amplitude of the profile starts to decrease. Under isothermal conditions, the rate of decrease can be evaluated to yield a surface self-diffusion coefficient.⁷ As long as the anisotropy of the surface energy of the system is small, the profile is sinusoidal in shape and its amplitude decays exponentially with time.⁷ This amplitude A is measured *in situ* via the intensity distribution of a laser diffraction pattern.⁸

The results of periodic surface profile decay are presented as plots of $\log A$ versus time, according to Mullins's theory.⁷ Prior to comparison of different experimental data, it is important to realize that the annealing variables, such as time and temperature, are only scaling parameters for the decay process and as such are not significant for the general shape of the decay curve, $\log A$ vs t . On the other hand, the important parameters are the total range of amplitudes, over which the profile decays, and the profile periodicity. Both of these govern the range of crystallographic orientations of the profile and hence the possible influence of surface-energy anisotropy. These parameters, amplitude range, and periodicity, should be about equal for a comparison of different decay curves. Figure 1(a) shows two examples for a Cu(110) crystal where the diffusion direction is $[001]$, i.e., the profile grooves were parallel to $[1\bar{1}0]$. Straight-line behavior indicates that the theoretical decay law is obeyed and that therefore no significant anisotropy in the surface energy for this orientational range exists. The same straight-line behavior was observed for Cu(110) $[1\bar{1}0]$ and Pt(110) $[1\bar{1}0]$. However, for the Pt(110) $[001]$ diffusion direction a basically different dependence

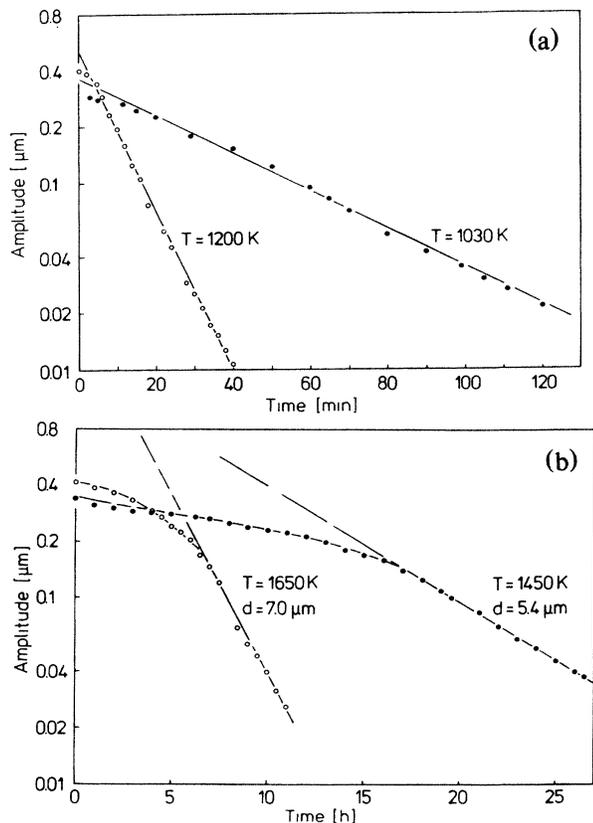


FIG. 1. Semilog plot of amplitude vs annealing time for periodic surface profiles annealed at constant temperature (experimental data). (a) Profiles of $5.4\text{-}\mu\text{m}$ wavelength on Cu(110) surfaces; diffusion direction is [001]. (b) Profiles of 5.4- and $7.0\text{-}\mu\text{m}$ wavelengths on Pt(110) surfaces; diffusion direction is [001].

was observed as illustrated in Fig. 1(b). There is no simple straight-line behavior for the data of $\log A$ versus time over the whole range of profile decay, although the small-amplitude data may still be described by a straight line. The Pt(110) [001] direction is the same in which the (1×2) reconstruction occurs which, according to the latest experimental investigations,^{9,10} is interpreted in terms of (111) microfaceting ("missing-row model").

The unusual amplitude dependence of the profile decay can be readily explained by our invoking a relatively high anisotropy in surface energy, $\gamma(\theta)$, along the [011] zone of Pt and by incorporating this $\gamma(\theta)$ into the phenomenological equation governing the diffusional profile decay.^{6,11,12} The physical conditions for this step are reasonable because the [011] zone contains the (111) orientation at 35.2° which always has the lowest surface energy for fcc metals. The orientation-dependent surface energy was approximated by

$$\gamma(\theta)/\gamma_0 = 1 + \alpha [1 - K(1 - \cos 4\theta)^\beta],$$

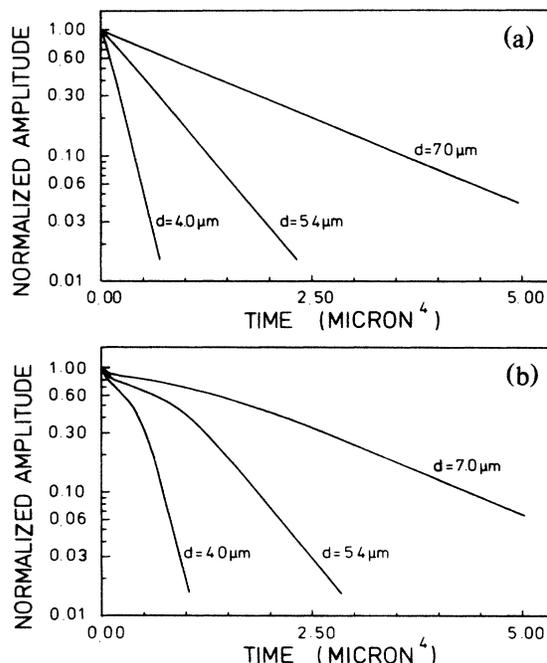


FIG. 2. Semilog plot of normalized amplitude vs annealing time for periodic surface profiles of different wavelength (theoretical data). The starting amplitude was $0.4\ \mu\text{m}$ in all cases. (a) The amplitude decay was calculated for an anisotropy in surface energy of 2.2% (simulation of Cu). (b) Analogous calculation for an anisotropy of 10% (simulation of Pt).

where $K = 2/[1 - \cos(4 \times 29.5^\circ)]^\beta$ is a constant and θ the polar angle of orientation. There are two parameters α and β which determine the degree of the anisotropy and the curvature of $\gamma(\theta)$ near its (111) cusp orientation. Further details of the calculation are reported elsewhere.^{11,13}

The results of the calculated profile-decay kinetics under the action of anisotropic $\gamma(\theta)$ are shown in Fig. 2 for several different conditions typical for the experiments. The initial amplitude is $0.4\ \mu\text{m}$ in each case, while the periodicity varies from 4.0 to $7.0\ \mu\text{m}$. All three decays were calculated for the same kinetic parameters, i.e., temperature and $\gamma(\theta)$. The time scale is in units of μm^4 and not directly amenable for a comparison with experiments. Two types of results are shown: Figure 2(a) depicts the decay of $\log A$ versus time for $\Delta\gamma(\theta)/\gamma_0 = 2.2\%$ and Fig. 2(b) for an anisotropy of 10%. In the first case, there is still a straight-line behavior, while the second case deviates significantly from the normal exponential decay; there are two sections to the decay kinetics, the first with a rather low rate which is not constant, and the second with a faster, constant rate. A comparison between the experimental and calculated decay plots, Figs. 1 and 2, shows that the observed amplitude-dependent decay curve for Pt(110) [001] is qualitatively similar to

that in Fig. 2(b). Again, we emphasize that this comparison is basically independent of annealing temperature and time scale. We conclude that the profile decay on Pt(110) in the [001] direction is influenced by the anisotropy in $\gamma(\theta)$ and that this anisotropy is of the order of 10%.

A further result of the calculated profile decay was the shapes of the profile. Figure 3 shows a set of examples for an initial amplitude of $0.4 \mu\text{m}$ and $5.4\text{-}\mu\text{m}$ periodicity. The $\gamma(\theta)$ anisotropy parameters were identical to those for Fig. 2. The shape of the initial profile was chosen to be sinusoidal, which, however, is of no consequence for the shape at $t > 0$. The initial profile converts very quickly to a profile of quasi steady-state shape, which is dictated by the particular anisotropy of $\gamma(\theta)$. This conversion can be noted in Fig. 2(b) at the very beginning of the profile decay curves which show a narrow region at higher curvature. The quasi steady-state shape of the profile at the end of this region is independent of the shape of the initial profile. The calculated profiles in Fig. 3(a), for a low anisotropy of $\gamma(\theta)$, remain almost perfectly sinusoidal during the entire decay. In Fig. 3(b), on the other hand, profiles of large amplitude show a substantial degree of (111) faceting—as expected on the grounds of the large anisotropy in $\gamma(\theta)$. This faceting vanishes at lower amplitudes because the orientational range of the profile shrinks and therefore moves away from the region of strong curvature near the (111)

cusps in $\gamma(\theta)$. Once the (111) facet ceases to be present, the profile decay is faster and purely exponential. Unfortunately, it was not possible to confirm experimentally the presence of (111) facets on Pt (110) [001] profiles, e.g., by optical interference microscopy. Since facets are only expected to exist at large amplitudes ($0.2\text{--}0.4 \mu\text{m}$) they cannot be seen, because the interference fringes are very closely spaced and exhibit a very high slope.

The important consequence of the comparison of experimental and theoretical results of profile decay becomes apparent when all data for Cu and Pt as well as previously studied Ni (see Latta and Bonzel¹⁴) are taken together. Time-dependent amplitude decay was *only* observed for the Pt(110) [001] direction, but not for Cu(110) and Ni(110) in either [1 $\bar{1}$ 0] or [001], and also not for the Pt(110) [1 $\bar{1}$ 0] direction. Hence, out of six possible cases only one demands the noticeable influence of anisotropic $\gamma(\theta)$ on profile decay, and that one case is the Pt(110) [001] direction which reconstructs to (1 \times 2). Hence we argue that the (1 \times 2) surface reconstruction and the amplitude-dependent decay in the [001] direction on Pt(110) are interrelated and are both due to a large anisotropy in $\gamma(\theta)$ along the [0 $\bar{1}$ 1] zone of Pt. Both phenomena are characterized by (111) facets, microscopic in one case and macroscopic in the other.

Such a possible correlation between the large anisotropy in $\gamma(\theta)$ and surface reconstruction is quite remarkable, because it is also a relationship between a phenomenological, macroscopic quantity and a microscopic, atomic scale, physical phenomenon. On the other hand, the surface energy in a microscopic picture depends on the interatomic forces of the solid and should therefore also be applicable in atomic dimensions. In those terms one would expect to find a high anisotropy in $\gamma(\theta)$ and surface reconstruction for the same crystallographic azimuth of a metal, consistent with the conclusion of this paper. Increased theoretical efforts in calculating surface energies of metals and their orientation dependencies would hence be highly desirable. For example, it would be extremely interesting to know why the anisotropy in $\gamma(\theta)$ should be substantially larger for Pt than for Cu, Ni, or other metals.

Because of the link between highly anisotropic $\gamma(\theta)$ and surface reconstruction for Pt, one may ask whether the (1 \times 2) periodicity of reconstruction is anywhere near an equilibrium state or whether a larger (1 \times n)-type reconstruction, with $n > 2$, would lead to an even lower energy state. Reports about (1 \times 3)- and (1 \times 4)-type corrugations on reconstructed Au(110) are in the literature,¹⁵ in general support of this idea.

Invoking a larger anisotropy of surface energy for Pt than for Cu (or Ni) in order to rationalize faceting and reconstruction is not unreasonable in view of experi-

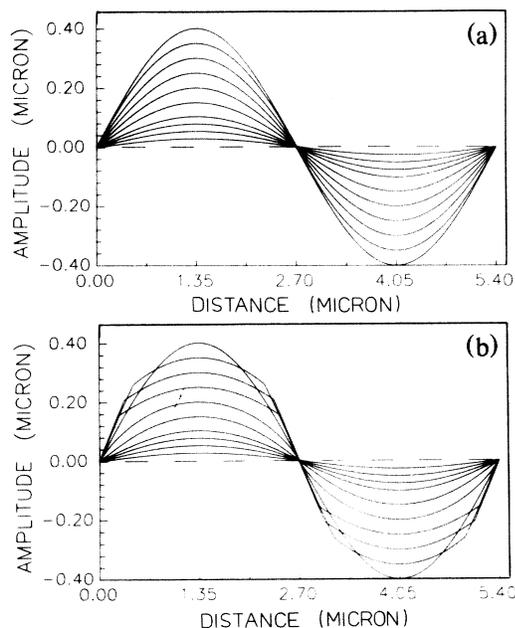


FIG. 3. Calculated profile shapes for various annealing times and different anisotropies in surface energy. The initial profile was chosen to be sinusoidal. (a) Anisotropy in $\gamma(\theta)$ is 2.2% (simulation of Cu). (b) Anisotropy in $\gamma(\theta)$ is 10% (simulation of Pt). Note extensive (111)-type facets.

mental measurements of this quantity.¹⁶⁻¹⁸ Unfortunately, the data reported for Pt are relatively old and may not be representative of the clean surface, but a maximum anisotropy of the order of 10% is given.¹⁶ On the other hand, measured anisotropies for Cu and Ni which are more reliable from this point of view are considerably lower and range between 2.1% and 3.4%.^{17,18} Thus, the agreement between these experimental numbers and the values needed above to explain the amplitude-dependent profile decay is good.

¹C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C. S. Smith (Univ. of Chicago Press, Chicago, 1953), p. 8.

²W. W. Mullins and R. F. Sekerka, *J. Phys. Chem. Solids* **23**, 801 (1962).

³J. F. Nicholas, *Aust. J. Phys.* **21**, 21 (1968).

⁴H. P. Bonzel and S. Ferrer, *Surf. Sci.* **118**, L263 (1982).

⁵M. A. van Hove, R. J. Koestner, P. C. Stair, J. P. Biberian, L. L. Kesmodel, I. Bartos, and G. A. Somorjai, *Surf. Sci.* **103**, 189 (1981).

⁶H. P. Bonzel, E. Preuss, and B. Steffen, *Surf. Sci.* **145**, 20 (1984).

⁷W. W. Mullins, *J. Appl. Phys.* **30**, 77 (1959).

⁸H. P. Bonzel and N. A. Gjostein, *J. Appl. Phys.* **39**, 3480 (1968).

⁹H. Niehus, *Surf. Sci.* **145**, 407 (1984).

¹⁰G. L. Kellogg, *Phys. Rev. Lett.* **55**, 2168 (1985).

¹¹H. P. Bonzel, E. Preuss, and B. Steffen, *Appl. Phys. A* **35**, 1 (1984).

¹²A. D. Brailsford and N. A. Gjostein, *J. Appl. Phys.* **46**, 2390 (1975).

¹³E. Preuss, N. Freyer, and H. P. Bonzel, to be published.

¹⁴E. E. Latta and H. P. Bonzel, *Phys. Rev. Lett.* **38**, 839 (1977).

¹⁵W. Moritz and D. Wolf, *Surf. Sci.* **88**, L29 (1979); G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Surf. Sci.* **131**, L379 (1983).

¹⁶M. McLean and H. Mykura, *Surf. Sci.* **5**, 466 (1966).

¹⁷E. D. Hondros and M. McLean, *Colloq. Int. C.N.R.S.* **187**, 219 (1970).

¹⁸T. Barsotti, J. M. Bermond, and M. Drechsler, *Surf. Sci.* **146**, 467 (1984), and in *Proceedings of the Twenty-Ninth International Field Emission Symposium*, edited by H.-O. Andren and H. Norden (Almqvist and Wilsells, Stockholm, 1982), p. 51.