Surface Morphology of Ag(110) Close to Its Roughening Transition

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We have investigated the thermal roughening of the Ag(110) surface using synchrotron x-ray diffraction. The data taken out of plane (nonzero perpendicular momentum transfer) show a clear two-component line shape below the roughening transition at $T_R = 790$ K. We interpret this as coexistence of flat (110)-oriented regions and slightly inclined, rough regions on the surface below T_R. The temperature dependence of the angle between the components and their relative amplitudes implies that roughening takes place by the gradual replacement of the (110) faceted regions by the rough phase.

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Roughening of certain metal surfaces at high temperatures is expected for simple thermodynamic reasons: In spite of the energetic cost of creating extra surface area, the free energy can be lower because of the configurational entropy of the many ways in which a rough surface can be constructed. Studies of the equilibrium crystal shapes (ECS) of small Au and Pb crystals have shown that only (100) and (111) facets are present at temperatures close to the melting point [1], implying that all other orientations are rough there. All these high-index faces must have roughening temperatures below the melting point, since the configurational-entropy term vanishes at zero temperature. Roughening transitions have been observed by x-ray and He diffraction experiments on various surfaces including Ag(110) [2], Cu(113) [3], and Ni(113) [4,5].

Prior to these experiments were theoretical predictions originating from the work of Burton and Cabrera [6]. Chui and Weeks [7] (CW) used the solid-on-solid (SOS) approximation, whereby a surface has one and only one discrete height h at each site of a square lattice, and a short-range repulsive potential between nearest-neighbor sites with different heights. They showed that such a surface has a phase transition at a temperature T_R above which the average height variation should diverge logarithmically with distance across the surface, r:

$$\langle [h(r) - h(0)]^2 \rangle = X(T)\ln(r)\,, \qquad (1)$$

where $X(T)$ increases with T for $T > T_R$ and has the value $1/\pi^2$ at $T = T_R$. The theory of capillary waves can be used to show that the same functional form applies to the equilibrium state of any rough surface in which the configurational entropy dominates the lattice interactions associated with steps. This property of height divergence at large distance is a useful definition of a rough surface.

Calculations were also made of the expected form of the He diffraction [8] and x-ray diffraction [4] from rough crystal surfaces described by Eq. (1). Ignoring the effects of resolution in the latter case, the diffracted intensity I is given by a power-law form:

$$I(q_\parallel, q_z) \approx [A(T)/\sin^2(q_z/2)]\,|q_\parallel|^{\eta - 2}\,, \qquad (2)$$

where $q_\parallel$ and q_z are the reciprocal-space displacements from the nearest Bragg peak in the parallel (Q_x or Q_y) and perpendicular (Q_z) directions [9], respectively, in dimensionless units whereby the zone has width 2π. The first term in Eq. (2) is the familiar crystal truncation rod (CTR) [10] describing the q_z dependence of the diffraction from an ideally flat surface, while the second term describes the broadening due to roughness. Previous x-ray measurements on Ag(110) [2] were made of the in-plane line shape at $(0,1,Q_z)_r$ [9] for small Q_z. Held *et al.* [2] found line shapes that could be satisfactorily fitted by Eq. (2) convolved with a fixed resolution function over the whole temperature range, suggesting consistency with the CW model of logarithmic height divergence. The Q_z dependence was not tested in that work. Our study originally sought to verify the prediction [4] $\eta = X(T)q_z^2$, but found instead that a totally different description was needed.

These theories of roughening presuppose that isolated steps, by virtue of their entropy, can exist at low density in thermal equilibrium on the $(110)_c$ crystal face under consideration. Stated differently, it is assumed that all crystal directions near $(110)_c$ exist in the ECS of Ag [11,12]. While this would be correct in many situations, it can happen that a range of orientations near a facet is forbidden, giving it sharp edges in the ECS. This happens, for example, at high temperature around the (111) and (100) facets of Au [1]. If this is the case, steps are mutually attractive and will always congregate *away* from the facet, leading to phase separation into a "hill-and-valley" configuration [11]. Thermal roughening of such a facet would then take place by a redistribution among the coexisting phases as the stable facet orientation disappears from the ECS. We present evidence that suggests that this is the mechanism appropriate to the case of Ag(110).

Our sample was carefully aligned and polished before mounting in a block of solid silver that contained a Pt resistance thermometer. It was heated radiatively with a filament. The precision of the temperature setting achieved was 0.3 K, while the accuracy was estimated to be ±3 K. The surfaces were prepared in ultrahigh vacuum (UHV) by sputtering, and then annealed at 1000 K for several hours. Significant sublimation took place that left visible deposits on the interior of the vacuum vessel. The mosaic spread was greatly reduced by this treatment. The x-ray-diffraction measurements were made on beam line X16A of the National Synchrotron Light Source (NSLS) using a UHV diffractometer [13] in the five-circle diffraction geometry [14]. The sample was aligned using the $(101)_r$ and $(011)_r$ bulk Bragg peaks [9]. By comparing the crystallographic alignment with the macroscopic orientation of the polished face, given by its reflection of a laser beam, the sample was found to be misoriented by 0.186° ± 0.05° towards the $(010)_r$ azimuth and by 0.098° ± 0.05° towards the $(100)_r$ azimuth. All measurements were made with x rays of 11 keV and a NaI scintillation detector behind 2×10-mm slits 600 mm from the sample, giving a longitudinal resolution half-width of 0.009 Å^{-1}. The results presented here were transverse scans for which the resolution was limited by the sample mosaic function, which was best described by the square of a Lorentzian function with a half-width of 0.05°. The unit-cell parameters were adjusted at each temperature for thermal expansion of the lattice.

Figure 1 shows room-temperature diffraction at $(1,0,Q_z)_r$ for $Q_z=0.1$, 0.4, and 0.7, as a function of $q_\parallel$ along $(010)_r$. Superimposed on the first of these is a fit by the power-law form of Eq. (2), convolved with the measured mosaic function, which gives $\eta=0.79$ and a least-squares residual of $\chi^2=13$. While this experimental curve is similar to that used in the previous study [2], our fit gives a much larger value of η, largely because of differences in the handling of the instrumental resolution. While the fit at $Q_z=0.1$ is reasonable, the power-law description is totally unsuitable for the $Q_z=0.4$ and 0.7 data, where a pronounced asymmetry is apparent. We need to use two components with separated centers as shown. The $Q_z=0.1$ data can also be explained satisfactorily with a two-component line shape, giving $\chi^2=7$.

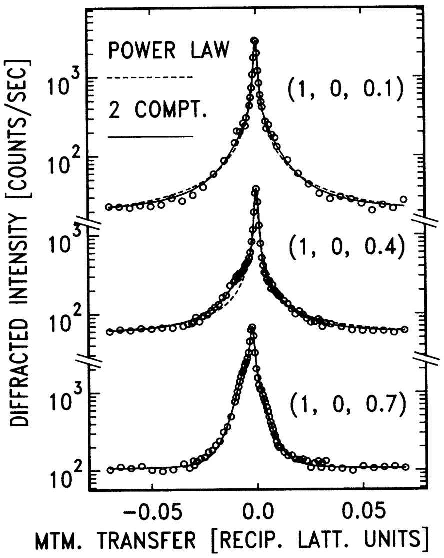

FIG. 1. Scans along $(010)_r$ of the $(1,0,Q_z)_r$ crystal truncation rod of Ag(110) at low temperature. Two components are necessary to fit the data at $Q_z=0.4$ and 0.7.

Two-component line shapes can arise for several reasons. Surfaces that are flat *in the long range* give rise to the sharp resolution-limited component. These may contain, in addition, a superimposed *local* roughness in the form of steps [15]. This kind of roughness is seen as the result of HF etching of Si surfaces [16] or during epitaxial growth [15,17]. An alternative explanation is that the surface is phase separated into flat and rough regions, larger in size than the x-ray coherence length (1000 Å here), as was seen in x-ray studies of the vicinal Ni(111) surface [18]. In the first scenario, the broad diffraction component arising from the steps should have a minimum intensity at the Bragg points where all atoms of the crystal scatter in phase, and a maximum far away. The second possibility is just the reverse: Both components have the intensity profile of CTRs [Eq. (2)], with maxima near the Bragg nodes [10]. The latter is what we see: Both the broad and narrow components increase in amplitude from $Q_z=0.1$ to 0.7.

The asymmetry of the out-of-plane line shape is the key to understanding the roughening of Ag(110). The sharp Bragg component is always exactly aligned with the crystallographic $(110)_c=(001)_r$ direction. Both the displacement and the width of the broad component are proportional to the distance from the $(101)_r$ bulk Bragg peak [19]. This is consistent with a diffuse rod of scattering *inclined* to the surface by 0.25° towards $(010)_r$ at room temperature. For the $(2,0,0.5)_r$ measurement of the nearest bulk Bragg peak is the in-plane $(200)_r$, so the diffuse rod should be located on the opposite side. This was indeed observed [19]. The curve at $(1,0,0.1)_r$ appears symmetric because there are roughly equal contributions from opposite sides of two diffuse rods emanating from $(101)_r$ and $(10\bar{1})_r$.

A series of fits was made to the line shape at $(1,0,0.5)_r$ to obtain in Fig. 2(a) the temperature dependence of the tilt angle, derived from the difference between the two component centers. The fitted line shape was a sharp Lorentzian-squared function representing the mosaic plus a broad Lorentzian with its width constrained to the low-temperature value. The largest χ^2 for the series was 3. The tilt angle was found to become progressively smaller with increasing temperature while the intensity of the sharp component diminished. Above 790 K the Bragg peak had disappeared and the tilt angle remained constant at about 0.14°, which is within error of the miscut angle of our sample. In this temperature regime the surface was aligned with the direction of its original cutting and was in a single (rough) phase since there was only one component remaining. When the sample surface was cooled, it phase separated once again into flat $(110)_c$ facets and more steeply tilted rough ones. The surface areas of the two phases are reflected by the respective in-

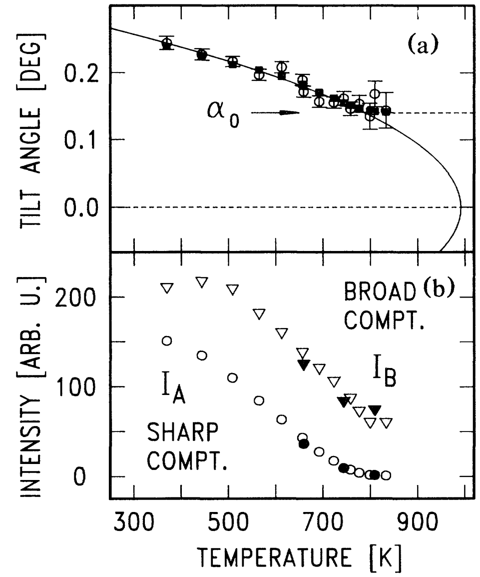

FIG. 2. Temperature dependence of the diffraction line shape fitting parameters at $(1,0,0.5)_r$. (a) The angle of tilt between the two surface phases, as measured from the separation of the two components (open circles) or from their relative intensities (solid squares) using Eq. (4). (b) Integrated intensities of the sharp and broad components corresponding to the flat and rough phases. Open symbols are heating; solid are cooling.

tegrated intensities of the peaks, shown in Fig. 2(b), and also in the resulting angle of the rough region.

We can use the Wulff construction [11,12] of the ECS to understand the variation of angle with temperature near T_R. We consider first the situation above T_R by assuming the rough phase to be locally isotropic with a free energy per unit area, f_R, independent of orientation. This gives a spherical free-energy surface (FES) and a spherical ECS, shown in Fig. 3. If we now introduce an interior cusp on the FES along the $(110)_c$ direction, this not only leads to a facet on the ECS [11] but also to a sharp corner [12] B and a band of forbidden directions [11] AB in the FES [dashed line in Fig. 3(a)], so that the cusp is present only in the virtual sense with its apex A as the single well-defined point. Any local orientation that happens to lie between A and B is unstable and will phase separate into A and B according to a lever rule, giving an energy lying on the dotted curve inside the virtual FES [11]. The small angle of inclination α of phase B to the $(110)_c$ direction is related to the depth of the cusp, Δf_{110}, by the simple geometric relation [20]

$$\alpha(T)=[2\Delta f_{110}(T)/f_R]^{1/2}. \tag{3}$$

If our sample has a miscut of α_0, then so long as $\alpha_0<\alpha$ it will phase separate into flat $(110)_c$ facets and rough B facets with orientation α, as shown in Fig. 3(b). As Δf_{110} changes with temperature, so will α and therefore the ratio of the areas of the A and B phases, as Fig. 3(c) suggests. When $\alpha(T)$ becomes equal to α_0, the whole surface will be in the rough B phase at angle α_0, so α does not change further. Equation (3) is shown as the curve through the data in Fig. 2(a), where we have assumed a linear reduction of Δf_{110} with T and have adjusted $T_0=992$ K, the point of disappearance of the cusp, and f_R for a good fit. We can identify T_0 with the temperature at which the true $(110)_c$ direction would roughen. The roughening temperature of our sample is the labeled point at which Eq. (3) meets $\alpha(T)=\alpha_0$, giving $T_R=790\pm20$ K.

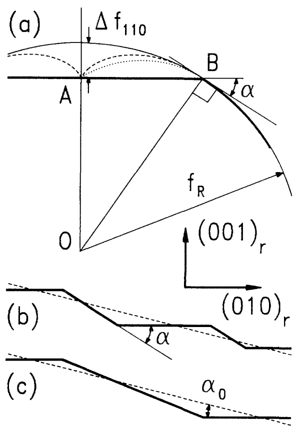

FIG. 3. (a) Wulff construction of an equilibrium crystal shape (thick line) containing a flat facet with a sharp edge. The thin line is the spherical free-energy surface of the rough phase, which is also its ECS. The addition of a cusp leads to forbidden orientations (dashed line) and the facet. (b),(c) Resulting hill-and-valley morphology for different values of $\Delta f_{110}(T)$: (c) is a higher temperature than (b).

The lever rule [11] allows us to make a second, independent estimate of the surface tilt angle from the knowledge of the relative surface areas of the A and B phases, given by the integrated intensities of the two line-shape components, I_A and I_B in Fig. 2(b). Since the macroscopic angle of the combination of A and B is always α_0 (see Fig. 3),

$$\alpha'=\alpha_0(I_A+I_B)/I_B. \tag{4}$$

α' is plotted alongside α in Fig. 2(a) after adjustment of α_0 to 0.139° ± 0.01°. The values agree well with both the direct measurements and Eq. (3).

Our results are consistent with those of Ref. [2], which observed a very similar linear decline of the Bragg-peak intensity with temperature, ending at a slightly smaller value of T_R. The authors chose to fit the $T<T_R$ line shape with a power law instead of two components and so failed to see the two-phase coexistence. We expect from Fig. 2(a) a significant dependence of T_R with miscut: They determined $T_R=723$ K, which is consistent with the stated miscut of $<0.3°$. Above T_R they observed the line shape of Eq. (2) convolved with resolution; since this is the shape expected for any rough surface, the observation is consistent with the present interpretation. We looked carefully for evidence of this line shape both for $T > T_R$ and by numerically subtracting the sharp component from the experimental curve for $T < T_R$, to leave the contribution of the rough B phase. We saw nothing that was significantly different from the Lorentzian shape, nor any temperature-dependent change in width [19].

The rearrangement from a hill-and-valley morphology to a uniformly sloped one has also been seen in x-ray reflectivity experiments on Cu(110) [21], and largely explains the controversy of whether or not there is a roughening transition on Cu(110) [22]. A related experiment on a series of Si(111) vicinal surfaces [23] observed a phase diagram similar to that of Fig. 2(a); here the reconstruction plays an additional role that can lead to "magic angles" [24]. The steep dependence of T_R with α_0 implied by Fig. 2(a) means that we cannot determine the T_R of the exact $(110)_c$ direction of Ag with much certainty, especially since our experiment did not reach the precise vanishing point of the cusp from the FES in Fig. 3. The tiny angular range of Fig. 2(a) also implies that any $(110)_c$ facets that might appear in the ECS of spherical crystals would be extremely hard to see, subtending much less than 1° along $(010)_r$. Microscopically the $(110)_c$ face is highly anisotropic with close-packed chains of atoms along $(010)_r$ and more openly spaced along $(100)_r$. The step energy along $(100)_r$ is correspondingly lower. The facets might therefore be very anisotropic too, or even have the round-edged character in the $(100)_r$ direction, implying the absence of forbidden angles. It is even possible that CW roughening could take place along $(100)_r$, at the same time as flat-rough coexistence dominates the behavior along $(010)_r$.

The approach to roughening of Ag(110) is now understood to involve the *coexistence* of rough and flat phases, and the roughening transition takes place by the gradual replacement of one phase with the other. Part of the phase boundary between rough and smooth phases in (α,T) has been elucidated [Fig. 2(a)]. The theories of roughening that construct equilibrium populations of steps within otherwise flat faces appear not to be applicable to this surface because of the forbidden regions of its FES: Isolated steps would always segregate from the flat regions.

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