From hill-and-valley faceting to global faceting of a crystal: oxygen-covered tungsten

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A tungsten crystal with a curved surface (radius of curvature = 0.2 μm), exposed to 1.3 ± 0.2 Langmuir of oxygen, undergoes massive atomic rearrangement upon annealing. Hill-and-valley faceting in the form of {211} steps is observed between (211)–(121), (121)–(112), (112)–(211) crystal facets. As the annealing temperature is increased, the number of steps decreases. Finally only one step remains and the crystal assumes a globally faceted shape for temperatures between 1400 K and 1600 K. For higher temperatures the number of steps increases with temperature.

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I. INTRODUCTION

The theory of equilibrium crystal shapes predicts that a crystal in equilibrium is a convex body. The shape of the crystal is such that the surface free energy is minimal[1, 2]. If the surface energy per unit area is highly anisotropic, the crystal develops large facets for orientations of low surface energy. We will call this process *global faceting*.

In practice, mass transport mechanisms (adsorption/desorption, surface diffusion) are often not efficient enough for the equilibrium crystal shape to be attained. If the surface energy per unit area is highly anisotropic, the crystal assumes a steady-state form which is not convex. Numerous small facets of low surface energy develop on the surface, forming pyramid-like or steplike structures. (The facets are small compared to the crystal size.) This process is called *hill-and-valley faceting* [1–3].

In this work we demonstrate that hill-and-valley faceting and global faceting can be observed on the same crystal, if only one parameter is changed – the temperature. This behaviour, uncommon in experimental studies, is possible due to specific features of the system we have chosen: oxygen-covered tungsten crystal, with radius of curvature smaller than 1 μm. A layer of oxygen causes high surface energy anisotropy, leading to pronounced faceting [4–6]. Oxygen remains on the tungsten surface at temperatures higher than 1800 K, while faceting is already observed at 800 K [4]. This wide temperature range, in addition to high surface energy anisotropy, makes the oxygen on tungsten system a good example for studying the phenomenon of faceting. Moreover, if crystals of small radius are studied (not exceeding a few μm), surface diffusion suffices to reshape the crystal globally, and global faceting can be observed.

II. EXPERIMENTAL

The experiment was carried out in a field ion microscope [7, 8]. The sample crystal was prepared by electropolishing a ⟨111⟩-oriented tungsten wire, 0.13 mm in diameter, into a 2 mm long needle. The apex of the needle was approximately hemispherical, with the average radius of curvature 230 ± 80 nm. (Only the apex of the crystal is observed in a field ion microscope[7, 8].) All measurements reported here were carried out on the same sample, whose radius was constant throughout the experiments.

The base pressure in the microscope was $3 \cdot 10^{-10}$ Torr. During faceting the average pressure was higher: $1 \cdot 10^{-9}$ Torr, due to the residual presence of gases used for imaging (helium and neon) and for adsorption (oxygen).

The sample was cleaned thermally[9]. Sample purity was verified by observations of field emission and by carrying out blank experiments: annealing in vacuum of a clean tungsten crystal in the temperature range 900–1800 K does not cause faceting.

III. RESULTS

The results of this work are summarised in Fig. 1. In this figure, each point represents a separate experiment of the following scheme: (1) The tungsten crystal was cleaned by annealing at 1950 ± 100 K. (2) The crystal was cooled to ∼80 K. (3) The crystal was exposed to 1.3 ± 0.2 Langmuir of oxygen. (4) The oxygen atmosphere was removed. (5) The crystal was annealed for 80 s at a temperature T (indicated on the graph). (6) The faceted configuration was frozen by cooling the crystal to ∼80 K. (7) The crystal surface around the ⟨111⟩ crystal pole was observed by field ion microscopy.

Global faceting is observed in the temperature range 1400–1600 K. In this range three crystal facets: (211), (121), (112), which surround the ⟨111⟩ crystal pole, are extended so much that they form a single, three-sided pyramid. The edges of the pyramid are sharp on the atomic scale, most probably formed by a single chain of oxygen atoms. The vertex of the pyramid is truncated. Details of the shape of the vertex could not be observed in our experiment. A model of the crystal surface is shown in Fig. 2 (b), and the corresponding microscopic image is shown in Fig. 3 (d).

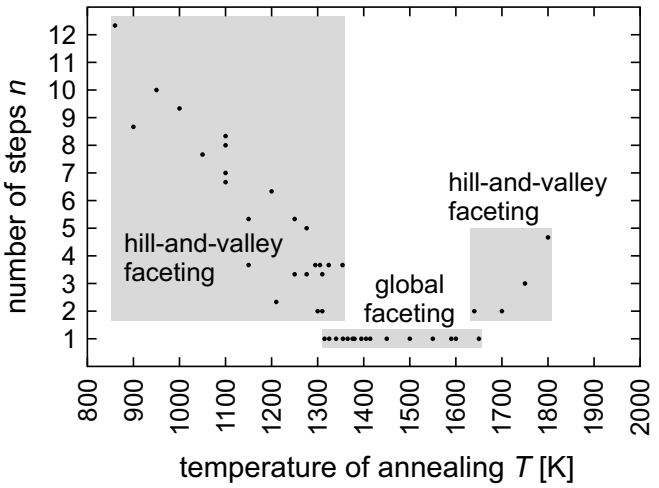

FIG. 1: Number of {211} steps in the vicinity of the ⟨111⟩ pole. If $n = 1$, a single (211)-(121)-(112) pyramid is formed (global faceting).

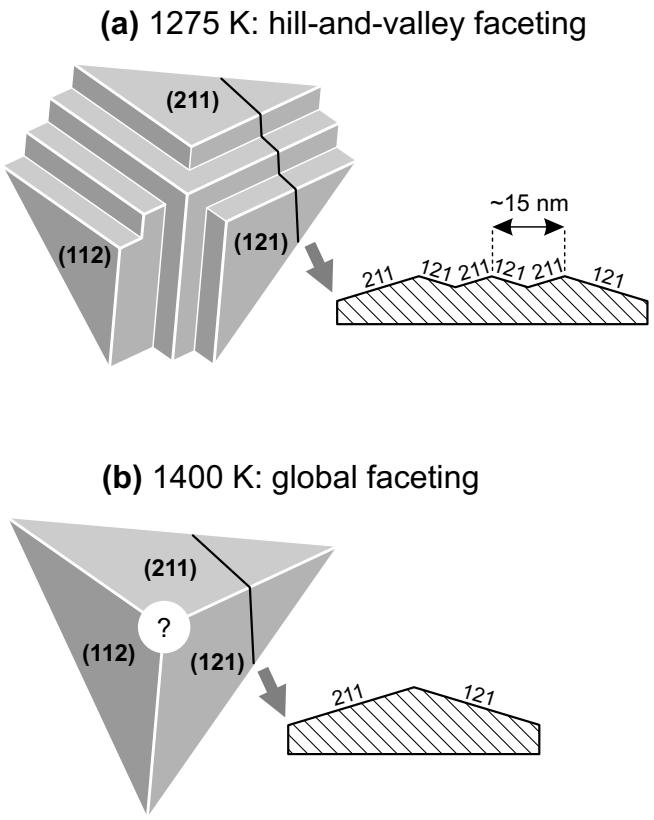

FIG. 2: A simplified model of the crystal topography in the vicinity of the ⟨111⟩ pole. The crystal cross-sections shown on the right run along the (113) plane (perpendicular to the facet edges). The detailed shape of the vertex region in (b) could not be determined in this experiment.

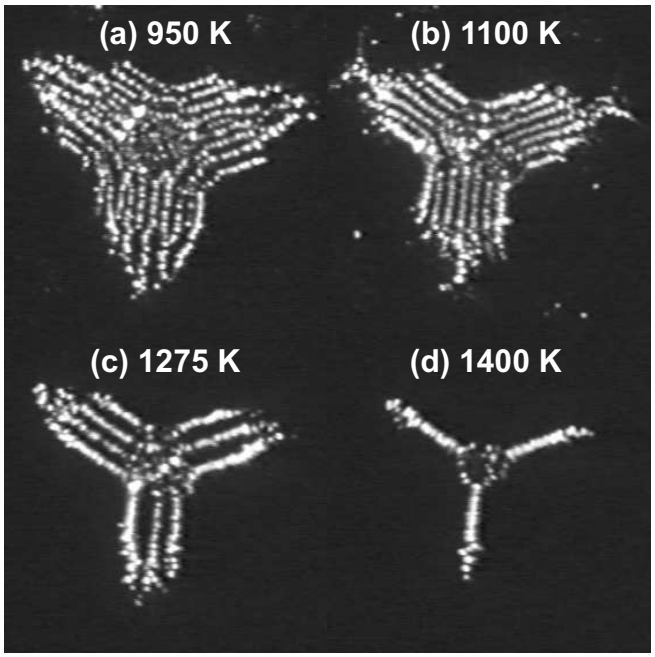

FIG. 3: Microscopic images of the crystal surface in the vicinity of the ⟨111⟩ pole. Edges of the facets are imaged as bright lines. The interpretation of these images is proposed in Fig. 2.

Hill-and-valley faceting is observed in the temperature ranges 860–1300 K and 1640–1800 K. The global {211} crystal facets are enlarged, but remain separated by a steplike hill-and-valley region built of {211} microfacets (Fig. 2 (a)). In light of the previous work carried out on flat crystals[4–6] it is probable that the ⟨111⟩ pole is covered by a pyramid-like hill-and-valley region built of small alternating convex-concave (211)-(121)-(112) pyramids. This could not be observed in our experiment due to the limitations of the experimental technique. The overall hill-and-valley topography can be described as a three-sided pyramid with multiple edges (steplike faceting) and multiple vertices (pyramid-like faceting). The number of steps n, which appears in Fig. 1, describes the multiplicity of the pyramid edge. For example, in Fig. 3 (c) there are two triple edges and one quadruple edge, so n = average number of steps = average number of edges = $(3 + 3 + 4)/3 = 3\frac{1}{3}$.

In the temperature range 1850–1950 K the crystal does not undergo faceting because the oxygen layer desorbs from the crystal surface.

IV. DISCUSSION

From Figure 1 it is evident that in the temperature range 860–1300 K the number of steps (edges) on the surface decreases with increasing temperature. This has been observed before on curved crystal surfaces [9, 10]. On the other hand, on flat crystals it has been observed that the sizes of the facets increase with increasing tem-

perature [11, 12]. The underlying mechanism of these two processes is probably the same. It has been proposed that the driving force for such surface evolution is the minimization of the total edge energy [11]. A recent solid-on-solid model of adsorbate-induced faceting[13] confirms that the reduction of the total length of the facet edges lowers the total energy of the crystal (this is not obvious, since in a hill-and-valley topography there exist both convex edges and *concave* edges).

At higher temperatures (1400–1600 K) surface diffusion is efficient and the hill-and-valley faceting yields to global faceting. This process is driven by the minimization of both the surface energy and the edge energy. Such transformation has not been observed for other adsorbates (Au/W [10], Pd/W [9]) because of the thermal desorption of the adsorbate.

A surprising feature seen in Figure 1 is that in the temperature range 1640–1800 K the number of steps *increases* with the increase of the annealing temperature. Such behaviour has not been predicted in the literature. Further experiments need to be carried out to study this phenomenon. A possible explanation of this process may be the following. From the definition of the free energy: $F = E - TS$, it follows that at high temperature T the free energy of the crystal can be considerably lowered by the increase in entropy S, even at the cost of increasing the energy E. A hill-and-valley topography has a lower degree of order, higher number of possible atomic configurations and higher entropy than the globally faceted topography. It is thus possible that at high temperature the free energy can be lowered by the breakup of the globally faceted shape into hills and valleys.

In summary, we have demonstrated that the theoretically anticipated transition from hill-and-valley faceting to global faceting can be experimentally observed with a suitable choice of adsorption system, crystal size and temperature range. We have found that the oxygen on tungsten adsorption system demonstrates a wealth of faceting phenomena, depending on the annealing temperature. In particular, we have found that the number of steps is not a monotonic function of the annealing temperature.

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