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The kinetics of hill-and-valley faceting of oxygen-covered tungsten

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ABSTRACT

The coarsening kinetics of steplike faceted O/W(332) surface is investigated using field ion microscopy. The spatial density of facets is measured as a function of time (10–320 s) and temperature (1100–1400 K). The results are discussed in terms of the temporal coarsening exponent and the activation energy for the coarsening process.

1. Introduction

Faceting of a flat crystal surface of a given orientation (*hkl*) is defined as the break-up of this surface into a hill-and-valley structure which exposes surfaces (facets) of different orientations $(h_1k_1l_1)$,(h_2, k_2, l_2), … Faceting sometimes occurs spontaneously for a pure crystal [1–3], but most often it is observed when adsorbate is present on the surface. In both cases faceting is most often explained by the minimization of surface free energy [4–7]. However, the absolute minimum, corresponding to a convex shape – the equilibrium crystal shape [8,9] – is not attained due to kinetic constraints — the limitations of mass transport on the surface (note that the equilibrium shape depends on the temperature). In the experiment, the crystal as a whole remains flat (in the millimeter length scale), while the typical size of the hill-and-valley facets (sometimes called microfacets) is from a few nanometers to hundreds of nanometers.

As a non-equilibrium shape, the faceted topography evolves with time. This time evolution is usually very slow and in practice a faceted crystal is often regarded as a steady-state shape. The models predict that the size of the facets increases with time following a power law $L \sim t^{\phi}$, where $0<\phi<1$ [2,10–13]. There are only a small number of experimental reports on the time evolution of a faceted surface. The experimentally determined coarsening exponents fall in the range 0.1–0.5 (typically 0.1–0.2) [2,3,14–17]. In the experiments it is difficult to capture the weak effect of time on faceting, because it is easily obscured by the stronger effect of impurity adsorption.

The influence of temperature on the faceted shape is much stronger than the effect of time. Increasing temperature substantially increases surface diffusivity, which results in a longer range of material transport and larger facets (this simple rule may be complicated by temperature desorption effects). There exist numerous studies showing the effect of temperature on facet size (eg. [1,18–25]). The effect of increasing temperature is most often irreversible — when the temperature is lowered, the facets do not shrink to the previous size. This is another consequence of the fact that the faceted crystal is not in equilibrium.

A curved crystal surface can be considered as a collection of surfaces of different orientations, so hill-and-valley faceting occurs in local regions of the surface similarly as for corresponding flat crystals. On curved surfaces hill-and-valley faceting is accompanied by the enlargement of macroscopic crystal facets [21,26–28]. It is experimentally possible to obtain a convex, equilibrium crystal shape, with only macroscopic (global) facets and no hill-and-valley regions [8,9,26] (this is also possible for oxygen-covered tungsten [22,29,30]).

The aim of the present work is to study quantitatively the effect of time and temperature on hill-and-valley faceting of oxygen-covered tungsten. We perform the experiments on a microcrystal with a curved surface, focusing on its three crystallographically equivalent {332} orientations in the vicinity of the (111) region. The {332} orientations are not stable and facet into a hill-and-valley structure built of {211} microfacets. We observe this structure for a wide range of times (10–320 s) and temperatures of annealing (1100–1400 K).

2. Experimental

The sample crystal had the form of a [111]-oriented, 2.6 mm long needle. The apex of the needle was approximately hemispherical,

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with the average radius of curvature 270 nm. The apex region was observed using Field Ion Microscopy (FIM) [31,32]. Within the field of view there was the [111] crystal pole, surrounded by three stable facets of the {211} type. In between the {211} facets there are three unstable {332} regions which were the subject of study. After each faceting experiment, the crystal was quenched to 80 K (quenching rate = 6000 K/s [30]), argon was introduced (1.5×10^{-5} Torr) and high voltage was applied to the sample (28–32 kV) to obtain the FIM image of the crystal surface. The ion images were intensified by a microchannel plate and captured by a CCD camera with exposure time of 6 s.

The temporal evolution of facets under annealing is a weak effect. We found that self-consistent and reproducible facet sizes are obtained only if strict surface cleaning procedures are followed. In the present work the sample, connected to a liquid nitrogen reservoir, was cleaned thermally by annealing at least twice at 2050–2200 K for at least 5 s, with rapid temperature rise and fall (time constant $\tau<1$ s). Although it is known that carbon impurities may remain on tungsten even at 2200 K, the repetitive application of oxygen in the course of experiments removes the carbon atoms. Occassionally it was found that the temperature rise and fall rates had to be lowered ($\tau=20$ s) to obtain a clean surface. The effectivity of the cleaning procedure had to be constantly verified. "Blank" experiments without oxygen adsorption were carried out [21] (a contaminated surface undergoes faceting, a clean surface remains smooth). A sensitive indicator of surface purity is the field electron emission microscopy (FEEM) image [33,34] (impurities alter the emission pattern). We observed the FEEM pattern and measured the integral brightness b of the image at a fixed voltage (6.7 kV). We found that as the cleaning temperature is increased, the total image brightness first increased and then saturated — at this point the regular pattern of a clean tungsten surface was observed. The brightness test was repeated in the course of experiments. Fig. 1 shows the FEEM images observed 80 s after cleaning.

The base pressure of the metal vacuum chamber was 3×10^{-10} Torr. The faceting experiments were carried out immediately after cleaning to minimize residual gas contamination. During the experiment, the exposure to residual gases was 0.01–0.1 Langmuir. At the temperatures of the faceting experiments (1100–1400 K) the sticking coefficients of residual gases is low and we did not notice any influence of residual gas adsorption — for example, the results did not appear sensitive to the variation of the chamber background pressure caused by variation of the laboratory ambient temperature.

After cleaning, the tungsten crystal was cooled to 80 K. Such prepared crystal surface is smoothly rounded except for small {211} facets. Subsequently the surface was exposed to 1.4 ± 0.3 Langmuir of oxygen.

At this low oxygen exposure tungsten oxides are not formed [37]. The adsorbed oxygen film was stable upon subsequent temperature treatment (80–1400 K), because the desorption temperature of atomic oxygen from tungsten is 2200 K [37]. The oxygen adsorbate is mobile above 800 K — it forms a two-dimensional lattice gas [38,39]. In this work the oxygen exposure is constant — the effect of exposure change on O/W faceting was discussed in Ref. [40]. A review of the O/W adsorption system can be found in Ref. [41], Ref. [23] summarizes information on O/W faceting, while Refs. [29] and [30] discuss the temperature-dependent equilibrium crystal shape of O/W.

After cleaning and oxygen exposure, the actual faceting experiment was simple. The crystal temperature was raised for time t to a fixed value T. During this time, the smooth {332} regions quickly (in less than 10 s) underwent a transformation to a hill-and-valley structure built of {211} microfacets; this was followed by slow coarsening process, when the facets collide and merge into larger ones, leading to the increase of the average facet size and the decrease of the facet density. Finally, the surface configuration was frozen by quenching

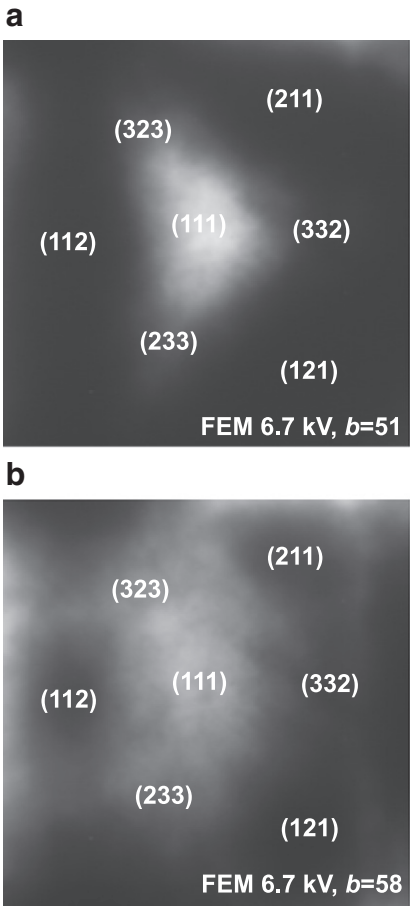

Fig. 1. Field electron emission images for assessing the initial cleanness of the crystal surface, 80 seconds after cleaning. (a) Contaminated surface, integral image brightness $b=51$. Reconstructed (111) region leads to locally increased brightness, but total electron emission is low due to adsorption. (b) Well cleaned surface, integral brightness $b=58$. Smooth surface, high total electron emission. After cleaning a small amount of residual hydrogen adsorbs on the surface (sticking coefficient ≈0.1 at 80 K [35]), but it is removed at temperatures applied in subsequent experiments (1100–1400 K) [36].

of the crystal at the rate of 6000 K/s and observed using FIM. The steplike facets are interconnected by extended edges which are resolved in FIM. By counting the number of edges, the spatial density of facets was determined.

In Ref. [30] it was shown that the observed frozen crystal shape may depend on the quenching rate if the atomic mobility is high. However, in the experiments reported here the observable coarsening of the faceted surface occurs on the timescale of seconds, tens of seconds or even hundreds of seconds. The present quenching time is so short (≈0.1 s) that during quenching no observable changes occur in the arrangement of facets.

To ensure proper vacuum conditions, only one faceting experiment per day was carried out. For the next experiment with different t or T, the whole procedure of cleaning and oxygen adsorption was repeated.

3. Results

Fig. 2 presents example FIM images obtained in the faceting experiments. In the {332} regions the surface is completely reconstructed into a steplike structure built of {211} microfacets. The edges of these facets are imaged as bright parallel lines. Each of the {211} microfacets is a few nanometers wide (~5 nm for $t=160$ s, $T=1400$ K) and 40–60 nm long. The length of the microfacets is determined by the average radius of curvature of the sample