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Oxygen-covered tungsten crystal shape: Time effects, equilibrium, surface energy and the edge-rounding temperature

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ABSTRACT

The equilibrium crystal shape (ECS) of an oxygen-covered tungsten microcrystal is studied as a function of temperature. A specially designed ultrafast crystal quenching setup with the cooling rate of 6000 K/s allows to draw conclusions about ECS at high temperatures. The edge-rounding transition is shown to occur between 1300 K and 1430 K. The ratio of surface free energies $\gamma(111)/\gamma(211)$ is determined as a function of temperature.

1. Introduction

The study of equilibrium crystal shape (ECS) yields information on temperature-dependent surface free energy, which is one of the fundamental quantities in surface physics and chemistry [1]. Understanding ECS is an important step in the ongoing challenge to construct realistic models of solids. The problem of ECS for pure one-component crystals is already complex (see e.g. reviews [1–3]). Even more challenging is the consideration of ECS with adsorption, which is important for the understanding of fundamental processes on catalyst surfaces [4,5]. There exist only few models and experimental reports concerning ECS with adsorption [3,5–12].

The general property of ECS is that it evolves with temperature. At absolute zero polyhedral shapes are predicted [2,13], with atomically sharp vertices and atomically sharp edges. As the temperature is increased, entropic effects cause rough regions to appear on the crystal surface. At a certain temperature the vertices and the edges become rounded. We will denote by T_v the *vertex rounding temperature*, and by T_e the *edge rounding temperature*. The proposed dependence of ECS on temperature is illustrated in Fig. 1(a)–(f) (see also [2]).

Given the difficulty of experiments on ECS with adsorption, it is reasonable to choose an exprimentally simple and well studied adsorption system — O/W (for a review on O/W, see Ref. [14]). We treat O/W as a model system, which gives insight into general properties of thermal evolution of ECS predicted by theory. On the other hand, O/W is one of the candidate adsorption systems for the fabrication of atomically sharp tungsten electrodes applied as practical electron and ion point sources [15–24], and understanding of the temperature dependence of O/W ECS allows one to control the sharpness of the electrode.

The adsorption of oxygen on tungsten is qualitatively different for low and high oxygen exposures. Thermal desorption spectroscopy studies reveal that after low exposures (<2 L) the adsorbate is all desorbed as O atoms, while with higher exposures oxygen is removed as tungsten oxides [25]. In the present work we concentrate on the low exposure case: 1.4 L, where no alloying occurs. The desorption temperature of atomic oxygen is 2200 K (much higher than the desorption temperature of oxides) [25]. The exposure of 1.4 L corresponds to a coverage of less or equal to $5 \cdot 10^{14}$ molecules/cm^2.

Oxygen is known to increase the anisotropy of the surface free energy of tungsten and thus to induce pronounced thermal faceting of the surface (see Ref. [26] and references therein). The O/W faceting is observed in a very wide temperature range: it is already observed at 800 K [27], while annealing at 1800 K still leaves enough oxygen on the surface for faceting to occur. Oxygen adsorbate is mobile above 800 K — it forms a two-dimensional lattice gas [28,29].

Oxygen-induced faceting of tungsten observed in experiments often takes the form of steplike (hill-and-valley) faceting, where steps or pyramids/pits are formed on the surface. These non-convex shapes are steady-state, non-equilibrium forms. Only under special conditions it is possible to observe a convex, equilibrium crystal form [11,30] (global faceting). It is known that the vertex-rounding transition occurs at $T_v = 970 \pm 70$ K [11].

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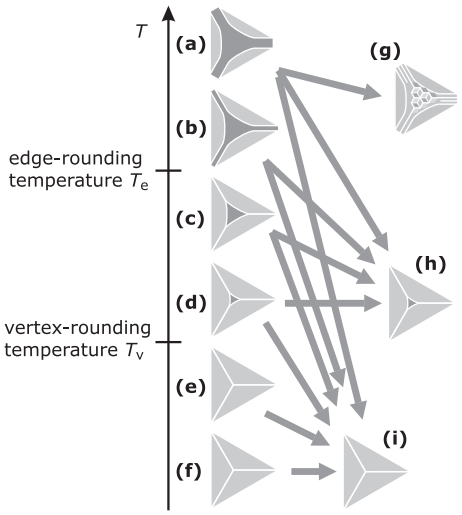

Fig. 1. (a)–(f) The proposed equilibrium crystal shape in the vicinity of the crystal vertex depends on temperature. (g)–(i) The actual crystal shape observed after quenching. The observed shape depends on the cooling rate and may differ from the equilibrium shape. During quenching small steplike facets may be formed as shown in (g).

Still, there remain unsolved some interesting questions about the ECS of O/W crystals.

- As the temperature is increased, the transition from non-equilibrium steplike crystal surface to a convex equilibrium shape may be observed [30]. But as the temperature is increased further, it appears that a reverse transition is taking place — a single crystal edge is again disassembled into a non-convex group of parallel edges (steplike faceting) [30], apparently violating theoretical predictions for ECS.
- With the present state of microscopic techniques, if one needs at the same time high spatial resolution (~1 nm), high sample temperatures (~1500 K) and good control of surface impurities, the only way to observe the ECS is to observe the crystal after quenching (rapidly cooling) the crystal to a lower temperature. The question is: what is the necessary cooling rate for the atomic configuration to be preserved? Is the cooling rate applied in previous work sufficient? (400–800 K/s [11,30]).
- Is it possible to extract from microscopic observations any quantitative information about the dependence of the surface free energy on temperature? (the problems are: microscope image deformations and doubts whether the cooling rate is sufficient).
- Is it possible to observe the edge-rounding transition? (Not to be confused with the vertex-rounding transition observed before [11].)

The main purpose of the present paper is to answer the above questions. In this work the crystal is mounted on a special support allowing for extremely high cooling rates: 6000 K/s. As will be shown, for high crystal temperatures this does make a difference.

2. Experimental

2.1. The sample crystal

The tungsten crystal had the form of a 2.6-mm long needle, with the cone half-angle not exceeding 10°. The axis of the needle was oriented along the [111] direction. The apex of the needle was approximately hemispherical, with the average radius of curvature 270 nm. In this work we focused on the changes in topography near the apex of the needle – in the vicinity of the (111) pole – where the crystal shape is a good approximation of the equilibrium crystal shape. The surface of the crystal was observed using Field Ion Microscopy (FIM) [31,32].

The base pressure of the vacuum chamber was 3×10^{-10} Torr. The experiments were carried out at fast pace to minimize residual gas contamination. The whole process of crystal formation, from crystal cleaning to crystal quenching, took about 5 min.

The sample was carefully cleaned in situ immediately before every experiment. Cleaning by field evaporation, which is applied with great success in FIM studies of low temperature single-atom diffusion (see e.g. Ref. [33]), is not appropriate for faceting studies, because at high temperature impurities from the sample shank contaminate the field-evaporated tip apex. For this reason we cleaned the sample thermally — separately for each experiment. This consisted of annealing at sufficiently high temperature (1950–2200 K), where impurity-induced faceting is no longer observed. Surface cleanliness was verified by performing "blank" experiments [34]: the crystal was annealed at 1100 K without adsorbate, and no faceting was observed. Although it is known that carbon impurities may remain on tungsten even at 2200 K, it is unlikely that carbon influences our experiment, for two reasons: first, carbon induces characteristic surface faceting on tungsten [6], which was not observed in this work, and second, the surface was repeatedly treated with oxygen, which is known to remove carbon impurities.

After cleaning, the tungsten crystal was cooled to 80 K and exposed to oxygen (1.4 ± 0.3 L). This provided the starting point of all experiments described in this work. The adsorbed oxygen film was stable upon subsequent temperature treatment (80–1800 K), because the desorption temperature of atomic oxygen is 2200 K (much higher than the desorption temperature of oxides) [25].

2.2. Sample mounting for ultrafast cooling

The main idea behind the ultrafast cooling setup constructed for this work is to heat the sample while maintaining a very high temperature gradient in the sample support. When the heating stops, high temperature gradient causes efficient conduction of heat from the sample, leading to a rapid decrease of the sample temperature. The realization of this idea is shown in Fig. 2. Four molybdenum rods ($\phi=1.5$ mm) are kept at low temperature (80 K) and act as efficient heat sink. The sample is mounted on a short (6 mm) tungsten wire ($\phi=0.1$ mm), which acts both as a resistive heater for the sample and as a heat conductor for sample cooling. Additional two tungsten potential leads ($\phi=0.1$ mm) are used to measure the resistance, and thus to monitor the temperature [31].

Fig. 3 shows the calculated temperature distribution along the 6 mm long heating/cooling wire, the details of which are described in Section 2.3. Note that along the short 3 mm distance the temperature changes by almost 2000 K. This high temperature gradient is desirable for ultrafast sample cooling, but it complicates the measurement of the sample temperature. The standard method [31] must be modified to account for temperature gradients, as described in the next section.

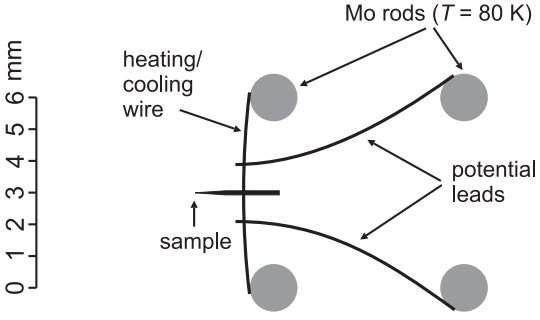

Fig. 2. Sample mounting for temperature control and ultrafast cooling.