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Anisotropy of the spatial distribution of CO molecules desorbing from tungsten

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The desorption of CO from an anisotropic surface of polycrystalline tungsten after different periods of annealing has been studied. Anisotropy in the spatial distribution of CO molecules in the desorbing flux was detected at early stages of annealing. Smoothing out of the surface texture during annealing recorded by means of STM resulted in the disappearance of the spatial distribution anisotropy. The results are quantitatively explained by the model of a rough surface.[7]

Key words: carbon monoxide, desorption from tungsten; desorption flux, anisotropy of spatial distribution.

The study of the spatial distribution of desorption flux (SDDF) is of great interest for understanding dynamics of the interaction of gases with surfaces. This distribution is in many cases nonequilibrium and provides information about processes preceding desorption.[1–4]

For smooth surfaces the SDDF is often observed to be concentrated normal to the surface and is described by the model of Van Willigen[5]:

$$I/I_0 = \frac{\varepsilon + \cos^2\varphi}{(\varepsilon + 1)\cos\varphi} \exp(-\varepsilon\, \mathrm{tg}^2\, \varphi), \qquad (1)$$

where $\varepsilon = E/kT$, E is the chemisorption activation energy, k is the Boltzmann constant, T is the sample temperature, I_0 and I are the flux intensities normal to the surface and at an angle φ with it, respectively.

In practice the following equation is often used:

$$I/I_0 = \cos^n \varphi, \qquad (2)$$

in which the parameter n ($n > 1$) characterizes the degree of SDDF concentrated normal to the surface.

With the appropriate selection of the values of n and ε the functional dependences (1) and (2) are close to each other.

On isotropic single crystal faces the SDDF is isotropic, this being shown by the example of H_2/Ni(111).[6]

In the case of a rough surface, an increase in the roughness coefficient (γ) leads to widening the distribution of the desorption flux, and the effective value of n decreases.[7] Thus, anisotropy of the surface relief can lead to anisotropy of the SDDF.

Azimuthal anisotropy of SDDF was observed for CO_2 molecules formed in the oxidation of CO on anisotropic faces of Pt(110), Ir(110), and Pd(110).[8–11]

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In the present work an attempt was undertaken to experimentally detect the anisotropy of SDDF on a rough surface with anisotropic relief having characteristic dimensions of 100 Å.

For this purpose a rolled polycrystalline tungsten ribbon was used with grooves, strictly oriented in the direction of rolling produced by mechanical treatment.

Experimental

The basic experiments were carried out using a stainless steel UHV system described previously.[3] The exact procedure for sample preparation and the design for its support were of great importance for this work.

Specimens with dimensions of 10×3 mm were cut out from a 0.01 mm thick tungsten ribbon. Two specimens were fixed at the same time in the support: one of them was cut along the rolling lines, the other — transverse to them. In this way simultaneous annealing of both samples was achieved.

The direction of the rolling lines was determined with a light microscope. After annealing the specimens were investigated with a tunneling microscope to determine the surface relief parameters. The specimens were heated resistively by alternating current. Their temperatures were measured by means of W-Re thermocouples spot welded to the back sides of the specimens.

In the experiments parameters of SDDF were determined for CO molecules evolving from tungsten due to the recombination of carbon and oxygen dissolved in the specimens. In one series of specimens the distributions were measured in the plane which passed through the surface parallel to the rolling lines of the tungsten ribbon and in the other one — at right angles to them.

Desorption measurements were alternated with annealing in the ultra high vacuum at 2000 K. To obtain a desorption flux of a sufficient intensity the temperature in every subsequent series of experiments was increased by steps from 900 to 1700 K.

Results and Discussion

Investigation of the initial specimens showed that the defects on their surfaces were too large for determination of the surface relief by means of tunneling microscopy. Annealing for 1 h smoothed out the specimen surface substantially.

Figure 1, *a* shows the surface relief of the tungsten ribbon specimen after annealing for 1 h. In this figure we notice that the discontinuities of the relief are oriented along the rolling lines of the tungsten ribbon and are 30—50 Å in size. The roughness coefficients estimated along (γ_1) these furrows and normal (γ_2) to them are equal to 1.010±0.005 and 1.20±0.05, respectively.

After annealing for 5 h the surface smooths out (Fig. 1, *b*), the surface relief anisotropy nearly disappears, and the values of γ_1 and γ_2 approach unity, becoming equal to 1.004±0.003 and 1.020±0.005, respectively.

According to preliminary calculations one would expect a marked difference between the parameters of SDDF for the two mutually perpendicular planes. In fact, when the surface is strongly anisotropic (Fig. 1, *a*) significant anisotropy of the spatial distribution is observed in the initial stage of annealing (Fig. 2). Approximating the SDDF using Eq. (1) gives the values of the exponents $n_1 = 3.2$ and $n_2 = 1.6$ in the planes parallel and perpendicular to the lines of rolling, respectively.

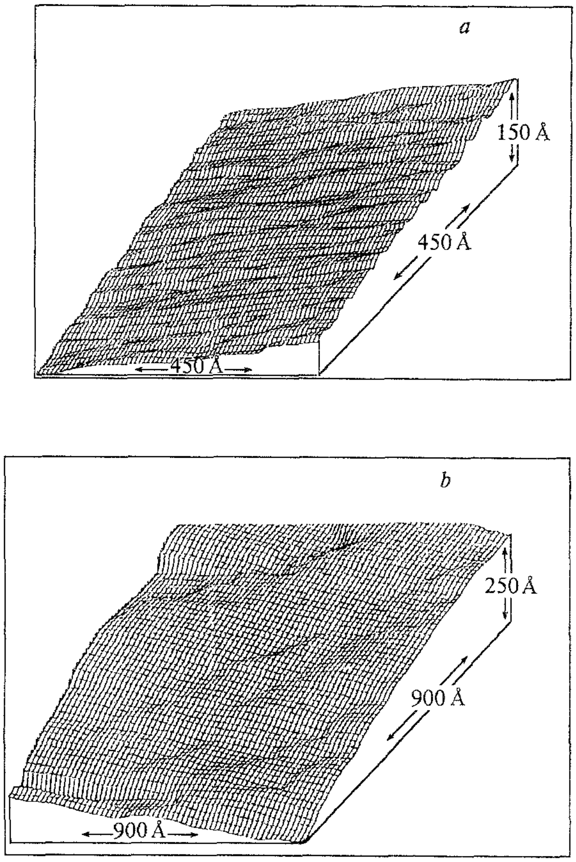

Fig. 1. Surface relief of a tugsten polycrystalline ribbon recorded by a tunneling microscope after annealing at 2000 K for 1 h (*a*) and 5 h (*b*).

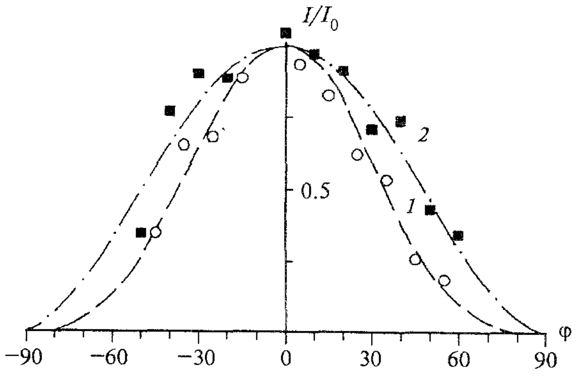

Fig. 2. Spatial distributions of the fluxes of CO molecules desorbing from tungsten recorded in planes parallel (*1*) and perpendicular (*2*) to the rolling lines (annealing time 1 h)

Table 1. Spatial distribution parameters of CO desorption flux from tungsten

Annealing time/h	n_1	γ_1	n_2	γ_2	T/K
1	3.2±0.3	1.01	1.6±0.2	1.2	900
1.5	2.2±0.2	—	1.4±0.2	—	1200
3	1.7±0.2	1.006	1.4±0.2	1.07	1400
5	1.6±0.2	1.004	1.7±0.2	1.02	1600

The data obtained here are in complete agreement with those estimated previously[7]: with an effective exponent $n_{\text{eff}} = 1.6$ and the value of $\gamma = 1.2$ one would expect for a smooth surface, according to the calculations, that $n = 3.2$. The value of n_1 experimentally determined for the surface which could be considered practically smooth ($\gamma_2 = 1.01$) was also equal to 3.2.

In Fig. 3 the distributions of CO registered in two mutually perpendicular planes along the rolling lines and transverse to them are shown as a function of total previous annealing time. Table 1 lists the parameters (n_1 and n_2) of these distributions, the surface roughness coefficients (γ_1 and γ_2) corresponding to the two chosen directions, and CO desorption temperatures.

As can be seen from Fig. 3 and Table 1, on the initial stages of annealing when the surface is substantially anisotropic considerable anisotropy of SDDF for CO is observed. Hereafter as the specimen surface smooths out as a consequence of annealing, the values of n_1 and n_2 become equal to each other within the limits of experimental error.

It could be assumed that with the smoothing out of the specimen surface during annealing the value of n_2 would increase approaching n_1, but actually the opposite effect was observed, *i.e.*, n_1 decreased and these parameters approached a level corresponding to the initial value of n_2 (see Table 1).

In order to understand the observed dependence an important peculiarity of the procedure in these experiments should be noted: during annealing the content of oxygen and carbon in the specimen decreased, therefore to obtain a measurable CO desorption flux the specimen temperature in every subsequent experiment had to be increased from 900 K (at the initial stage of annealing) to 1600 K (after annealing for 5 h). Increasing the temperature decreases the value of ε in Eq. (1); this should result in the "expansion" of the spartial distribution of the desorption flux. Since during approximation of the same experimental data the values of n and ε change in parallel the parameter n in Eq. (2) should also decrease. Accounting for the increase in the desorption temperature gives a decrease of n_1 from 3.2 to 2.4, which only partially explains the regularities observed.

According to the available data[12] during CO desorption from tungsten a complex spectrum is observed in the temperature range between 700 and 1600 K, which is characteristic for several forms of dissociatively adsorbed CO. The parameters of SDDF in different parts of this range are substantially different. Thus at 700—950 K the angular distribution is described by Eq. (2) with the exponent $n \approx 4$; at 950—1100 K $n \approx 3$, and at 1100—1500 K n = 1 to 2. These data are in agreement with the experimentally obtained results for the parameter n_1 corresponding to a smooth tungsten surface (see Table 1).

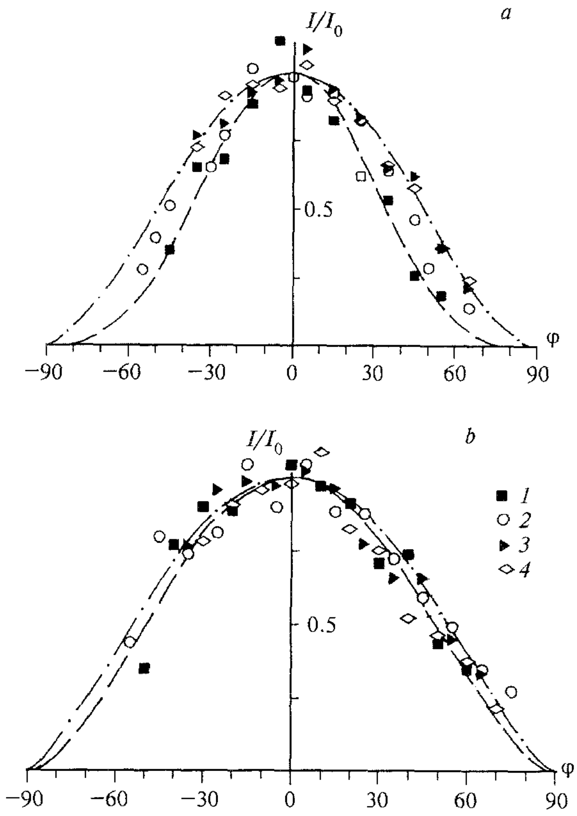

Fig. 3. Spatial distributions of CO desorption fluxes as a function of annealing time recorded in planes parallel (*1*) and perpendicular (*2*) to the rolling lines at annealing time (h): 1 (*1*), 1.5 (*2*), 3 (*3*), 5 (*4*).

One can similarly explain the constancy of the value of n_2 despite the marked smoothing out of the surface during annealing (the value of γ_2 changed from 1.2 to 1.02). The surface was initially very rough; detectable distinctions between the exponents n_1 and n_2 were observed. One could expect that with flattening of the surface the exponent n_2 would increase. However, at high temperatures desorption of firmly bound forms of CO characterized by lower values of n was observed. The effects of surface flattening and the effect of desorption at high temperatures of firmly bounded forms of CO compensated for each other in such a way that the value of n_2 remained practically constant.

The agreement between the results of SDDF measurements for CO formed during the recombination of C and O atoms with previously obtained data[12] on the desorption of dissociatively adsorbed CO molecules makes it possible to assume the presence of a common rate limiting step for both processes. This, very probably, is the recombinational desorption of C and O adatoms.

It is of interest to note that the simple geometrical model of a rough surface used in this work can be used to describe the experimental results obtained in the study of CO_2 desorption from anisotropic faces of single crystals where the characteristic size of the surface relief is several interatomic distances[8–11].

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