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Thermal desorption of dysprosium from tungsten microcrystal

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Abstract

Activation energy for thermal desorption of dysprosium from a tungsten microcrystal of about 300 nm diameter was determined by means of the field-emission method. The desorption was detected from the whole W emitter surface in the temperature range 1490–1665 K for dysprosium average coverage $\theta < 0.06$ monolayer. The average activation energy was determined to be 4.09 ± 0.06 eV/atom and the frequency factor to be about 10^{11} s^{-1}. The energy may mainly concern the desorption from the atomically rough regions of the microcrystal.

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Keywords: Field emission; Thermal desorption; Dysprosium; Tungsten

1. Introduction

Extensive experimental studies of dysprosium-metal systems concerned mainly dysprosium adsorbed on the planar substrates [1–9]. The field-emission microscopy method (FEM) for tip surfaces was also applied [10–13]. Early FEM results were related to the average work function change during the adsorption of dysprosium on the W emitter tip surface and thermal desorption of Dy atoms [10]. Then the surface diffusion of Dy on W emitter tips and the surface self-diffusion of dysprosium were also investigated [11,12].

Recently, further results on the surface diffusion of dysprosium on the rough W(1 1 1) facet have been obtained using the field-emission current fluctuation method [13]. The method allows studying the motion of adspecies in dynamic conditions. Studies of thermal desorption of adsorbed atoms give information on the kinetics and dynamics of the adsorbates and interactions in the adsorbate layer. For such investigations, the temperature programmed desorption (TPD) technique is mainly used [14–17], apart from the field-emission method [10,18–22]. Analysis of the experimental results based on the application of the well-known Polanyi–Wigner equation provides the desorption kinetic parameters. Recently, for studying the desorption processes, the kinetic Monte Carlo simulation scheme was applied [23–25].

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We present experimental results concerning studies of the thermal desorption of dysprosium from the tungsten tip surface by the FEM method. In this method, the surface – a field emitter microcrystal tip surface – has a diameter of the order of several hundreds of nanometers. Such objects constitute the core of heterogeneous catalysts. The nearly hemispherical apex of the field emitter tip is just a suitable example of the model catalysts. Although this method provides with only average values of thermal desorption parameters, for a total emitter tip surface that consists of several facets of various types, the knowledge of such data can be useful for understanding various processes occurring selectively just on such complex surfaces. Our results concern the desorption parameters corresponding to the low Dy coverage limit $\theta < 0.06$. Thus, they may be connected mainly with interaction between the adsorbed atoms and the substrate.

Studies of the thermal desorption of Dy from W are useful for planning and interpretation of the results of investigation of field-emission current fluctuations for adsorption systems like this. They help to define the influence of thermal effects on the current fluctuations and also to find the temperature range suitable for surface diffusion, which is of importance in surface modification for nanotechnology applications.

2. Experimental

The thermal desorption was investigated using a sealed-off glass field-emission microscope equipped with a source of dysprosium to be deposited under UHV conditions. The emitter tip temperature was determined by measuring the changes of resistance of an emitter loop segment [26,27]. In order to control the thickness of the dysprosium submonolayer, the work function versus the deposition time (corresponding to Dy coverage) was measured [13].

The experimental procedures of the thermal desorption and calculations were similar to those applied by Gomer and coworkers [28,18,20]. After the thermal cleaning of the tungsten emitter surface a submonolayer of dysprosium was deposited. Then the emitter was heated at about 700 K in the absence of the electric field to enable equilibration by surface diffusion of dysprosium. Thermal desorption of dysprosium from the tungsten emitter tip surface was examined within the temperature range from 1490 to 1665 K. For this purpose, the emitter surface was heated for some time t at a convenient temperature T in the absence of the high electric field and then the emission high voltage U for a fixed emission current was measured. In this way, the dependences of U on the annealing time t of the emitter at constant temperatures T were obtained.

The kinetic parameters of thermal desorption were determined basing on the Polanyi–Wigner equation, which describes the desorption rate:

$$r_{\mathrm{des}} = -\frac{\mathrm{d}\theta}{\mathrm{d}t} = \nu\theta^n \exp\left(-\frac{E}{kT}\right) \tag{1}$$

where E is the activation energy for thermal desorption, ν the desorption attempt frequency, θ the adsorbate coverage in monolayers, n the desorption order and k is the Boltzmann constant. The desorption order reflects the adlayer phases present during desorption. For systems with no (in fact, very weak) lateral interactions the first-order desorption ($n = 1$) is assumed [21–25]. Although we did not examine the order of the kinetics, the field-emission method allows to obtain information on the temperature range of desorption and the activation energy of the process. Assuming the first-order kinetics for desorption of Dy at a constant temperature T and the coverage θ_1 at time t_1 and θ_2 at time t_2 ($\Delta t = t_2 - t_1$), we can write the above equation in the form:

$$\ln \Delta t = \frac{E}{kT} - \ln \nu + \ln\left(\ln\left(\frac{\theta_1}{\theta_2}\right)\right) \tag{2}$$

The activation energy for desorption and the desorption attempt frequency ν were determined for dysprosium coverage below 0.06 ML from the Arrhenius-type plots $\ln \Delta t$ versus $1/T$.

3. Results

An important parameter in desorption studies is overlayer coverage. Average coverage has been determined arbitrarily assuming that 1 ML of dysprosium on the W microcrystal corresponds to the minimum of the average work function of the system. Such approach is applied in Ref. [10] for Dy/W and to