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Diffusion and field desorption of barium atoms from an inhomogeneous rhenium surface

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Using field desorption microscopy, it is shown that the nature of desorption by an electric field of adsorbed barium atoms on a quasi-spherical surface of a rhenium single crystal that is inhomogeneous in work function depends on the rate of diffusion of adsorbate atoms over the surface. In the absence of diffusion of barium atoms over the surface ($T = 300\,\mathrm{K}$), a pulse character of desorption is observed. At rhenium temperature $T = 700\,\mathrm{K}$ migration equilibrium is established on the surface, at which the concentration of barium adatoms on the faces of a rhenium single crystal can be different. It has been shown that in this case, a stationary field desorption mode is realized, in which the emission of barium ions comes from faces with higher work function.

Keywords:field desorption, microscopy, diffusion, work function, rhenium, barium.

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1. Introduction

Desorption in an electric field of atoms of alkaline earth metals, in particular, barium, pre-adsorbed on the surface of chemically resistant refractory metals, the study of the effect of substrate parameters on ion formation processes are of both scientific and practical interest. Currently, the production of ion fluxes as a result of field desorption is widely used in various fields (ion beam technologies, mass spectrometry, field microscopy, etc.) [1–5].

Desorption in an electric field (field desorption) is usually understood as the removal of adsorbed atoms or molecules in the form of ions from the surface (ion emission). Fields with a strength of $\sim 10^7 - 10^8$ V/cm and more are needed to implement field desorption, and it exists in a wide range of temperatures, including low ones. To obtain such a high electric field strength on the surface of the sample, it is made in the form of a tip with a radius of curvature of $10-1000$ nm. The surface of the tip after temperature treatment acquires a quasi-spherical monocrystalline shape. Inhomogeneities present on the surface of the tip, such as flat low-index faces of a single crystal, various nanostructures (microgrowths, graphene and graphite nanostructures, etc.) affect the process of field desorption due to changes in the local electric field strength, intercalation of adsorbate atoms by graphene nanostructures, which makes it possible to visualize the modification of the emission surface. It follows from the theory of image forces for field desorption that the magnitude of the electric field strength required for desorption depends on the heat of evaporation of the adatom, the ionization potential of the adatom, the work function of the surface and the polarizability of the adatom and the ion formed. The adatom and the free ion polarizability values of alkali metals are small (less than $5\,\text{Å}^3$) [6,7], and they do not significantly affect the magnitude of the electric field strength. The situation with barium adatoms is different. The barium adatom polarizability exceeds the polarizability of the free ion by an order of magnitude and decreases sharply with an increase in the degree of coating, which should affect the intensity of the desorbing field.

The use of field desorption to obtain an enlarged image of the surface of the sample from which desorption occurs (field desorption microscopy) is of particular interest. In continuous desorption microscopy, metals whose atoms are relatively weakly bound to the surface, diffuse over the surface and desorb from it at relatively low temperatures and electric field strengths are mainly used as an ion source (depicting adsorbate). Alkali metals are the most convenient in this regard and are most often used. At the same time, alkaline earth metals have some potentially useful features for field desorption microscopy. Alkali metal atoms during adsorption on a metal substrate are in an ionized state and interact with each other and with the substrate almost completely electrostatically. Alkaline-earth atoms can carry out chemical interaction due to the second valence electron. Interaction with surface defects, crystal steps, impurities and adsorbate structures can reveal these objects. In this regard, it is of interest to study the features of field desorption of alkaline earth metals.

2. Experiment procedure

A field emission microscope was used to obtain field desorption and field electron images of the surface on a nanometer scale [8]. The enlarged image is formed due to the projection of the sample surface onto the luminescent screen by emitted electrons (field electronic image) or ions (field desorption image). To register weak currents, an assembly of two microchannel plates with a diameter of 56 mm was located in front of the fluorescent screen. A sample in the form of a tip with a vertex radius of about 500 nm was made of rhenium wire by electrochemical etching. Then, in a high vacuum (pressure $p \approx 5 \cdot 10^{-9}$ Torr), the sample was annealed directly in the chamber of a field emission microscope at a temperature of $T = 2500$ K. The sample was cleaned and a single-crystal quasi-spherical surface of the tip with flat low-index faces was formed during annealing. The formation of a single crystal vertex of the rhenium emitter was accompanied by the appearance of a [9] field electron image, which is standard for crystals with a hexagonal densely packed lattice. The field electron image was visualized in the field electron microscope mode, the field electron emission current was measured and the volt-ampere characteristics of the Fowler–Nordheim were obtained to determine the work function of the surface and the parameters of the tip. The field desorption microscopy mode [10] made it possible to visualize the process of field desorption of barium from the surface on a nanometer scale, to determine the localization of the emission of barium ions, to determine the intensity of the electric field at which desorption occurred. Comparison of field desorption images with field electronic images made it possible to determine the effect of local work function and electric field strength on the localization of desorption on the surface of the emitter.

3. Results and discussion

To estimate the magnitude of the electric field strength F on the surface of the rhenium sample, the electric field factor β was calculated from experimentally taken Fowler–Nordheim characteristic for a pure emitter with a known value of the work function [11]. β value for the field emitter used in the experiments turned out to be equal to $\beta = 3600\,\mathrm{cm}^{-1}$. The strength of the desorbing field F was calculated using the formula

$$F = \beta \cdot U_\mathrm{d}, \tag{1}$$

where $\mathrm{U_d}$ — the voltage at the field emitter at which desorption is observed. The maximum voltage applied to the emitter in the field microscope used was 30 kV, which corresponds to the maximum value of the electric field strength F on the sample surface $\sim 1.1 \cdot 10^8$ V/cm. The dependence of φ work function on the time of barium deposition was obtained to assess the degree of surface coating (θ) of rhenium with barium. This dependence, characteristic of alkaline and alkaline earth metals, passes through the minimum in the region of the optimal coating corresponding to ~ 0.7 monolayer coating [12]. φ sample work function after spraying of barium atoms was determined using the formula

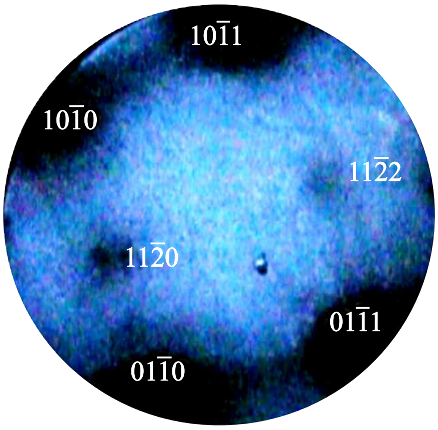

Figure 1. Electronic field image of a rhenium sample.

$$\varphi = \varphi_0 \cdot (U/U_0)^{2/3}, \tag{2}$$

where φ_0 — work function of the pure rhenium surface ($\varphi_0 = 5$ eV), U_0 — voltage at the pure emitter, and U — voltage on the emitter after adsorption of barium atoms, measured at the same field electron emission current [13]. Figure 1 shows a field electronic image of the surface of a rhenium sample at a voltage of 10 kV. The flat low-index faces of the rhenium single crystal are represented by dark areas on which the face indices are indicated.

After spraying a small dose of barium at rhenium temperature $T = 300$ K, the emitter voltage was lowered to $U = 8.4$ kV. The work function calculated by the formula (2) was $\varphi = 4.5$ eV, which corresponds to the degree of barium coating $\theta = 0.05$ from the monolayer coating. In this case, the field electronic image practically did not change, since the deposition was carried out by a uniform flow of barium atoms onto the sample, and there was no diffusion of barium atoms over the surface. The voltage polarity changed (plus on the sample) in field desorption microscopy mode. The voltage was gradually increased, and at the emitter voltage $U_\mathrm{d} = 27$ kV, field desorption of barium in the form of a flash was observed (Fig. 2). The electric field strength calculated using the formula (1), at which field desorption of barium was observed at a temperature of $T = 300$ K, was $0.97 \cdot 10^8$ V/cm.

As can be seen from Fig. 2, the field desorption of barium at $T = 300$ K occurs over the entire area of the emitter within the recording area. There are no clearly identified areas where there is a more intense emission of barium ions.

The energy barrier $Q_n(F)$, which should be overcome during thermal activation to remove the adsorbed atom in the form of a n-multiply charged ion in the image forces

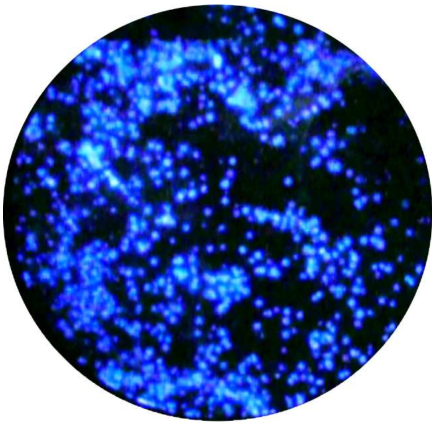

Figure 2. Flash of barium field desorption at the degree of coverage $\theta = 0.05$, 300 K and $U_{\mathrm{d}} = 27$ kV.

model, is determined by the expression [7]:

$$Q_n(F) = \Lambda(\theta) + \sum I_{\mathrm{n}} - n\varphi(\theta) - (ne)^{3/2}F^{1/2} + \Delta E_{\mathrm{p}}(\theta), \tag{3}$$

where Λ — heat of evaporation of the atom, $\sum I_{\mathrm{n}}$ — sum of ionization potentials, φ — work function of the surface, e — electron charge, F — intensity of the applied electric field, ΔE_{p} — polarization correction equal to $1/2(\alpha_{\mathrm{a}} - \alpha_{\mathrm{i}})F^2$, where α_{a} — polarizability of the adsorbed atom, α_{i} — polarizability of the desorbed ion. The time τ required for field desorption during thermal activation is determined using the Arrhenius equation

$$\tau = 1/\nu_0 \cdot \exp(Q_n/k_{\mathrm{B}}T), \tag{4}$$

where ν_0 — vibration frequency, k_{B} —Boltzmann constant, T — temperature. It is possible to write an expression from the ratios (3) and (4) to estimate the magnitude of the electric field strength required for desorption

$$(ne)^{3/2}F^{1/2} = \Lambda + \sum I_{\mathrm{n}} - n\varphi - k_{\mathrm{B}}T \cdot \ln(\tau\nu_0) + \Delta E_{\mathrm{p}}. \tag{5}$$

Field desorption of barium (Fig. 2) is observed throughout the registration area, including from the rhenium faces of type $(10\bar{1}0)$. Therefore, to estimate the electric field strength F using the formula (5), the heat of evaporation of barium atoms Λ, work function of the surface φ, we take the known values for the rhenium face $(10\bar{1}0)$ [14]. The desorption time τ in our experiments did not exceed 1 s, and the value of the vibration frequency ν_0 is assumed to be equal to $\nu_0 = 10^{13}\,\mathrm{s}^{-1}$ [15]. α_a polarizability value of the adsorbed barium atom depends on the degree of coating θ and is $\alpha_{\mathrm{a}} = 30\,\text{Å}^3$ (at a concentration of $n = 2 \cdot 10^{13}\,\mathrm{cm}^{-2}$) and becomes less than $3\,\text{Å}^3$ at a concentration of barium $n > 2 \cdot 10^{14}\,\mathrm{cm}^{-2}$ [6]. The polarizability value for a double-charged barium ion α_{i} is $1.7\,\text{Å}^3$ [16]. The results of calculating the desorbing field F for single-charge and double-charge barium ions at the rhenium tip temperature $T = 300$ K are given in Table 1 (the values of the electric field strength F are given in parentheses without taking into account the polarization correction ΔE_{p}).

The calculated strength of the desorbing electric field F in the region of small coatings for double-charged barium ions coincides fairly well with the experimentally obtained value ($F = 0.97 \cdot 10^8$ V/cm). It should be noted that the value of the polarizability of the adsorbed barium atom is significantly more important in the region of small coatings ($30\,\text{Å}^3$) compared with the polarizability of a two-charged ion ($1.7\,\text{Å}^3$). Therefore, the polarization correction ΔE_{p} in the formula (5) is important only in the area of small coatings $\theta < 0.1$.

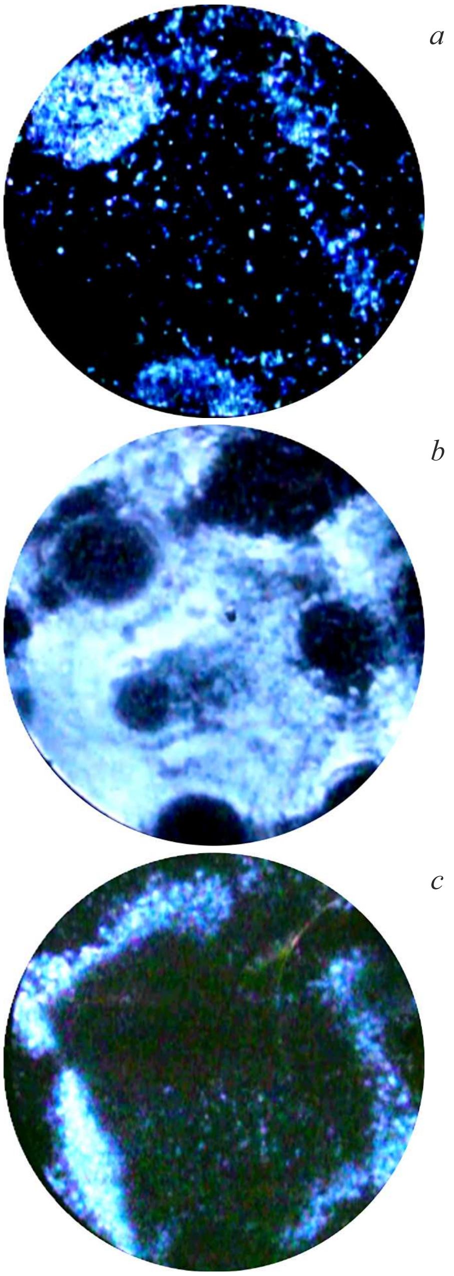

Figure 3. Field desorption of barium at $T = 700$ K, degree of coverage 0.1 and the voltage of the desorbing electric field: *a*) 21 kV; *b, c*) 24 kV.

Table 1. Calculated values of the intensity of desorbing fields F for Ba ions^{++} and Ba^{+} at the rhenium tip temperature $T = 300\,\mathrm{K}$

θ	~ 0.01 ($< 10^{13}\,\mathrm{cm}^{-2}$)	0.1 ($1 \cdot 10^{14}\,\mathrm{cm}^{-2}$)	0.2 ($1.8 \cdot 10^{14}\,\mathrm{cm}^{-2}$)
Λ, eV	4.8	4.4	4.2
φ, eV	5.1	3.9	2.9
Ba^{++}; F, $\mathrm{V \cdot cm^{-1}}$	$0.9 \cdot 10^8$ ($0.7 \cdot 10^8$)	$1.1 \cdot 10^8$ ($1.1 \cdot 10^8$)	$1.4 \cdot 10^8$ ($1.4 \cdot 10^8$)
Ba^{+}; F, $\mathrm{V \cdot cm^{-1}}$	$1.7 \cdot 10^8$	$1.9 \cdot 10^8$	$2.3 \cdot 10^8$

Table 2. Values of desorbing fields F for Ba ions^{++} and Ba^{+} at rhenium tip temperature $T = 700\,\mathrm{K}$

θ	~ 0.01 ($< 10^{13}\,\mathrm{cm}^{-2}$)	0.1 ($1 \cdot 10^{14}\,\mathrm{cm}^{-2}$)	0.2 ($1.8 \cdot 10^{14}\,\mathrm{cm}^{-2}$)
Λ, eV	4.8	4.4	4.2
φ, eV	5.1	3.9	2.9
Ba^{++}; F, $\mathrm{V \cdot cm^{-1}}$	$0.7 \cdot 10^8$ ($5.4 \cdot 10^7$)	$0.9 \cdot 10^8$ ($0.9 \cdot 10^8$)	$1.2 \cdot 10^8$ ($1.2 \cdot 10^8$)
Ba^{+}; F, $\mathrm{V \cdot cm^{-1}}$	$1.2 \cdot 10^8$	$1.5 \cdot 10^8$	$1.9 \cdot 10^8$

The field desorption process significantly changes at the emitter temperature $T = 700\,\mathrm{K}$, when the migration equilibrium of barium atoms is established due to surface diffusion on a surface that is inhomogeneous in its work function. In migration equilibrium conditions, the concentration of adsorbate is redistributed on various surface areas depending on the local heat of evaporation of adatoms Λ from these areas [17]. After spraying the barium ($\theta = 0.1$ monolayer coating), the voltage of the appearance of the field electronic image decreased to 7 kV, which corresponds to the work function $\varphi = 3.9\,\mathrm{eV}$. A stationary emission of barium ions appeared from the region of faces of type $(10\bar{1}0)$ in the field desorption mode at an emitter voltage of 21 kV and a temperature of 700 K (Fig. 3, *a*).

The desorbing electric field strength at which desorption occurred decreased compared to room temperature and amounted to $F = 0.8 \cdot 10^8\,\mathrm{V/cm}$. This value is consistent with the calculated values in the region of small coatings given in Table 2, at the emitter temperature $T = 700\,\mathrm{K}$ for double-charged barium ions.

The calculated values of the electric field strength F are provided in brackets in table 2 without taking into account the polarization correction, which turn out to be underestimated in the area of small coatings ($\theta < 0.1$). Taking into account the polarization correction leads to a slight leveling of the intensity on the surface with different concentrations of adsorbate, which may affect an increase in the desorption area. The stationarity of the observed process confirms the establishment of migration equilibrium on the surface due to the diffusion of adsorbed barium atoms from the peripheral areas of the emitter surface to the top. At the same time, it turns out that the most favorable conditions for field desorption are realized mainly on the rhenium faces of type $(10\bar{1}0)$ (higher values of the work function φ and lower values of the heat of evaporation of adatom Λ). The conditions for field desorption from the entire surface of the emitter vertex are created when the concentration of barium adatoms decreases due to field desorption with a further increase of the emitter voltage (24 kV) and avalanche-like desorption (flash) from the emitter vertex is observed (Fig. 3, *b*). In this case, a fairly clear field desorption image of the emitter surface is formed. The dark areas in the field desorption image during the flash correspond to the flat low-index planes of the rhenium single crystal, which have a higher work function. The occurrence of dark areas during an avalanche-like flash indicates a higher rate of barium desorption from the flat low-index faces of the emitter compared to other areas, and barium desorption from these areas before the flash. An avalanche-like flash occurs from the emitter region, where the electric field strength exceeds the threshold value for desorption. Therefore, a field desorption contour remains after the flash (Fig. 3, *c*), where the electric field strength is of sufficient importance for desorption, at which the diffusion and desorption fluxes on the surface of the emitter are balanced. Barium adatoms move from the side surface of the emitter to the top in an inhomogeneous electric field and are desorbed on the contour. A similar behavior of field desorption was observed in the field desorption of alkali metals [18,19]. A second stationary state is formed, which is characterized by the absence of barium adatoms inside the contour. All barium entering the top of the emitter is desorbed at the boundary of the contour. With a slight change in the emitter voltage, it was possible to visually observe how the contour boundaries diverge from the center or converge to the center, practically following the voltage change and visualizing the diffusion process (migration of barium adatoms in an inhomogeneous electric field).

4. Conclusions

1. Using field desorption microscopy, it was found that the nature of the field desorption of barium adatoms from the rhenium surface depends on the rate of diffusion of the adsorbate on the surface.

2. At the temperature of the rhenium sample $T = 300\,\mathrm{K}$, the pulse character of desorption (ion emission) is realized from places where the electric field strength reaches the values necessary for desorption. At a sample temperature of 700 K, when migration equilibrium is established due to surface diffusion, at which the concentration of adatoms on different parts of the emitter surface depends on the local heat of evaporation, in addition to pulsed, stationary desorption can also occur.

3. The stationary mode is implemented from surface locations with greater work function, which, according to the model of image forces for field desorption, requires lower values of the intensity of the evaporating electric field.

4 If the intensity of the electric field is increased in the steady-state stationary mode, then at some intensity an avalanche-like (pulsed) desorption of barium occurs from the entire surface of the sample, where there is a sufficient electric field. The second stationary state occurs (in the form of a contour) after the avalanche-like flash, when the rate of entry of barium adatoms into the desorption zone becomes equal to the rate of field desorption.

5. It is shown that the polarizability of barium adatoms in the region of the submonolayer coating should be taken into account when estimating the electric field strength required for desorption.

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Conflict of interest

The authors declare that they have no conflict of interest.

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