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Formation of cluster caesium ions in an electric field on a nanostructured rhenium surface

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Using field desorption microscopy and time-of-flight mass analysis of ions formed during field desorption, it was shown that the adsorption of caesium atoms on the quasi-spherical nanostructured surface of a rhenium single crystal results in the formation of polyatomic cluster caesium ions (Cs^+ , Cs_2^+ , Cs_3^+ , Cs_4^+ , Cs_5^+). The intensity of the electric field required for the desorption of caesium ions corresponds to the calculated values obtained in the image forces model for the field desorption of alkali metals. Polyatomic caesium clusters are formed at a higher desorbing electric field strength than monatomic ones, despite the fact that they have a lower ionization potential. This indicates a greater value of the binding energy of these clusters to the surface. It was found that the mass distribution of clusters during field desorption depends on the magnitude of the electric field strength.

Keywords: cesium, rhenium, field desorption, clusters.

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1. Introduction

Interaction of atoms adsorbed on surface of solid body is of importance in many areas of science and technology, such as heterogeneous catalysis, crystal growth, nanotechnology, microelectronics. For major of adsorbates the formation of two-dimensional and three-dimensional associates (islands, clusters) on the surface was identified. But this does not relates to the alkali metals. Atoms of the alkali metals are either randomly scattered over the surface or form ordered two-dimensional lattices [1]. The multilayer structures are formed at low (cryogenic) temperatures only.

The clusters consisting of metal atoms are interested for scientific studies and have wide application in different nanotechnologies [2–4]. So, during last decade great attention is focused on study of processes of clusters formation [5].

Interaction of adsorbed atoms on surface affects the predominant structures of clusters as compared to clusters in vacuum. In present paper using time-of-flight mass-analysis and field desorption microscopy [6,7] the formation of ionic clusters of caesium on nanostructured surface of rhenium single-crystal in electric field is studied. It is known that formation of caesium ions during field desorption requires relatively low desorbing fields ($\sim 10^7$ V/cm). In model of image forces for field desorption this is explained by the low ionization potential of caesium atom and weak bond of adsorbed atoms with metal surface [7].

This paper relates to identification and study of clusters formation of alkali metals (Cs), which have lower potentials of ionization as compared to atoms [8]. The cluster ions in described experiments are formed during field desorption from nanostructured and inhomogeneous by work function

surface. Surface of single-crystal close in shape to semi-sphere, on which clusters are formed, comprises crystalline planes with size 1–100 nm and steps of monoatomic height.

2. Experimental procedure

A field electron and desorption microscope with a wide-angle atomic probe was used to conduct the study [9]. Increased image of surface of rhenium sample in form of spike, which tip has quasispherical single-crystal shape, is formed on the luminescent screen by surface projection with emitting electrons (field electronic image) or ions (field desorption image). To register weak currents from samples, an assembly of two microchannel plates with a diameter of 56 mm was located in front of the luminescent screen. The sample is manufactured from rhenium wire with diameter of 0.1 mm, its one end is welded to tungsten loop. Another end of the rhenium wire is loaded into solution for electrochemical etching. As a result of electrochemical etching of the rhenium the spike with tip radius about 500 nm is formed. Then, in a high vacuum (pressure $p \sim 5 \cdot 10^{-9}$ Torr), directly in the chamber of the field emission microscope the emitter is annealed at a temperature of $T = 2500$ K.

During annealing the sample was cleaned, and a single-crystal quasi-spherical surface of the spike tip with flat low-index faces of rhenium crystal was formed. Figure 1 shows the diagram of faces in standard projection for crystals with hexagonal close-packed lattice with central axis (1120) [10]. The formation of the single crystal tip of the rhenium emitter was accompanied by the appearance of field electron image, which is standard for crystals with hexagonal close-packed lattice [11].

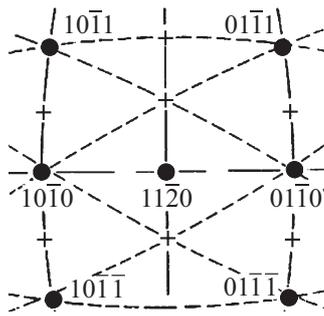


Figure 1. Standard projection for hexagonal crystals with central axis (1120) (central part).

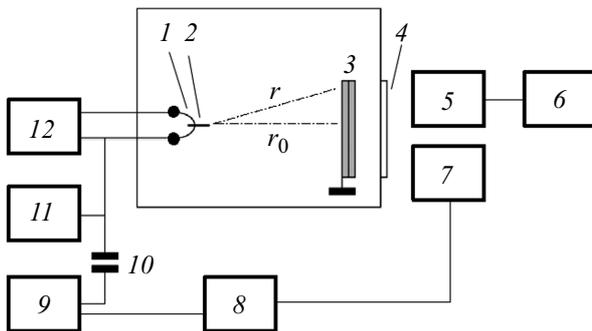


Figure 2. Diagram of the experimental set-up.

Diagram of experimental set-up is shown in Figure 2, where 1 — loop, to which the rhenium spike is welded, 2, 3 — assembly of two microchannel plates with diameter of 56 mm, 4 — luminescent screen, 5 — video camera, 6 — computer, 7 — photoamplifier with amplifier, 8 — storage oscillograph, 9 — adjustable generator of HV nanosecond pulses, 10 — buffer capacitor, 11 — adjustable HV DC source, 12 — sample heating unit.

The field electron image was registered in the field electron microscope mode, the field electron emission current was measured, and the current-voltage curve (CVC) was taken to plot Fowler–Nordheim graphs, the work function of the surface and the field parameters of the sample were determined. Mode of field desorption microscopy [12] ensured visualization of the field desorption process of adsorbed caesium atoms from surface, determination of the electric field strength, at which desorption was performed, monitoring of migration of adsorbed caesium atoms over surface. Comparison of field electronic images with field desorption images ensured determination of the desorption localization place on the sample surface in nanometer scale.

In mode of wide-angle atomic probe by time-of-flight measurement (t) of desorbed ions from surface of sample to the detector comprising two multichannel plates (MCPs) and luminescent screen, we can evaluate mass of desorbed ions. For this we used the formula

$$t = r_0(2q\Sigma U/m)^{-1/2}, \quad (1)$$

where r_0 — distance from sample surface to detector, q — ion charge, $\Sigma U = U_0 + U_p$ — difference of potentials

between sample and MCP, U_0 — permanent voltage, U_p — pulse voltage, m — ion mass [13]. Potentials difference between sample and detector was created using constant voltage (0–30 kV) from source 11 and pulse voltage from source 9 via buffer capacity 10. Parameters of voltage pulse can vary by amplitude (0–4 kV) and duration (2–20 ns).

For field desorption of adsorbed atom in form singly charged ion it is necessary to overcome energy barrier $Q(F)$, which in model of image forces will be determined by expression [7]:

$$Q(F) = \Lambda(\vartheta) + I - \varphi(\theta) - e^{3/2}F^{1/2} + \Delta E_p(\theta), \quad (2)$$

where Λ — heat of atom desorption, I — potential of atom ionization, φ — work function of the surface, e — electron charge, F — strength of the applied electric field, θ — degree of surface coverage by the adsorbate, ΔE_p — polarization correction $1/2(\alpha_a - \alpha_i)F^2$, where α_a — polarizability of adsorbed atom, α_i — polarizability of desorbed ion. For desorbed caesium atoms the polarizability α_a is low and does not exceed 3 \AA^3 [14], and for caesium ion α_i the same does not exceed 3 \AA^3 [15]. So, polarization correction ΔE_p in expression for $Q(F)$ can be omitted. Time τ required for field desorption during thermal activation is determined by Arrhenius equation

$$\tau = 1/\nu_0 \exp(Q/kT), \quad (3)$$

where ν_0 — vibration frequency, k — Boltzmann constant, T — temperature. It is possible to write an expression from the ratios (2) and (3) to estimate the magnitude of the electric field strength F required for desorption of selected adsorbate

$$e^{3/2}F^{1/2} = \Lambda + I - \varphi - kT \ln(\tau \nu_0). \quad (4)$$

Temperature correction $\Delta E = kT \ln(\tau \nu_0)$ at room temperature $T = 300 \text{ K}$ is in range 0.78–0.5 eV [16]. At sample temperature $T = 300 \text{ K}$ rather intensive surface diffusion of adsorbed caesium atoms occurs, and migration equilibrium of caesium atoms on nanostructured and inhomogeneous by work function surface is set. Under conditions of migration equilibrium the concentration distribution of adsorbate in surface areas of sample corresponds to evaporation heat of adsorbed atoms Λ (the higher Λ is the larger surface concentration of adsorbate is) [17]. The mode of migration equilibrium of adsorbate on sample surface is characterized in that during adsorbed atoms desorption from the surface, as a result of adsorbed atoms diffusion in inhomogeneous electric field the adsorbate concentration restores on top of sample due to ingress of adsorbed atoms from side surface. At that value of desorbing field F , depending on degree of coverage, do not change, and the process of field desorption can go rather long.

To obtain mass-spectrum of caesium ions desorbing in the electric field the constant voltage and pulse voltage are applied to sample. The voltage pulse from generator 9 (Figure 2) enters the sample resulting in adsorbate

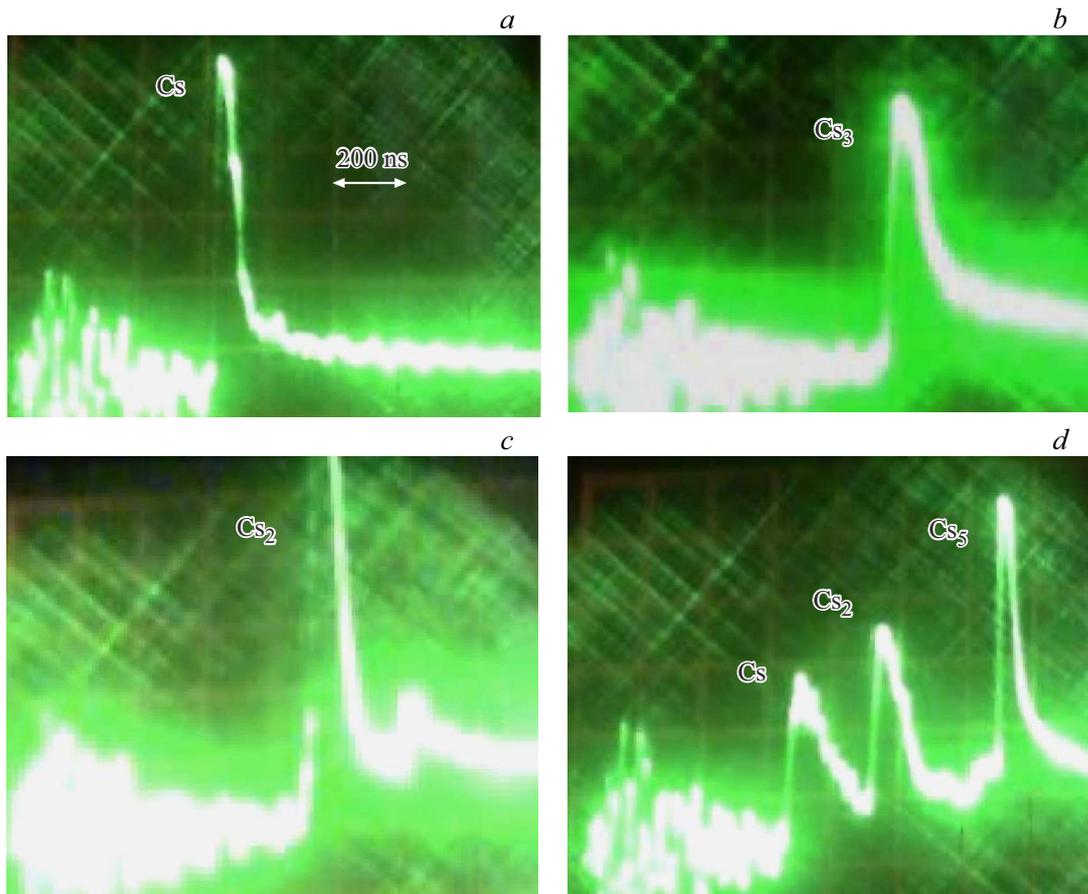


Figure 3. Mass-spectra of polyatomic caesium ions. The spectra can contain monoatomic ions (a), single clusters (b) or several clusters (c–d).

desorption and simultaneously starts sweep of storage oscillograph 8. After time period t caesium ions enter the detector, where voltage pulse is generated and enters the storage oscillograph. Measuring time-of-flight of ions t on calibrated sweep of the oscillograph we can evaluate the mass of ions. Due to the fact that in wide-angle atomic probe the ions move along radii from the quasi-spherical surface of the sample, and the detector is flat surface of MCP, the distances from the sample to the MCP for ions desorbed from different parts of the surface will be different (r_0 and r in Figure 2). This will introduce uncertainty in identifications of polyatomic clusters. If necessary, this uncertainty can be decreased limiting region of registration using diaphragms.

3. Results and discussion

To determine the electric field strength F on surface of rhenium sample we calculate the factor of electric field (β) based on the experimentally obtained Fowler-Nordheim characteristics [18]. β value for the field emitter used in the experiments turned out to be equal to $\beta = 3600 \text{ cm}^{-1}$. The electric field strength F was determined by formula $F = \beta U$, where U — voltage on sample. The voltage on

the sample can be increased to 30 kV, which corresponded to the maximum value of the electric field strength F on surface of sample $\sim 1.1 \cdot 10^8 \text{ V/cm}$. To evaluate degree of coverage (θ) of sample surface by caesium we take dependence of work function (φ) on time of caesium sputtering. This dependence, characteristic of alkaline and alkaline earth metals, passes through the minimum in the region of the optimal coverage. The work function of the sample surface during sputtering of caesium atoms was determined by formula

$$\varphi = \varphi_0(U/U_0)^{2/3}, \quad (5)$$

where φ_0 — work function of surface of pure rhenium sample ($\varphi_0 = 5 \text{ eV}$), U_0 — voltage on pure sample, U — voltage on sample during caesium atoms adsorption, measured at same current of field electronic emission from emitter [19].

According to expression (4), the value of desorbing field has minimum value at large work function of sample surface this corresponds to minimum values of surface coverage by caesium (degree of coverage $\theta \sim 0.1$). For theoretical evaluation of the electric field strength required for desorption at selected coating θ , we assume work function of sample surface $\varphi = 4.3$, $\Lambda = 3 \text{ eV}$ [20]. Substituting values φ , Λ temperature correction $\Delta E_T = 0.78 - 0.5 \text{ eV}$,

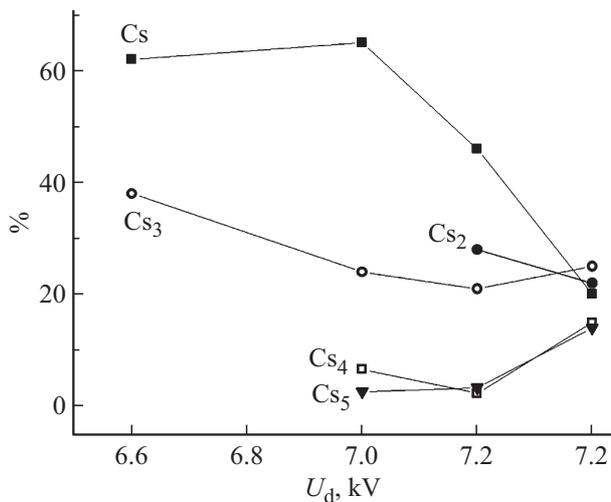


Figure 4. Percentage content of clusters in spectra vs. voltage of sample.

ionization potential of caesium atom $I = 3.89$ eV into expression (4) we obtain interval of desorbing field strength $F = 2.4 - 3 \cdot 10^7$ V/cm. Considering the obtained electric field factor β the voltage on sample shall be $6.7 - 8 \cdot 10^3$ V. In experiment the characteristic mass-spectra of polyatomic caesium ions shown in Figure 3 were obtained in range of voltages $\Sigma U = U_0 + U_p$ from 6.6 to 7.4 kV, which is in good coincidence with theoretically predicted values.

Processing of arrays of spectra obtained at different voltages is shown in Figure 4. On horizontal axis total voltage $\Sigma U = U_0 + U_p$ applied to sample is shown, and vertical axis shows change in number of different clusters of caesium ions from Cs^+ to Cs_5^+ in percents of total number of registered ions at given voltage.

From shown graph the following moments can be specified. First of all, when voltage increases only monoatomic (ionization potential 3.89 eV) and triatomic caesium ions (ionization potential 3.2 eV [8]) appear. Apparently, this is a manifestation of the dependence (4) of the desorbing field strength on the ionization potential, desorption heat and surface work function. Then, upon voltage increasing to 7 kV, in spectrum ions Cs_4^+ and Cs_5^+ are added. When voltage increases to 7.2 kV in mass-spectrum ions of cluster Cs_2 appear, in it the ionization potential is a little lower (3.8 eV) than in monoatomic caesium, but higher than in Cs_4 and Cs_5 . At voltage on sample 7.4 kV converging of dependences for ions of monoatomic and polyatomic clusters is observed. From dependence (4) it follows that formation of ions will be affected also by value of evaporation heat Λ of adsorbed particles, and by presence of polyatomic steps on nanostructured surface, and by diffusion of adsorbed atoms in inhomogeneous electric field.

Under experiment conditions the vapor pressure of caesium is much lower 10^{-9} Torr. So, ingress of atoms or clusters of caesium from vacuum into desorption area on surface during desorbing pulse 10 ns is practically impossible. All processes of cluster ions formation occur on surface

of rhenium sample. In paper [21] theoretically by method of molecular dynamics the formation and distribution by sizes of polyatomic clusters of caesium under conditions of critical state of substance were studied. In this paper the percent ratio for Cs and Cs_3 in gas phase was 65% and 7.5%, respectively, which differs from the obtained in this paper during clusters formation in surface in ratio 62% Cs and 38% Cs_3 .

Feature of caesium adsorption on metal surface is that adsorbed atoms are in ionized state, and electrostatic repulsion occurs between them [22]. Formation of any associates of caesium atoms was not detected. It is possible that the formation of clusters is affected by the presence of crystalline steps and the external electric field. The latter is in conflict with the fact that the field of the applied polarity increases the electric charge of adsorbed atoms, and, consequently, their repulsion. Probably, there is a significant influence of the surface nanostructure — the presence of steps.

4. Conclusion

1. Using the time-of-flight mass-analysis and field desorption microscopy it is shown that on nanostructured surface of single-crystal rhenium during caesium atoms adsorption the polyatomic cluster ions of caesium are formed under conditions of migration equilibrium of the adsorbate.

2. In mode of the wide-angle atomic probe the polyatomic clusters of caesium ions (Cs^+ , Cs_2^+ , Cs_3^+ , Cs_4^+ , Cs_5^+) are identified.

3. Effect of ionization potential of adsorbed particle on processes of formation of polyatomic cluster caesium ions is shown.

4. We determine the electric field strength on sample effect on percentage content of polyatomic clusters of caesium and converging of clusters content if strength increases.

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Conflict of interest

The authors declare that they have no conflict of interest.

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