High Temperature Field Evaporation of the Metals and its Correlation with Surface Ionization

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Abstract: High temperature field evaporation of Ir and Pt was investigated at the $T = 1400 - 1700$ K and electric fields $F \sim 1$ V/Å by field electron, ion and evaporation microscopy. The Arrhenius plot was obtained for the process of field evaporation of Pt in these conditions. This plot gives the activation energy of the evaporation $Q_n = 3.05 \pm 0.1$ eV and preexponential factor $\nu_0 = 3 \times 10^{15}$ 1/s. The value of the heat of evaporation at the presence of high electric field λ_F for the Pt-ions was obtained by means of image forces model and value of Q_n . The value of $\lambda_F = 3.15$ eV is less in comparison with sublimation energy of Pt - $\lambda_0 = 5.85$ eV. The reasons of the difference between λ_F and λ_0 and the mechanism of the evaporation process at these conditions are discussed.

1. THE INTRODUCTION

As high temperature field evaporation it is possible to name process of evaporation of ions from surface of field emitters at temperatures T appreciably above room (usually $T = 800-1800$ K for refractory metals) and fields $F \sim 1$ V/Å ($F = 0.8 - 1.8$ V/Å for same objects). This phenomenon is not practically investigated, though natural and it is rather interesting. The high temperature field evaporation lays in intermediate area between classical low temperature field evaporation (at cryogenic $T \leq 77$ K) and surface ionization in the presence of high electrical field. The surface ionization in high electric field is usually observed at $T \sim 1000$ K and $F = 10^{-4} - 10^{-2}$ V/Å. Thus the ion is evaporated over Schottky barrier, were on distance $x_c = (3,6 \text{ nF})^{1/2}$ from conditional surface of metal [1], n - the charge of an ion, and x_c is received in Å if F is expressed in V/Å. Easily to see, that in this case the Schottky barrier is located on distances $x_c = 10 - 100$ Å from surface. At low temperature field evaporation $F = 3-6$ V/Å and $x_c = 0.85$ Å in field $F = 5$ V/Å for single charged ion or $x_c = 1.2$ Å for double charged ion. These values are less than radii of the majority of atoms, in that case the concept of a Schottky barrier loses sense and is considered, that the evaporation occurs, when an external field removes a barrier practically up to zero. Both these processes give ions different charge, for example at field evaporation of W ions W^{+3} , W^{+4} , W^{+2} and never - ions W^{+1} [1] are received, whereas the surface ionization gives basically ion W^{+1} . The high temperature field evaporation at $F \sim 1$ V/Å and $x_c = 1.5 - 2$ Å describes that area, where the surface ionization in high electric field passes in field evaporation with change of a charge of evaporated ion therefore the experiments in this area are rather interesting. Besides the high temperature field evaporation can serve the rather effective tool in nanotechnology, as permits to create point sources of ions of various metals, continuously functioning during enough long-duration time. The sizes of emitting centers are usually $10 - 50$ Å or less, even emitting ions centers are possible, having on top from one up to several atoms. Thus the special interest is presented by the elements, not oxidized on air and "diffusion proof", when a circuit drawing on surface does not destroy owing to surface diffusion. The elements the most suitable with these points of view are Ir and Pt [2,3].

2. EXPERIMENTAL

The experiments were conducted on installation, which gives the possibility to combine modes field electron, ion and desorption (is more correct evaporation) microscopes. The installation contained single crystal tip - an object of research, which could be heated up to melting point or to be cooled up to $T = 77$ K, the amplifier of the brightness of the image from two microchannel plates and the screen on which is possible to observe the image of a tip surface by means of the electrons with resolution $20 - 50 \text{ \AA}$, ions of imaging gas He, Ne or H_2 with resolution $3 - 4 \text{ \AA}$ or evaporating own ions of a tip material. Vacuum conditions in device $\sim 10^{-9} - 10^{-10}$ torr, the current and voltage were measured with help of digital devices. The dynamically varying image of a surface at high T and F was registered by means of the videorecorder. Temperature of a sample was supported by high stability power supplies and was measured with accuracy $\sim 10 - 15^0$

3. RESULTS AND DISCUSSION

In our work [4] high temperature field evaporation Ir was investigated at $T = 1100 - 1600$ K and $F \sim 1 \text{ V/\AA}$. Thus measurement of an ion current $i = 3 \times 10^{-10} \text{ A}$ was made at $T = 1435$ K., that corresponds to rate of evaporation $v \sim 10^9$ ion/s. Taking into account, that we on surface have of the order 10^2 microprotrusions, evaporating of the ions the rate of evaporation from each microprotrusion with one or several atoms on top $v \sim 10^7$ ion/s. According to Arrenius law the value of the evaporation rate $v = v_0 \exp(-Q_n/kT)$, having assumed, that $v_0 = 10^{13} \text{ 1/s}$ we shall receive using the $T = 1435$ K and $F = 1 \text{ V/\AA}$ the value of the activation energy of the process $Q_n = 1,98 \text{ eV}$. The value of Q_n , according to image forces model is determined by expression [1]

$$Q_n = \lambda_0 + \sum I_n - n\phi - (n^3 e^3 F)^{1/2} + 1/2 \alpha F^2 \quad (1)$$

Where λ_0 - the heat of evaporation of an element, $\sum I_n$ - total potential of ionization of n -divisible charged ion, ϕ - work function of a surface, α - polarizability of surface atom. Having substituted known values λ_0 , I_n and ϕ for Ir [5] and having assumed, that in such weak fields basically single charged ions are evaporated, assuming $\alpha = 9.2 \text{ \AA}^3$ measured for atom W on the planes $\{110\}$ W [6] we shall receive $Q_n = 7.09 \text{ eV}$. About such distinction between calculated and experimentally appreciated the values Q_n have found out the authors of work [2] for high temperature field evaporation W, according to their valuations $Q_n = 2.4 - 2.7 \text{ eV}$ at the calculated value $Q_n = 8.0 \text{ eV}$.

For establishment of the reasons of similar distinction in Q_n it was necessary to determine experimentally this value, having obtained Arrenius plot in some interval T of evaporation, which has given real value Q_n and preexponential factor v_0 instead of used "theoretical" value $v_0 = kT/h \sim 10^{13} \text{ 1/s}$. However the plot of Arrenius has certain physical sense only in that case, when the temperature and the rate of the given process vary only. Thus the character and the conditions of the process must be invariable. For our case of high-temperature field evaporation at change T should not vary evaporating field F and condition of a surface. However, if to apply to metal tip a field $F \sim 1/\text{\AA}$ and $T \sim 1000$ K owing to processes of a surface diffusion and field crystal growth the complicated variation of the form of a tip surface takes place. It leads to the variation of F at constant voltage U between by tip and anode. The value $F = U/kr$, where r - the radius of the tip, k - the coefficient determined by the form of the tip. In process of thermo-field action both values, as r , and k vary. On surface of the tip $r \sim 1 \mu$ can form microprotrusions, having $r = 10 - 100 \text{ \AA}$, and the values of k can vary from $k = 2.8$ for smoothed by the heat tip [7] up to $k = 26$ for the tip with microprotrusions on top [8]. Thus, at constant U and various T the value F can essentially vary, as increasing, and being decreased. For correct determination of the Arrenius plot it was necessary to find such stage of the

form change of the tip, when at fixed U and varying T would not vary F . We had investigated high temperature field evaporation of Pt. Thus was shown, that in the beginning at low T and F a stage of usual build up in electric field [9], consisting in expansion of the close packed planes $\{100\}$ and $\{111\}$ is observed, in this case ions are emitted only by corners $\langle 012 \rangle$ reconstructed tip or microprotrusions, growing on these corners. Then, at higher T and F there comes a stage of formation of the large macrooutgrowths first of all on the planes $\{100\}$ and $\{111\}$. The macrooutgrowths are covered by microprotrusions, which emit of the ions. Thus the macrooutgrowths as whole periodically are evaporated and growth again, this phenomena is observed on the emission picture as "effect of collapsing rings" [4]. We have made measurements of the values of an evaporating fields F at various T for Pt-tip. Thus was shown, that at the stage of, where growth and evaporation of the macrooutgrowths is observed the value of F does not practically vary, as the form of a surface does not vary. The values of F were determined by means of Fowler-Nordheim plots after cooling of the tip up to room T . We assumed that the form of the microprotrusions does not vary at cooling. It is complicated question what value of work function ϕ may be used for microprotrusion with one or some atoms on the top because the emission is coming only or mainly from a small area corresponding to the top of the microprotrusions. There are not experimental data of absolute values of ϕ for the microprotrusions. The average ϕ for annealed tip was used to determine F . The microprotrusions grow mainly on the rough planes and the values of ϕ of these planes are similar to average values of ϕ . On Fig. 1 the plot of dependence F from T is shown at constant U for stage of growth and evaporation of macrooutgrowths on the surface of Pt-tip. It is visible, that in this case the value of $F = 1.1 \pm 0.14$ V/Å for Pt in interval $T = 1400 - 1700$ K. Consequently, condition of a surface at the stage of growth and evaporation of the macrooutgrowths permits correctly to obtain the Arrhenius plot in that interval T , in which this stage of form change is observed, as a condition of a surface and the value of F do not practically vary. On Fig. 2 the similar Arrhenius plot for Pt-tip is shown at $F = 1.1$ V/Å and $T = 1400-1700$ K. The values of activation energy $Q_n = 3.05 \pm 0.1$ eV and preexponential factor $\nu_0 = 3 \times 10^{15}$ 1/s were obtained by this plot.

Fig 1

The dependence of evaporating field F on the temperature of Pt-tip at the constant voltage $U=14$ kV for the stage of the growth and evaporation of the macrooutgrowths.

Fig 2

The Arrhenius plot for high temperature field evaporation of Pt for the stage of the growth and evaporation of the macrooutgrowths.

According to (1), the value Q_n should be equaled 5.75 eV at known for Pt value $\lambda_0 = 5.85$ eV, $I_1 = 9.0$ eV and $\phi = 5.3$ eV in field $F = 1.1$ V/Å in assumption, that only single charged ions are evaporated. Received experimentally the value $Q_n = 3.05$ eV is much less. It is represented to us, that the most probable reason of a similar divergence is dependence of heat of evaporation on field, therefore $\lambda_F = Q_n - I_1 + \phi + (e^3 F)^{1/2} - 1/2\alpha F^2 = 3.15$ eV. Thus, field $F = 1.1$ V/Å decreases the value of evaporation heat from value of heat of evaporation in absence of a field $\lambda_0 = 5.85$ eV up to $\lambda_F = 3.15$ eV. The value of potential of ionization I_n should it is hardly probable depend on field, as is property of atom. As to work function of a surface ϕ in work [11] dependence ϕ from F is supposed, as a field of positive polarity, penetrating deep into of the emitter causes reduction of electron density near to surface, that results in increase ϕ . According to [12], $\phi_F = \phi_0 + neF\chi$, where χ -depth of penetration of F . However, having assumed validity of a similar assumption, the value $\delta\phi = neF\chi \approx 0.5$ eV at typical for the metals value $\chi \approx 0.5$ Å thus, assumption of dependence ϕ on F cannot explain distinctions in calculated and experimental values of Q_n . Follows to note, that in same work [11] it is supposed also dependence λ on F and even approximate expression of this dependence $\lambda_F = \lambda_0 - bF$ is given, where b - some constant value. This possible dependence is explained by that an external electric field moves off the electrons from surface atoms deep into of metal, from each atom is moved off ~ 0.5 electron in field some V/Å. It results in reduction of binding energy of atom with surface, however experimental corroboration of a similar hypothesis was not made. It would be interesting to determine the dependence λ from F at various F , however the change of value F can result in change of a stage of a form change of a surface, and in this case can not be observed invariability of conditions on surface, necessary for correct determination of the Arrenius plot.

As is known, the heat of evaporation of atom corresponds to evaporation it from kink position. The process of evaporation of atom consists from migration transition it from kink position to adsorbed position, from which atom is evaporated. Hence, the heat of evaporation consists of energy of transition to adsorbed position and energy of evaporation from this position, i.e. $\lambda = Q_M + Q_{EV}$. On which of these values can influence a field? According to model of pair interaction, atom in kink position has in f.c.c.- lattice of Pt 6 neighbours of the first order and 3 neighbours of the second order, and in adsorbed position on the plane (100) Pt (we shall conduct consideration only for this central plane of Pt-tip) - 4 neighbours first and 1 neighbour of the second order. Thus, transition of atom from kink position to adsorbed position corresponds to break of the bonds with two neighbours first and two - second order, i.e. $Q_M \approx 1/3\lambda$ and $Q_{EV} \approx 2/3\lambda$. External electric field decreases energy of migration Q_M on the value, named " the field addition " [12]

$$Q_M(F) = Q_M - 1/2\alpha (K_t^2 - K_b^2) F^2 \quad (2)$$

The similar approach is based on assumption of Drechsler [12] that a field changes a potential barrier for migrating atom on "top" and in "bottom" differently, for the top $K_t > 1$ and for the bottom $K_b < 1$, however the valuation under formula (2) as a rule will be poorly agreed experimental data. There is the experimental work on determination $Q_M(F)$ and Q_M for the process of build up of Pt-tips in electric field: $Q_M = 1.28 \pm 0.13$ eV and $Q_M(F) = 1.14 \pm 0.11$ eV, i.e. $\delta Q_M = 0.14$ eV in the fields $F = 0.3 - 0.5$ V/Å [13]. As Q_M depends on F^2 , in field $F = 1.1$ V/Å the value of δQ_M should lay in interval 0.8 - 1.2 eV. Thus, it is possible to evaluate, that the total decrease of λ on the value 2.7 eV will consist of the decrease of Q_M on ~ 1 eV and Q_{EV} on ~ 1.7 eV.

Can exist other reason of distinction between λ_0 and experimentally determined λ_F , on which paid attention and in work [2]. We determined value F from Fowler-Nordheim theory, which means a uniform electric field at surface. However in work [14] was specified, that the electron leaving the surface of the tip, "sees" a surface as a flat, since radii of curvature $r \geq 500$ Å. At smaller r the case of a uniform field already will not be realized, but typical values of r for the microprotrusions, with which ions are evaporated, are equal some tens Å. Applying the Fowler-Nordheim theory for the

microprotrusions, we replace the real emitter with non-uniform field by the equivalent emitter with uniform field [18]. Thus, the values of a current density J and F for equivalent emitter always are less than those for real. In [17] it is shown, that J of the real emitter at $r = 100 \text{ \AA}$ exceeds J equivalent emitter in 10 - 20 times. But it means, that taking into account exponential dependence of value J from F , real F will be more F , determined on Fowler-Nordheim method on 10 - 15 % at $\phi = 5.3 \text{ eV}$ for Pt. Thus, our real field will be $F = 1.21 - 1.27 \text{ V/\AA}$ and we shall receive $\lambda_F = 3.34 - 3.43 \text{ eV}$, i.e. it is less than λ_0 on 2.51 - 2.42 eV. Exists and other method of determination F on the basis of fixing of a best image field (BIF), at which the atomic structure of a surface is observed in imaging gas with best sharpness. The values of F_{BIF} are known for all imaging gases, used in field ion microscopy. We observed the images of microprotrusions of Ir in Ne and on basis $F_{\text{BIV}} = 3.5 \text{ V/\AA}$ for Ne it was possible to make a conclusion, that, determined in such a way F exceeds F , determined by Fowler-Nordheim method in ~ 1.6 times. The authors of work [2], observing microprotrusions W in He, have shown, that similar excess makes ~ 1.7 time. It is necessary thus to note, that accuracy of fixation of a condition of the best image for microprotrusion with one atom on top is not high. For example, observing microprotrusion of WSi_2 on the plane $\{110\}$ W in Ne it was possible to make a conclusion, that F , determined on field of the best image was less F , determined on Fowler-Nordheim method on 10 %. However even if to assume, that indicated by us $F = 1.1 \text{ V/\AA}$ actually in 1.6 times more then we shall receive $\lambda_F = 3.9 \text{ eV}$, smaller than λ_0 on 1.95 eV.

All consideration by us is conducted in assumption, that only single charged ions are evaporated. Generally speaking, the charge of the evaporated ions at high $T \geq 1000 \text{ K}$ and fields $F \sim 1 \text{ V/\AA}$ - the question practically unstudied, exists extremely few works in this area. The charge of the evaporated ions is determined by a ratio their energies of evaporation Q_n . In itself temperature does not influence on Q_n , if to neglect temperature dependence of ϕ , the increase T causes only decrease F , necessary to have the same rate of evaporation, and the value F influences on a charge of an ion. In absence of an external electric field (case of surface ionization without field) only single charged ions are evaporated practically, as $Q_1 = \lambda + I_1 - \phi$, and for double charged ions $Q_2 = \lambda + I_1 + I_2 - 2\phi$. The value Q_1 always is less Q_2 as second potential of ionization $I_2 \geq 10 \text{ eV}$ for all elements, and the value ϕ always is less 10 eV. Increase T at the presence of electric field results in change of a ratio between Q_n for ions different charges. At low temperature field evaporation very high fields are used, to reduce Q_n practically up to zero (in fields $F = 4 - 5 \text{ V/\AA}$ the value $Q_n = 0.1 - 0.2 \text{ eV}$). For evaporation of Pt at $F = 4.8 \text{ V/\AA}$ and $T = 78 \text{ K}$ ions Pt^{+2} , Pt^{+3} and Pt^{+1} by way of decrease of intensity are observed. However already decrease F from $3 \text{ V/\AA}$ up to $1.6 \text{ V/\AA}$ results in decrease of a part of ions Pt^{+2} on 4 - 5 orders, and the ions Pt^{+3} at such F are in general not practically observed [5]. In case of fields $F \sim 1 \text{ V/\AA}$ can be observed double charged ions only of Ba, Ca, and rare-earth elements. Exists and experimental work on study of high-temperature field evaporation Pt in the field $F = 1.2 \text{ V/\AA}$ and in interval $T = 800-1500 \text{ K}$ by magnetic mass-spectrometer [16]. In given work was shown, that, for example, at $T=1320 \text{ K}$ on 8000 registered ions Pt^{+1} it was obtained only on the average 2,2 ions Pt^{+2} and 6,5 ions Pt^{+3} , hence the part of multi-charged ions was very small.

Thus, the mechanism of high temperature field evaporation consists of evaporation of atoms in kind mainly single charged ions from tops of microprotrusions or corners of reconstructed tip through potential barrier, lowered not only by Schottky effect, but also by decrease of heat of evaporation λ . The decrease of λ occurs as owing to decrease of energy of migration transition from kink position to adsorbed position, and owing to decrease of binding energy of adsorbed atom on the surface.

In conclusion it is necessary to say how to describe the process of evaporation of ions at $F \sim 1 \text{ V/\AA}$ and $T=1400-1700 \text{ K}$. Taking into account, that at field evaporation at $T \leq 77 \text{ K}$ and $F=3-5 \text{ V/\AA}$ the values of Q_n are only 0.1 - 0.2 eV, Schottky barrier position $x_c = 0.8 - 1.0 \text{ \AA}$ and will be formed basically multi charged ions, and in our case $Q_n = 3.05 \text{ eV}$, $x_c = 1.8 \text{ \AA}$ and practically only single

charged ions are formed or rather the given process to name as not high temperature field evaporation, and surface ionization in high electrical field. And, as in our case for single charged ions of Pt the value $I_1 < \varphi + (e^3 F)^{1/2}$ ($I_1 = 9.0$ eV, $\varphi = 5.3$ eV and $(e^3 F)^{1/2} = 3.78$ eV at $F = 1.1$ V/Å) we have case of easy ionization. The difference from case of surface ionization of the easy ionized elements (besides the complicated changes of F at the change of T and U) consists that there is not the incident flow of the atoms on a surface, the flow is formed by evaporation of the tip atoms. It results to exponential dependence of ion current from T and λ .

It is necessary yet to note, that the authors of work [17], who studied low temperature field evaporation of Rh at $T = 103$ K and $F = 4.1$ V/Å by the method of appearance potentials of ions have found out, that the value λ_F has appeared more than value λ_0 on 0.5 - 0.7 eV for the planes $\{111\}$ and on ~ 1.2 eV for the planes $\{001\}$. About such the excess λ_F above λ_0 is found out early and in work [18]. The authors [17] explain similar increase λ_F by the fact that the atom in kink position passes before evaporation not to adsorbed position, and on the contrary - to the position inside of the close-packed row of the step, where the binding energy is higher. From this position the atom are evaporated, and it results in the increase of λ . However in work [19,20] by means of laser time of flight atom probe the values of λ_F for Pt, Rh, Fe, Ni, Co and W were measured at $T = 150$ K and fields $F = 3.5 - 5.7$ V/Å. Thus was shown, that for all elements the values of $\lambda_F = \lambda_0$ within the interval of ± 0.2 eV, that corresponded to accuracy of measurements. However, if conclusions of the authors [17] are correct and the values of λ_F in case of evaporation at low T and high F increase, this one more attribute of distinction between low temperature and high temperature field evaporation.

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