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Stable forms and stationary emission of the ions of tantalum field emitter during exposure to an external electric field at high temperatures

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Using the methods of field electron microscopy, the change in the form of the field emitter from Ta was studied when exposed to high temperatures T and strong electric fields F. The aim of the study was to obtain a stable form of the emitter surface that would give a stationary ion current during field evaporation. Such a stable form was found at a certain combination of T and F, it could provide a stable constant ion current, but of relatively small magnitude.

Keywords: tantalum, field evaporation, field emission, ions.

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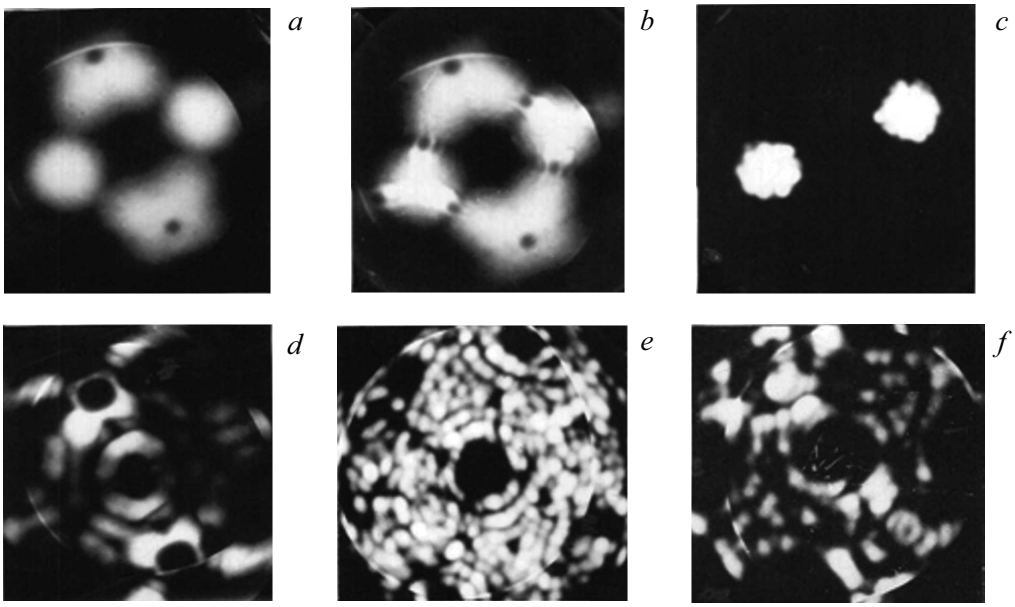
Field emitters of both electrons and ions are now used widely in various branches of science and technology [1]. Chemically inert emitters (e.g., Re, Ir, Ta) unaffected by residual gases are of special interest [2–4]. The effect of field evaporation of Ta and the process of production of various ions have been examined in our earlier study [4]. It has been demonstrated that Ta^{3+} ions are produced at room temperature. The ion charge was reduced to Ta^{2+} at higher T values, and a small amount of singly charged Ta^{+} ions was observed at the highest temperatures. While ion current i decreased rapidly at low (below room) temperatures in a constant applied field due to fast dulling of the emitter, the evaporation of ions at high T was continuous due to the constant diffusion influx of atoms to the apex of the pointed emitter. However, ion current i consisted of separate bursts of various amplitude, which followed each other with certain intervals ranging in length from several seconds to several tens of seconds. This nature of i was attributed to the formation of macro-outgrowths (tens of nanometers in size) on the emitter surface due to field crystal growth under simultaneous exposure to high temperatures strong electric fields (F). Pointed nanoprotrusions with curvature radius $r \sim 1-2$ nm form on the edges and cusps of these outgrowths, and the apices of nanoprotrusions, where local electric field F is maximized, act as sites of evaporation of atoms in the form of ions. However, if the equilibrium between the influx of atoms to the apex of a protrusion and their evaporation in the form of ions from the apex is disturbed, macro-outgrowths periodically evaporate and grow again [4]. This is the reason why ion current i features, while remaining continuous, bursts of varying „duty ratio“ and amplitude.

In the present study, we attempt to obtain a Ta emitter that would produce constant (or, at the very least, stationary) ion current i rather than a pulsed one. In order to achieve this, one needs to find a stationary time-independent state of the emitting surface; in other words, one needs to examine thoroughly the variation of form of a Ta emitter subjected to high T and F and identify the regions of F and T in which the sought-for stable forms occur.

The key experiments were performed using a setup combining all modes of field emission microscopy (electron, ion, and desorption modes). Single-crystal tantalum tips with curvature radius r of a fraction of a micrometer were prepared using common methods of DC electrolytic etching of small-diameter Ta wires in a mixture of sulfuric, acetic, hydrofluoric, and orthophosphoric acids. The temperature was measured by common optical pyrometry, and the magnitudes of external electric fields F were determined using the classical Fowler–Nordheim method [5].

Several electron microscopy images of the Ta surface are shown in the figure. These images represent the key stages of variation of form for an emitter under simultaneous exposure to various temperatures T and processing electric fields F. The well-known image of the initial form of Ta annealing, which is obtained after long-term exposure of the tip to $T = 2700$ K under high vacuum, is presented in panel *a*. This form is characterized by an anomalously large central region of face $\{110\}$ and the lack of faces $\{112\}$. The first visible change in faceting occurs at $F = 4.5$ V/nm and relatively mild temperatures ($T = 1130$ K). This change consists in the formation of faces $\{112\}$, which are seen most clearly in panel *b* in field $F = 5.5$ V/nm, on the surface. Raising F to 6.8 V/nm at the same temperature, one may observe the formation of a considerable number of nanoscale protrusions localized exclusively at faces $\{111\}$. These protrusions are sharp, and emitter field factor $\beta = 1/kr$ (r is the emitter curvature radius and k is a coefficient that depends on the tip shape) increases approximately two-fold from $\beta = 4421\ \mathrm{cm}^{-1}$ for the initial emitter to $\beta = 8273\ \mathrm{cm}^{-1}$. Therefore, only these protrusions are emitting and visible in the emission pattern (panel *c*).



Field electron images of the Ta emitter surface subjected to various T and F. *a* — Initial Ta emitter surface, *b* — processing at $T = 1130$ K and $F = 5.5$ V/nm, *c* — at $T = 1130$ K and $F = 6.8$ V/nm, *d* — at $T = 1500$ K and $F = 4.4$ V/nm with subsequent exposure to $T = 1000$ K for 15 s, *e* — at $T = 1700$ K and $F = 6.3$ V/nm, *f* — after exposing the surface from panel *e* to $T = 1000$ K for 15 s.

An increase in temperature is always associated with a reduction in F. At higher $T = 1320$ K and $F = 3.4$ V/nm, the tip undergoes a complete restructuring: it becomes faceted with only the most close-packed faces $\{110\}$ and $\{100\}$, and the emitter is „sharpened“ considerably. Since the field factor increases in this case to $\beta = 15\,870\,\mathrm{cm}^{-1}$, these angles are stationary, and the influx of atoms to the apex is offset by their field evaporation from the surface. This is confirmed by the fact that the field factor increases further to $\beta = 17\,340\,\mathrm{cm}^{-1}$ (due to a reduction in the flux of evaporating atoms) following a slight weakening of the field to $F = 3.1$ V/nm. Such angles may be used as efficient sources of electrons at room temperature, but the ion current is negligible and is hard to measure. When the field and the temperature reach $F = 4.4$ V/nm and $T = 1500$ K, a great number of nanoprotrusions emerge. Following their thermal smoothing, one may observe macro-outgrowths on all faces $\{110\}$ and $\{100\}$ (panel *d*); notably, outgrowths on faces $\{100\}$ are more thermally stable than the ones on faces $\{110\}$. The nature of the process remains unchanged at a higher processing temperature; the only difference is that the value of F decreases. At lower T and F, individual „large“ macro-outgrowths form, while the super-saturation of two-dimensional gas on the surface at higher $T = 1700$ K and $F = 6.3$ V/nm becomes more pronounced, and nanoprotrusions may be observed throughout the entire emitter surface (panel *e*). Following the thermal smoothing of nanoprotrusions in the course of short-term exposure to $T \sim 1000$ K, small outgrowths emerge on close-packed Ta faces (panel *f*). The pronounced reduction in F at higher T is attributable to the fact that an increase in T induces exponential growth of the field evaporation rate and a rapid growth of the emitter radius. Thus, the value of F needs to be reduced at higher T so as not to „ruin“ a pointed emitter completely. As was already noted, nanoscale protrusions may act as point sources of electrons with solid emission angles of several tenths of a steradian. The field needed to achieve a certain current in this case is several times lower than the field corresponding to the initial emitter and the same current [6]. In our view, a more intriguing possibility is that nanoprotrusions may serve as sources of ions of various charge states (doubly and triply charged at relatively low T and singly charged at the highest $T \sim 2000$ K). The mass of all ions will remain the same, since tantalum is a single-isotope material.

Ion current i is observed already in the state presented in panel *c* (when the temperature is just $T \sim 1130$ K), but this current is negligible and hard to measure. The state in panel *e*, which corresponds to $T \sim 1700-1800$ K and $F \sim 6.3$ V/nm, is rather intriguing. If one establishes a state similar to that presented in panel *e* and reduces F to $F \sim 3.0$ V/nm while maintaining the same temperature, current i may be obtained in the form of a stationary and almost time-independent flow of ions rather than in the form of individual bursts. This mode may be sustained for a considerable period of time (at the very least, for approximately an hour). At higher T and F, the mode of growth and evaporation of macro-outgrowths was established, and the current became „pulsed“. It should be noted that the magnitudes of a constant current from a single emitter in this mode are fairly low: $i \sim 10^{-13}-10^{-14}$ A with a stability of approximately 10%. However, these values may be sufficient for various nanotechnology purposes. The current magnitudes in the ion burst mode at higher T and

F may reach $i \sim 10^{-12}$ A. Thus, it turned out to be possible to sustain the mode of stationary field evaporation and stationary current for tantalum.

It was instructive and, apparently, helpful to determine the energy cost of emergence of macro-outgrowths with nanoprotrusions (i.e., activation energies Q for their growth). This was performed in accordance with the classical method that relies on Arrhenius plots $\lg t = f(1/T)$, where t is the time (in seconds) needed for an outgrowth to reach a certain growth stage and T is the emitter temperature (in kelvins). These plots had the form of straight lines (not shown here), and their slopes yield Q values at a fixed field magnitude F and various temperatures T. The obtained values were $Q = 1.8$ eV at $F = 3.2$ V/nm, $Q = 1.9$ eV at $F = 3.8$ V/nm, $Q = 1.4$ eV at $F = 4.2$ V/nm, and $Q = 1.3$ eV at $F = 4.6$ V/nm. It can be seen that energies Q are relatively small and apparently independent of F. This is likely attributable to the smallness of F in the process of formation of macro-outgrowths. However, higher F values cannot be set in the present case, since they would induce marked evaporation of ions, material loss, and an increase in the tip radius, thus rendering Arrhenius plots unusable. It would also be very instructive to determine activation energies Q for the growth of nanoprotrusions. However, the crystallographic localization of their growth and, to a certain extent, the nature of this process normally change with T, thus again rendering the Arrhenius method unusable.

To conclude, it was demonstrated that a stable state of the emitting surface may be obtained in the process of field evaporation of a Ta emitter. Therefore, it is also possible to produce a stationary constant ion current, although of a relatively small magnitude.

Conflict of interest

The author declares that he has no conflict of interest.

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