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M.V. Strikha[1,2], I.Ye. Oliynyk[1]

Reduction of Work Function in Nanostructured Modern Cathodes for the Field Emission (Based on the Example of Tungsten Oxide $W_{18}O_{49}$ "Nanopencils")

[1]*Taras Shevchenko National University of Kyiv, Faculty of Radiophysics, Electronics and Computer Systems, Kyiv, Ukraine*
[2]*V.Ye. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine,*
maksym_strikha@hotmail.com

Within the framework of a simple analytical model, an expression has been obtained that allows to calculate the work function near the tips of a nanostructured cathodes used in modern field emission devices. Numerical evaluations performed for tungsten oxide $W_{18}O_{49}$ "nanopencils" show that taking into account the considered decrease in the surface electron gas density near the nanotip leads to a decrease in the "bulk" value of the work function (~4.55 eV) by approximately 10%. This effect must be taken into account when calculating the emission current density according to the Fowler-Nordheim formula. It (as well as the electric field enhancement due to the tip geometry) leads to an increase in the emission current density and a decrease in the emission turn-on field.

Keywords: Work function, field emission, nanostructured cathodes.

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The phenomenon of cold emission has extremely important applications in modern vacuum technologies (see, for example, monograph [1] and references therein). The emission flux density from a metal surface is determined by the Fowler-Nordheim formula (hereinafter referred to as FN):

$$J = \frac{e^3}{16\pi^2\hbar\Phi}\beta^2F^2\varepsilon\xi\pi\left[-\frac{4\sqrt{2m_o}}{3e\hbar}\frac{\Phi^{3/2}}{\beta F}\right] \qquad (1)$$

Here e and m_o are the charge and mass of a free electron, $\hbar$ is the reduced Planck constant, and Φ is the work function. The field enhancement factor β is determined by the geometry of the emission surface. It determines the ratio of the intensity of the enhanced (due to the geometry of the surface) local field F_{loc} and the field intensity between the anode and the cathode $F = Vl$ (where V is the voltage at the anode, l is the distance between the anode and the cathode) through the expression:

$$F_{loc} = \beta F. \qquad (2)$$

As can be seen from (1), the work function Φ is a basic characteristic of the emitter, and today intensive efforts are underway to obtain surfaces with the lowest possible work function, which would allow obtaining high emission currents at sufficiently low turn-on fields (see, for example, review [2] and paper [3]). Another direction for obtaining highly efficient emitters is the use of nanostructured surfaces, which allow obtaining high values of the field enhancement factor β (see, for example, [4 – 7]).

However, in [7] attention was first drawn to an essential circumstance: in all previous works, to describe the experimental curves of the dependence of the emission current on the applied voltage, the values of the work function Φ obtained for a flat surface of a bulk material were substituted into the FN formula (1); this was done even for nanostructured cathodes (see, for example, [5, 6]). At the same time, it is well known that Φ is a characteristic not so much of the material as of its specific surface, and it is the difference of Φ for different surfaces with different densities of surface electron charge that the principle of operation of electron and ion emission

microscopes is based [8].

In this work, we will try to estimate the magnitude of the change in the work function for a nanostructured surface compared to the corresponding value for a flat surface of a bulk material based on the phenomenological model proposed in [9]. The initial assumptions of this model are as follows:

The emitter atoms are considered as an ordered set of spheres with classical radii *R* (ranging from 0.025 nm for hydrogen to 0.26 nm for caesium). At the same time, a layer of weakly bound electrons is associated with the surface atoms, not involved in strong interatomic bonds of the bulk; however, surface fields prevent them from leaving the surface. Such electrons form a 2D gas with Fermi energy [10]:

$$E_F = \frac{\pi\hbar^2}{m}N, \qquad (3)$$

where N is the number of electrons per m^2 , m is the effective mass of the electron.

In his classic "Treatise on Electricity and Magnetism" [11], James Clerk Maxwell solved the problem of the interaction of a charge -*e*, located at a distance *u* from the edge of a conducting sphere of radius *R*, with its image $+q$, located on the line connecting the centre of the sphere with the charge, at a distance *z* from the centre of this sphere. In particular, he showed that

$$+q = \frac{eR}{R+u}; \quad z = \frac{R^2}{R+u}. \qquad (4)$$

The distance between the charge and its image is

$$x = R + u - z, \qquad (5)$$

and the force of attraction between them is (in the SI units)

$$F(u) = \frac{qe}{4\pi\varepsilon_o(R+u-z)^2}, \qquad (6)$$

where ε_o *is* the dielectric constant of the vacuum.

The output work function is calculated in [9] as an integral over the distance *u* from the force (6) in the interval from infinity (the energy Φ corresponds to the electron being carried to infinity) to a certain minimum distance *d*, which is determined by quantum mechanical considerations:

$$\Phi = \int_d^\infty F(u)du. \qquad (7)$$

Note that zero in the lower bound of integration (7), due to the form of function (6), would lead to a divergence. Therefore, the distance *d* was chosen as the lower bound of integration in [9], which, when in product with the momentum corresponding to the Fermi energy (3), satisfies the uncertainty relation:

$$d = \frac{\hbar}{2\sqrt{2mE_F}}. \qquad (8)$$

We note the factor 2 in the denominator of (8), which corresponds to the exact modern writing of the uncertainty ratio: it was omitted in [9]. For the real values of the Fermi energy and effective mass included in (8), the parameter *d* is an order of magnitude smaller than the constant lattice. Integration of (7) taking into account (4), (5), (6), (8) leads to the result:

$$\Phi = \left(\frac{e^2}{8\pi\varepsilon_o}\right)\left(\frac{\sqrt{2mE_F}}{\hbar}\right)\left(1 + \frac{\hbar}{4R\sqrt{2mE_F}}\right)^{-1}. \qquad (9)$$

Taking into account (3), we rewrite (9) as follows:

$$\Phi = \left(\frac{e^2}{8\pi\varepsilon_o}\right)\sqrt{2\pi N}\left(1 + \frac{1}{4R\sqrt{2\pi N}}\right)^{-1}. \qquad (10)$$

Note that the surface concentration of electrons is included in (10) only, and not their effective mass, which is a consequence of the assumption of the 2D nature of the surface electron gas. This surface concentration *N* can be written in terms of the area of a unit cell of the surface lattice *A* and the number of electrons *n* that such a cell gives to the 2D gas:

$$N = {}^{n}/_{A}. \qquad (11)$$

Taking into account (11), we write (10) as follows:

$$\Phi(eV) = 1{,}8 \times 10^{-9}\sqrt{\frac{n}{A}}\left(1 + \frac{0{,}1}{R\sqrt{n/A}}\right)^{-1} \qquad (12)$$

where the values of *A* and *n* are substituted in SI units. When substituting the value of *R* = 0.132 nm for oxygen into (12), we see that for$N \geq 10^{18}м^{-2}$ (corresponding to standard metal concentrations in volume), the last factor of (12) is determined mainly by its first term

One of the most promising for the creation of modern high-performance cathodes is the tungsten oxide structure $W_{18}O_{49}$, the manufacturing process, structure, and determination of its properties are described in [12]. Using the thermal deposition method, structures in the form of "pencils" were grown on a silicon substrate. The average height of such "pencils", which are a combination of a rod at the base and a cone at the top, is approximately 15 μm, and the density of pencil nanostructures in the array is approximately 10^7 per cm^2. Typically, the distance between adjacent nanotips is approximately 5 μm.

Fig. 1 shows an image of the top of the "pencil" obtained in [12] using a tunneling electron microscope. It can be seen that the crystal was grown in the [010] direction.

As is well known, tungsten oxide $W_{18}O_{49}$ is an *n-type* semiconductor with a wide bandgap of 2.66 eV and a bulk electron concentration under normal conditions of about$1{,}9 \times 10^{29}m^{-3}$, due to the presence of a large number of defects. It has a monoclinic structure with unit cell parameters a = 18.28 Å, b = 3.775 Å, c = 16.98 Å, β = 115.14° [13] (Fig. 2). The area of such a cell in the (010) plane is $A = ac\sin\beta = 2{,}81$ nm^2. Based on these data, the output performance can be estimated using the above formulas.

Unfortunately, there is no single reliable method for determining the number of electrons *n* that a unit cell gives up to a 2D gas. The results of various model assumptions are compared with the tabulated value of Φ [9]. However,

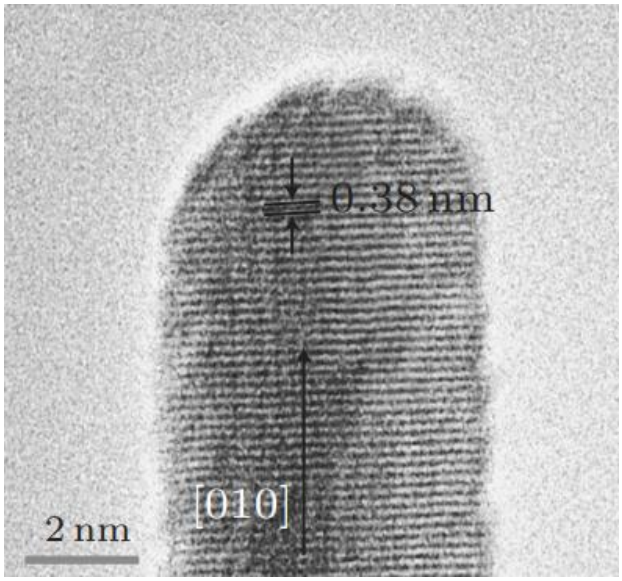

Fig. 1. TEM image of the top of a tungsten oxide "pencil" (adapted from [12]).

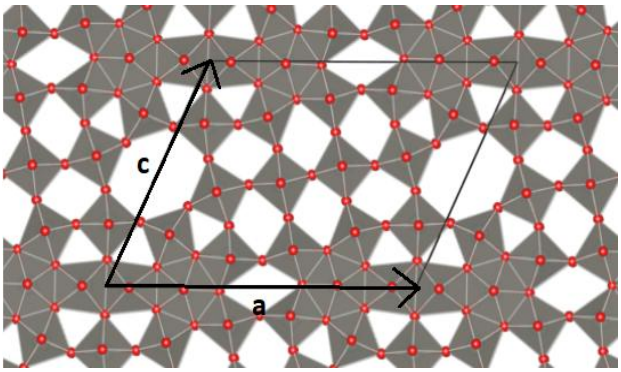

Fig. 2. Projection of the $W_{18}O_{49}$ structure onto the (010) plane and the corresponding unit cell (adapted from [13]).

there are also significant differences here for $W_{18}O_{49}$: from the value of 5.6 eV [9] to the newer values of 4.55-4.57 eV obtained by the approved methods [14]. Let us estimate the second of these values as more reliable. When substituting this value, formula (12) gives n = 27-28. Let's try to compare the obtained value of the number of electrons given up to a 2D surface gas by a unit cell with the features of the band structure of tungsten oxide.

Tungsten oxide $W_{18}O_{49}$ is an ionic crystal [13]. The grey octahedra WO_6 and the tetrahedra - pentagonal bipyramids WO_7 in Fig. 2 contain tungsten atoms in the +6 and +5 charge states, respectively. At the vertices of these polyhedra are oxygen atoms in the -2 charge state, where the 2p electron shell is filled with two additional electrons transferred by tungsten atoms. The Coulomb interaction between differently charged oxygen and tungsten atoms forms a monoclinic crystal structure characterised by the P2/m space group (see Fig. 2).

For oxygen atoms located in the vertices connecting the two octahedra, the binding energy of the two additional electrons is high enough that these atoms do not give up electrons to the free 2D gas.

However, for those oxygen atoms located in the vertices that protrude to the crystal surface and have tungsten atoms only on one side of them, one of the additional electrons can be transferred to a 2D gas of free surface electrons. Similarly, the binding energy for one of the additional electrons of those oxygen atoms belonging to two neighbouring octahedra and one decahedron is reduced (they have 10 oxygen atoms in the -2 charge state as their nearest neighbours, rather than 8 oxygen atoms in the vertices between two octahedra).

There are 18 oxygen atoms in the "surface" vertices of octahedra and pyramids per cell (14 atoms inside the cell, plus 8 at its edges, which belong to two neighbouring cells at once, so the cell accounts for half of them, 4 - see Fig. 2). The number of O atoms in the vertices belonging to two octahedra and a pyramid at the same time is 10 per cell (8 atoms inside the cell and 4 more atoms on its edges belonging to two cells at the same time). Thus, based on these simple assumptions, we obtain n = 28 and the value of Φ = 4.58 eV, which is a surprisingly good agreement with the value obtained from formula (12), taking into account the value of the work function of 4.55-4.57 eV obtained experimentally [14].

Based on the considerations outlined above, let us estimate the values of Φ for the other two crystallographic planes.

For the plane (100) we have: A 2D unit cell is a rectangle with sides b and c and an area of 0.64 nm^2. The 5 oxygen atoms located in the vertices facing the surface will give five electrons to the 2D electron gas. Another electron will be given by an atom belonging to two octahedra and a pyramid. In total, we get 6 electrons assigned to the area of the cell. As a result, using the above formulas, we obtain Φ = 4.41 eV.

For the (001) plane, the unit cell is a rectangle with sides a and b and an area of 0.69 nm^2. The contribution to the 2D electron gas here is made by 2 atoms from its left and right edges, which belong simultaneously to two neighbouring cells, 5 surface atoms, and one atom that belongs simultaneously to octahedra and pyramids. Thus, this cell gives up 7 electrons in total, and according to the above formulas, we have Φ = 4.63 eV.

As we can see, the work function for these two faces (100) and (001) is comparable to the known experimental values. Since the plane (100) is less densely packed than (010), the work function for it is also lower, which correlates with the known results for different types of surfaces [15]. On the contrary, plane (001) is denser, so the value of Φ for it is slightly higher.

Now let's try to use the previous considerations to evaluate the work function from the nanostructured surface. It should be noted that it is very difficult to reproduce such a structure exactly. Therefore, we used the simplest models to estimate the change in Φ due to the presence of nanostructured morphology. Fig. 1 shows that the surface in the vicinity of the nanopoint tip is close to spherical and has a certain asymmetry (which we will neglect in the following). We approximate the positive edge of the nanopoint by a set of steps and terraces. In this structure, the definition of a unit cell and the distribution of charges will modify. Now the total area of the unit cell will consist of the area of the step S_1 and the terrace S_2 (Fig. 3).

Let's estimate the area of the step S_1 through a parallelogram with sides a (1.828 nm) and d equal to 0.618 nm (this value is obtained as the hypotenuse of a right triangle with the legs b and h, which is the projection

of this hypotenuse onto the plane (010)). Then this area will be 1.129 nm^2.

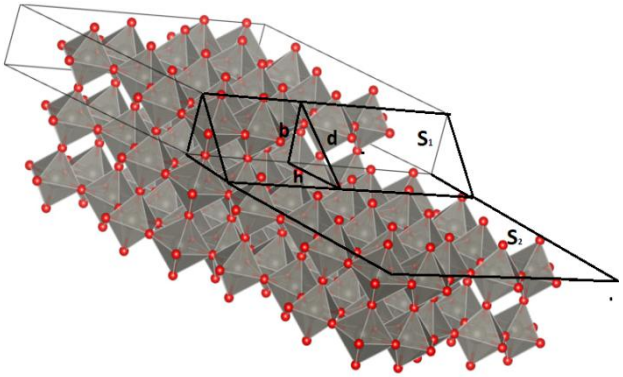

Fig. 3. Modification of a unit cell when a terrace S_2 and a step S_1 appear.

Let us calculate the number of atoms from which this inclined surface area will give up charge to the 2D fermion gas: the two outermost atoms of the top layer, simultaneously belonging to the adjacent top terrace and to the S_1 region. Four electrons will be given by the outermost atoms of the upper layer, which belong exclusively to S_1. Let us assume that electrons in a 2D gas are donated only by those atoms of the lower layer of the step that are almost on the surface of the inclined plane. These include five surface atoms and three intermediate atoms belonging to octahedra and tetrahedra simultaneously. Thus, in total, the inclined area S_1 gives up 12 electrons to the 2D gas.

The second area, the terrace S_2, is the usual tungsten oxide unit cell considered earlier in the (010) plane (see Fig. 2), from which the projection of the inclined area S_1 onto this plane has been removed. Its area S_2 = 1.89 nm^2. Excluding from the calculation the atoms belonging to the projection, as well as the last atom from the bottom edge, which will belong to the inclined area located in the layer below, we obtain that such a site will give up electrons to 2D gas from 12 atoms.

As a result, we have that the area with a total area of S_1+S_2 = 3.019 nm^2 accounts for 24 2D gas electrons. Substitution into formula (12) will give a value of Φ = 4.01 eV, which is approximately 0.5 eV less than the bulk value.

Now let us try to determine the area around the tip the nanowire $W_{18}O_{49}$ from which the effective field emission occurs. As is well known, the field enhancement actor, defined by expression (2), is maximal on the axis of the nanowire, where it is equal to β_a . When deviating from the top of the hemisphere by an angle θ, this coefficient decreases according to the cosine law [16]:

$$\beta(\theta) = \beta_a \cos\theta. \qquad (14)$$

Let us assume that the effective emission is limited to a region in the vicinity of the nanopoint axis, limited by the value of $\theta_{\max}$, for which the emission current according to the FN formula (1) decreases by one half. The value of the field enhancement factor can be estimated using the simplest relation $\beta_a \approx h/R$ [17], which includes the height of the nanopencil (h = 15 nm) and the radius of the tip (R = 5.7 nm). Hence, we obtain the value $\beta_a \approx 2631$.

Let us take the value of the work function as 4.55 eV [14], and the applied field of the turn-off order in [12] F = 3MV/m. Solving for the above values the trans-cendental equation, which is a consequence of (1), (13):

$$\cos(\theta_{\max})\left(\ln(2\cos(\theta_{\max})^2) + \frac{4\sqrt{2m}}{3e\hbar}\frac{\Phi^{1,5}}{\beta_a \Phi}\right) = \frac{4\sqrt{2m}}{3e\hbar}\frac{\Phi^{1,5}}{\beta_a \Phi}, \qquad (15)$$

we obtain the solution $\theta_{\max} = \mp 0.35$, or approximately 20°. Taking into account the form of the real nanotip shown in Fig. 1, this means that all emission comes from the highest one terrace oriented in the (010) plane, and therefore we can substitute the value of 4.01 eV obtained above into formula (1).

Let us also plot the dependence of the work function Φ on the radius of the nanotip R. Fig. 1 shows that a change in R leads to a change in the number of terraces and steps in the region that provides effective field emission, $\theta \leq \theta_{\max}$. Repeating the reasoning above for the number of terraces and steps corresponding *to* a certain value of R leads to the values shown in Fig. 4.

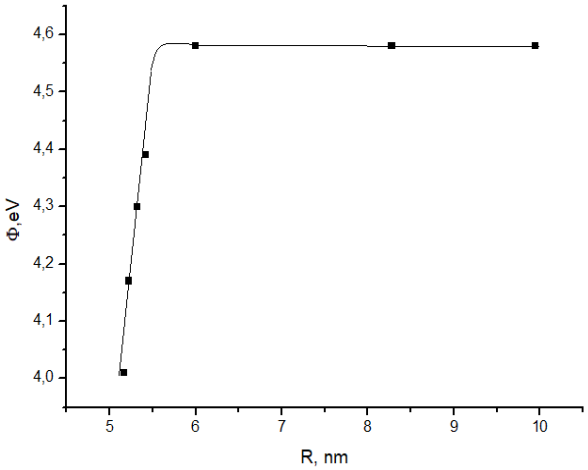

Fig. 4. The calculated dependence of the work function Φ on the radius of the nanotip R.

As can be seen from Fig. 4, for R smaller than about 5.5 nm, the work function decreases sharply, due to the above considerations, because of the decrease in the surface density of the 2D electron gas. However, for R larger than this value, the region near the axis has an almost constant surface gas density, and the work function thus reaches its "bulk" value.

Within the framework of a simple analytical model, we have obtained an expression that allows us to calculate the work function near the edges of a nanostructured cathodes used in modern field emission devices. Numerical estimates carried out for tungsten oxide $W_{18}O_{49}$ "nanopencils" show that taking into account the considered decrease in the density of the surface electron gas near the nanowire axis leads to a decrease in the "bulk" value of the work function (4.55 eV) by about 10%. This effect must be taken into account when calculating the emission current density using the Fowler-Nordheim formula for metals (or the modified FN formula for semiconductors [4, 5, 7]). It (as well as the electric field amplification due to the geometry of the tip) leads to an increase in the emission current density and a decrease in the emission turn-off field.

Strikha M.V. **–** Professor of the Department of Physical Electronics, Faculty of Radiophysics of Electronics and Computer Systems, Taras Shevchenko National University of Kyiv, Chief Researcher at the Lashkariov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine;
Oliynyk I.Ye. **–** is a student of the Faculty of Radiophysics, Electronics and Computer Systems of Taras Shevchenko National University of Kyiv.

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М.В.Стріха[1,2], І.Є.Олійник[1]

Зниження роботи виходу в наноструктурованих сучасних катодах для польової емісії (на прикладі «нанооліців» оксиду вольфраму $W_{18}O_{49}$)

[1]Київський національний університет ім. Тараса Шевченка,
факультет радіофізики, електроніки і комп'ютерних систем, Київ, Україна;
[2]Інститут фізики напівпровідників ім. В.Є.Лашкарьова НАН України, Київ, Україна, maksym_strikha@hotmail.com

У рамках простої аналітичної моделі одержано вираз, який дозволяє розрахувати роботу виходу поблизу вістрів наноструктурованого катода, використовуваного в сучасних пристроях польової емісії. Числові оцінки, проведені для «нанооліців» оксиду вольфраму $W_{18}O_{49}$, показують, що врахування розглянутого нами зменшення густини поверхневого електронного газу поблизу нановістря призводить до зменшення «об'ємного» значення роботи виходу (~4,55 еВ) приблизно на 10%. Цей ефект потрібно враховувати при обчисленні густини емісійного струму за формулою Фаулера-Нордгейма. Він (як і підсилення електричного поля за рахунок геометрії вістря) призводить до збільшення густини емісійного струму та зменшення поля вмикання емісії.

Ключові слова: Робота виходу, польова емісія, наноструктуровані катоди.