SOVIET PHYSICS JETP VOLUME 24, NUMBER 5 MAY, 1967

INVESTIGATION OF ADSORPTION OF CESIUM ON A TUNGSTEN SINGLE CRYSTAL

V. M. GAVRILYUK,* A. G. NAUMOVETS, and A. G. FEDORUS

Physics Institute, Academy of Sciences, Ukrainian S.S.R.

Submitted to JETP editor June 9, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 1332-1340 (November, 1966)

We have measured the work functions φ for the (110), (112), (100), and (111) faces of a tungsten single crystal as a function of the concentration n of cesium atoms adsorbed on the faces, by measuring the field-emission current from the faces of a single-crystal point. The lowest work functions of the various faces are in the range 1.35—1.55 eV; the concentration n in this case is respectively (in units of 10^{14} at/cm^2) 2.6 for the (100) plane, 3.2 for the (110) plane, 3.8 for the (112) plane, and 4.0 for the (111) plane. The effect of the structure and work function of the substrate on the shape of the φ(n) curve is discussed. The adsorption characteristics of cesium and lithium on tungsten are compared.

IT has become an urgent need in surface physics to obtain detailed quantitative data describing adsorption on substrates of a known crystal structure. The adsorption properties of the alkali elements on refractory metals have been studied particularly intensely in recent years. These systems are apparently the simplest from a physical point of view, and therefore it is natural to begin the study of the numerous unsolved problems with them. In addition, the electronic properties of adsorbed layers of the alkali metals have a tremendous practical importance. Particular interest is attached to cesium, which is widely used in thermionic energy converters.

The cesium-tungsten system has been the subject of a rather large number of investigations—from the classic article of Taylor and Langmuir[1] up to quite recent studies.[2,3] In spite of this fact, there are no quantitative data in the literature up to the present time on the adsorption of cesium on the individual faces of a tungsten crystal. The purpose of the present study was to obtain such data.

1. EXPERIMENT

Information on the work function was obtained by measuring the field-emission current from the individual faces of a single-crystal point in a Müller-type electron projection tube (Fig. 1). For this purpose the screen of the projection tube is equipped with an aperture 2 mm in diameter, beyond which is placed an electron collector screened by a suppressor grid. The idea for this design was borrowed from the work of Young and Müller.[4] The first experiments using a design of this type were made by us previously with lithium on tungsten.[5] The experimental tube has a narrow neck at the location of the point. Outside the tube at this neck is placed a magnetic deflecting system which can shift the field-emission image on the screen and direct electrons from a selected face of the point to the collector. The emission is collected from an area on the point having angular dimensions of ≈1.5—2° (the radius of the point was usually ≈2000 Å). Only the faces of types (110), (112), (100), and (111) closest to the axis of the point were studied.

The cesium was placed in a side arm of the experimental tube, from which it could enter the main region through a tube with an orifice 1.5 mm in diameter. The flat end of this tube could be covered with a nickel plate which was ground to make a close fit, thus isolating the cesium side arm from the main tube.

The cesium was obtained by reduction of CsF or CsCl by calcium and was subjected to four or five distillations in vacuum. The side arm was filled with cesium after the tube had received its final outgassing and was ready for seal-off ($p = 5 \times 10^{-9}$ torr, evacuation by a titanium pump). Here, at the limiting pressure of the vacuum system, no contamination of the cesium could be observed. After the tube was sealed off, pumping was continued by means of molybdenum and tantalum getters cooled by liquid nitrogen. The final pressure of active gases, estimated from the time dependence of the field emission, was no greater than 10^{-10} torr. Purity of the cesium from gaseous contaminants is also indicated by the appearance of

---

*Deceased

the field-emission pictures after desorption of a layer of cesium by the electric field (Fig. 2), which correspond to pure tungsten (the desorbing field for cesium is much smaller than that for gases).

In order to obtain the work function of the various faces as a function of the concentration, it was necessary to obtain a directed beam of cesium atoms. Since the pressure of saturated cesium vapor at room temperature is 10^{-6} torr, the walls of the apparatus had to be cooled to a rather low temperature (by dry ice, or by placing the tube in a closed vessel through which cold nitrogen was pumped, etc.). The temperature of the cesium side arm was maintained at a specified level by means of an ultrathermostat.

The atomic beam of cesium was calibrated by means of an ionization detector[6] placed in the path of the beam between the cesium source and the tungsten point. The geometry of the apparatus allows us to assume an inverse-square falloff of the flux of atoms with distance.[7]

The orientation of the point with respect to the beam was determined by the method described by Shrednik and Snezhko.[8] For this purpose a point cooled to T = 77°K to avoid mobility of the adsorbed atoms (adatoms) was exposed to a constant flux of cesium atoms, and the time intervals were measured for which the field-emission currents I reached a maximum for faces of the same type but differently oriented on the point.

After calibration of the atomic beam and determination of the orientation of the point with respect to it, the concentration of adatoms on any surface can easily be calculated.[8] The error in determining the surface concentration in our experiments is estimated as ≈10%.

The work function of surfaces covered with a cesium layer was calculated from the well known formula:[9]

$$\varphi = \varphi_0 (V / V_0)^{2/3},$$

where φ_0 is the work function of the clean surface, and V and V_0 are the voltages necessary to obtain a given current I from the surface covered with the layer and the pure surface, respectively. As we have verified by experiment, and also as has been shown in[3,5,8,9], in the absorption of alkali atoms on tungsten this formula gives values of φ practically identical with those calculated from the slopes of Fowler-Nordheim plots. The accuracy of determining the work function is 0.1 eV.

2. EXPERIMENTAL RESULTS AND DISCUSSION

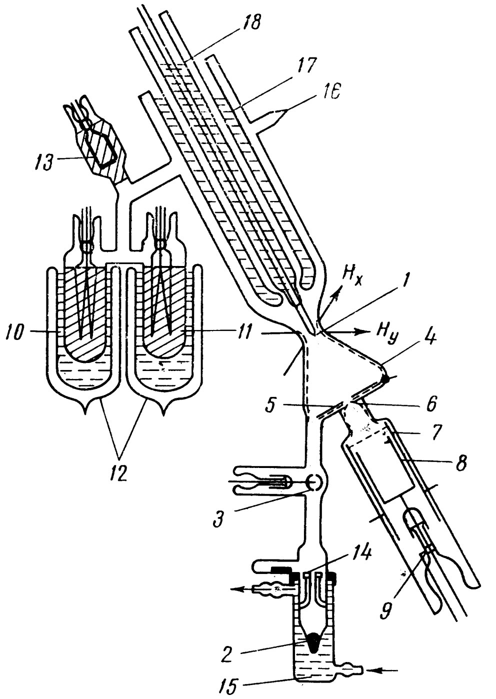


FIG. 1. Experimental tube. 1—point, 2—cesium, 3—ionization detector, 4—conducting layer, 5—screen, 6—diaphragm, 7—suppressor, 8—collector, 9—guard ring, 10, 11—molybdenum and tantalum getters, 12—Dewar vessel with liquid nitrogen, 13—barium getter, 14—vacuum gate, 15—thermostat, 16—seal-off tube, 17, 18—liquid nitrogen.

Figure 3 shows curves obtained for the work function as a function of the surface concentration of adatoms for deposition of cesium on different faces of a tungsten single crystal at T = 77°K. The curves have been drawn on the assumption that the work functions of the clean surfaces are respectively[10,11]: (111) — 4.4, (100) — 4.55, (112) — 4.8, and (110) — 5.4 eV (the reasons for taking $\varphi_{(110)} = 5.4$ eV will be discussed below).

It follows from the curves presented that the minimum work function $\varphi_{\min}$ at small concentrations occurs for the (100) face. This conclusion is also confirmed by visual observations of the field-emission pictures. Particularly graphic pictures can be obtained under these conditions, when the projection-tube walls are at room temperature and the point is cooled to 77°K. In this case cesium atoms previously deposited on the tube wall are evaporated and hit the point, producing on it a practically uniform covering (redistribution of the adatoms by migration over the point cannot occur at T = 77°K in the length of time occupied by the experiment). Thus, the pictures obtained (see Figs. 2b, c, d) reflect the distribution of the work function over the point for some fixed coverage of the point by cesium.

It is clear from examination of the photographs obtained at a constant projection-tube voltage that the (100) face is the first to emit strongly as ces-

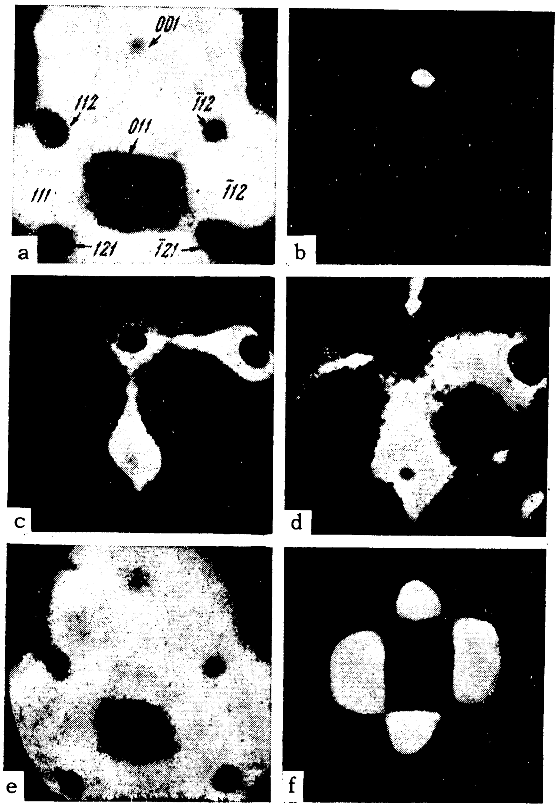


FIG. 2. Field-emission patterns: a–pure tungsten, b,c, d–successive stages of cesium deposition on tungsten at 77°K; d–after desorption of an optimum layer of cesium by an electric field of $\approx 5 \times 10^7$ V/cm; e–cesium crystallite grown in an electric field from a thick cesium layer.

ium is deposited, which indicates that $\varphi_{\min}$ is being achieved, and next the (110) and (111) faces. The minimum work function of the (112) faces is somewhat higher than the other faces mentioned, and for this reason they appear darker in the photograph. The emission from the (110), (111), and (100) regions is comparable, which indicates the closeness of their work functions. However, if we attempt to calculate $\varphi_{\min(110)}$ on the basis of the measured values of voltage for I = const, assuming $\varphi_{(110)} = 6.0$ eV,[4] we obtain a value of 1.7 eV. If this were actually the case, the (110) face at optimum coverage would appear darker than the other faces, for which there is no disagreement as to the initial work function in the literature. This is not observed, which inclined us to the choice $\varphi_{(110)} = 5.4$ eV.[10,11]

When cesium is deposited on a point at T = 300°K, the form of the field-emission pictures is completely different, which is due first of all to the fact that the adatoms are redistributed over the point by migration. A series of pictures obtained under these conditions for the cesium-tungsten system has been published previously.[2] The patterns observed by us are essentially the same as the published pictures.

Let us turn now to a more detailed discussion of the $\varphi(n)$ curves obtained at a point temperature of T = 77°K. The table lists the most important quantities characterizing these curves.

On all of the faces investigated, the $\varphi(n)$ curves have clearly expressed minima. The cause of this, in our opinion, lies in the following. As has been shown by[12,13], chemisorbed electropositive atoms at low coverages are bound to the substrate with a polar bond and have a certain positive charge. Thus, they have electronic properties which are different from the properties of the surface atoms of the massive adsorbate. The nature of the $\varphi(n)$ curve is determined evidently by how great this difference is and at what concentration of adatoms it begins to disappear as the result of overlapping of the electron shells (i.e., "metallization" of the film). If the positive charge of the adatom is sufficiently large, the work function of the surface can become lower than the work function of the massive adsorbate before the "metallization" of the layer begins, which leads to appearance of the minimum in the $\varphi(n)$ curve. Otherwise the $\varphi(n)$ curve is practically monotonic as, for example, in the adsorption of lithium on the (111) face of tungsten,[5] where the work function of all faces is lowered (on a per atom basis) 4–6 times more slowly than for cesium (for small coverages).

The greatest initial rate of reduction of the work function $|d\varphi/dn|_0$ in adsorption of cesium is observed on the (110) face, which has the largest work function. In this sense cesium behaves similarly to the other alkali metals—potassium,[14] sodium,[8] and lithium.[5]

It is clear from the table that $|d\varphi/dn|_0$ falls off with decreasing substrate work function. This parallelism can be considered as an indication that the chemisorption interaction, which leads to appearance of an effective positive charge in the cesium atom, is stronger when φ of the substrate is greater. Unfortunately, this interpretation is not completely unique, since the faces with lower work function are also characterized by looser packing, in view of which the effective distance from the center of the adatom to the surface (i.e., the dipole length) can also be smaller here. In other words, the atomic relief of the substrate must also have an influence in this case.

The role of this factor increases particularly in the transition to the region of large adatom concentrations, when the electron shells of neighboring atoms begin to interact directly. Thus, for example, it is difficult to detect a definite correlation

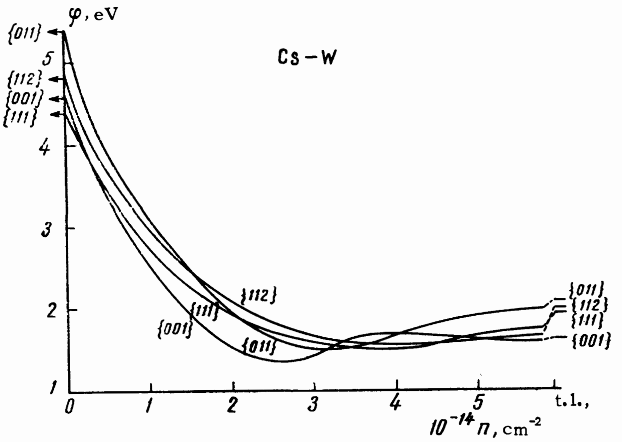


FIG. 3. Work function φ as a function of cesium adatom concentration n, for different faces of the tungsten crystal, T = 77°K; t.l.–thick layer, n = 3–5 n_{opt}.

between the work function of the substrate and the minimum work function of the film φ_{min} or the optimum concentration of adatoms n_{opt}. At the same time, comparison of the concentration of cesium atoms for the minimum φ—n_{opt}, and also the concentration at which a constant work function is reached—$n_{t.l.}$, with the concentration of tungsten atoms on the surface of the face—n_W, leads to interesting results. The table shows values of n_{opt}/n_W for the various faces. Our attention is drawn to the fact that within experimental error these ratios can be considered as multiples of 1/4; thus, for the (100) and (110) faces $n_{opt}/n_W \approx 1/4$, for the (112) face — 1/2, and for the (111) face — 3/4. A constant value of φ is achieved at concentrations, roughly speaking, of twice n_{opt}.

We recall that the lattice constant of cesium a_{Cs} = 6.05 Å,[15] while a_W = 3.16 Å, i.e., $2a_W/a_{Cs}$ = 1.05. Furthermore, cesium, like tungsten, crystallizes in a body-centered-cubic lattice. Therefore, if we assumed that adatoms of cesium have the same radius as in a massive single crystal (r^a_{Cs} = 2.62 Å), then the ratio n_{Cs}/n_W = 1/4 on the (110) face would correspond essentially to a close packed layer of cesium adatoms of the (110) structure, almost exactly reproducing the (110) face of a cesium crystal. However, we cannot forget that the work function of this layer still differs rather strongly (by 0.6 eV) from $\varphi_{t.l.}$ on the (110) face (see Fig. 3). Furthermore, experiments with a single-crystal tungsten ribbon, which we will report in detail later, have shown a dependence of the heat of adsorption of cesium atoms on their concentration on the (110) face — $q_a(n)$. It turned out that for optimum coverage q_a = 1.8 eV, i.e., more than twice the sublimation energy of cesium (0.8 eV). These facts indicate that the distribution of electron density in a cesium adatom under these conditions is still substantially different from that which is characteristic of the surface atoms of a crystal, and therefore the radius of the cesium adatom can in principle differ from the radius of the cesium atom in a crystal (we recall that the radius of the cesium ion is r^i_{Cs} = 1.7 Å).

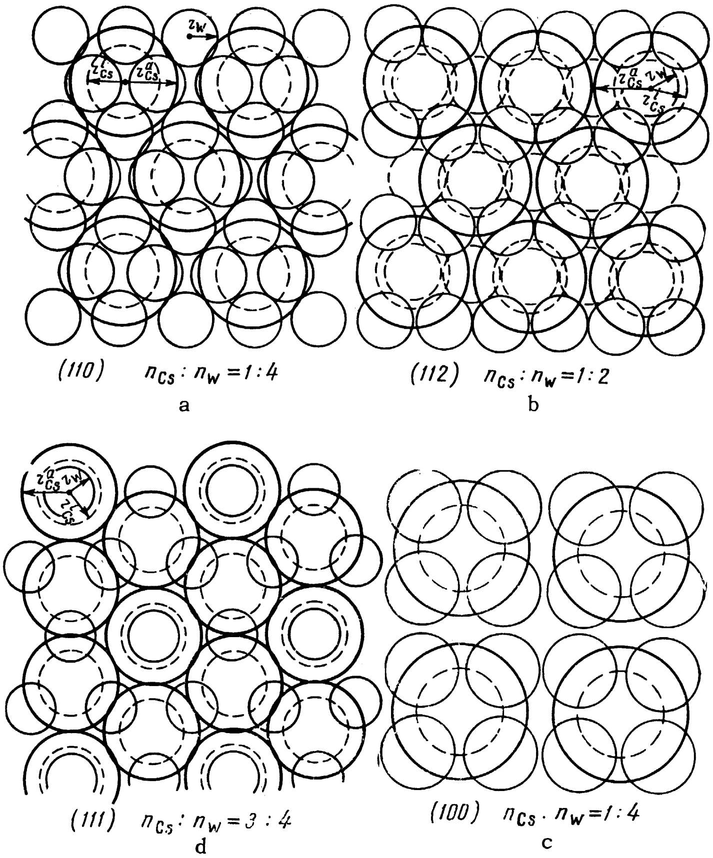
On the (112) face the minimum work function is reached at n_{Cs}/n_W = 1/2, i.e., at a concentration twice that corresponding to the (112) structure for cesium. The cause of this may lie in the fact that the (112) structure is characterized by a rather loose packing, for which an appreciable (on an atomic scale) portion of the tungsten substrate remains uncovered by the cesium film.

For the (100) face n_{opt}/n_W = 1/4, i.e., the same as for the (110) face, and for the loosely packed (111) face it is roughly 3/4.

The values found by us for the concentration n_{opt} are in good agreement, for all faces except (111), with the n calculated for a "monolayer" by Shrednik[16] from crystal geometry considerations, and by Gavrilyuk[17] from energy considerations.

Hypothetical ordered structures corresponding to the concentration ratios given above are presented in Fig. 4. It should be noted that the structure of cesium layers deposited on a substrate cooled to 77°K has not yet been studied by a direct method. Therefore it is still difficult to answer reliably the question as to what effect a possible disorder of the film structure exerts on the results presented. However, we can note that the activation energy for migration of cesium atoms over a chemisorbed layer is ≈ 0.2 eV,[2] so that at 77°K cesium atoms can shift by one lattice constant in a time of ~ 10^2 sec. The duration of the individual experiments was usually ~ 10^3 sec, and we can therefore assume that cesium atoms which fell at random on a portion of the surface already occupied by adatoms will move rather quickly to an energetically more favorable state in the first layer. (Possibly, the fact that the cesium atoms incident on the point

Face; φ_0, eV	$\lvert d\varphi/dn\rvert_0$, $10^{-14}\,\frac{eV}{at/cm^2}$	φ_{min}, eV	n_{opt}, 10^{14} cm^{-2}	n_W, 10^{14} cm^{-2}	$n_{opt} : n_W$	$\varphi_{t.l.}$ eV
(011); 5.4	5.5	1.5	3.15	14	0.9 : 4 (1 : 4)	2.1
(112); 4.8	3.5	1.55	3.8	8.2	0.93 : 2 (1 : 2)	2.0
(001); 4.55	3.0	1.35	2.6	10	1.04 : 4 (1 : 4)	1.65
(111); 4.4	2.3	1.5	3.95	5.8	2.72 : 4 (3 : 4)	1.95



(110) $n_{Cs} : n_W = 1:4$
a

(112) $n_{Cs} : n_W = 1:2$
b

(111) $n_{Cs} : n_W = 3:4$
d

(100) $n_{Cs} \cdot n_W = 1:4$
c

FIG. 4. Hypothetical structures of cesium films corresponding to φ_{min}, for different faces of the tungsten crystal.

have an energy corresponding to T ≈ 300°K may also be important here.) These considerations permit us to assume that under the conditions discussed the cesium layer is not completely amorphous. This conclusion is supported by the fact that the work functions of thick layers of cesium differ considerably on the different faces of tungsten (see the table). It is interesting to note that $\varphi_{t.l.}$ of cesium on the (110), (121), and (100) faces decreases in the same sequence as the work functions of the clean faces of the tungsten crystal (the (111) face is an exception). It is possible that epitaxial layers of cesium are formed in this case. The ratio of lattice constants is rather favorable for this, but it is difficult to estimate the energy conditions for epitaxy,[18] since the necessary quantities are unknown.

We have also succeeded in observing the growth of cesium crystals from a cesium film on tungsten under the action of a strong electric field, similar to that previously observed for lithium.[19] The cesium crystals are produced in the form of protuberances $\sim 10^{-5}$ cm in size standing out from the surface of the tungsten point. Field-emission pictures of these crystals (see Fig. 2e) are obtained at voltages 3—4 times smaller than those at which pictures of uniform thick layers of cesium are observed.

It is interesting to compare the $\varphi(n)$ curves for cesium and lithium on tungsten.[5] As a consequence of the small size of the lithium atom, its absorption characteristics are much more sensitive to the structure of the surface than in the case of cesium. Adatoms of lithium rapidly reduce the work function of the (110) face, up to 4×10^{14} cm^{-2}, where $n_{Li}: n_W \approx 1:4$. This structure is extremely loose ($r^a_{Li} = 1.52$ Å, $r^i_{Li} = 0.76$ Å). However, further increase of n up to 7×10^{14} cm^{-2} ($n_{Li} : n_W = 1:2$) has practically no effect on the work function. D. A. Gorodetskiĭ, who has studied the Li-(110)W system by diffraction of slow electrons, has kindly informed us that in this concentration interval the lithium adatoms are aligned in rows on the substrate. The distance between the lithium atoms in the rows is 3.16 Å, i.e., it corresponds almost to close packing (on the assumption that $r^a_{Li} = 1.52$ Å), and the distance between the rows is 4.45 Å. Thus, in formation of this structure, an unusual compensation effect occurs; although the number of adatoms increases, the effective dipole moment per atom decreases, so that $\varphi \approx$ const.

The structure $n_{Li} : n_W = 1:2$ also is rather loose, although according to Shrednik[16] it is a monolayer. However, it has been shown by diffraction of slow electrons that at larger concentrations a second layer of lithium atoms is not yet formed, but that only a crowding of the first layer and formation of more compact ordered structures take place. Here the work function increases to φ for a thick layer of lithium (this is reached at $n_{Li} : n_W \approx 1$). The structure of lithium films on the (121) and (111) faces has not yet been studied, and therefore we can only state some ideas about its effect on the behavior of $\varphi(n)$. Thus, the work function of the (112) face decreases rapidly only up to $n \approx 4 \times 10^{14}$ at/cm^2, and then remains practically constant over a wide region of n (up to 8×10^{14} cm^{-2}). If we assume that the adatoms occupy the energetically most favorable sites in the "grooves" of this face (Fig. 4b), this would mean that in the interval $4 \times 10^{14} < n < 8 \times 10^{14}$ at/cm^2 lithium atoms are being packed into dense rows similar to those described above for the (110) face, while φ remains ≈ const. With further increase of n, the lithium atoms are compelled to occupy less favorable sites on projecting tungsten atoms, and φ begins to change again.

On the (111) face the work function changes only up to n ≈ 6×10^{14} at/cm^2, when there is one lithium atom per surface atom of tungsten. Beyond this the work function remains almost unchanged.

CONCLUSION

The experiments described show that the behavior of φ(n) is affected both by the work function of the substrate and by its crystal structure. The initial rate of reduction of the work function of tungsten by cesium is greater when the work function of the crystal face is higher. The strong distortion of the electron shell of the adatom as the result of interaction with the substrate results in the existence on all faces of a minimum in the work function.

In the case of lithium on tungsten a simple correlation between $|d\varphi/dn|_0$ and φ does not exist: apparently the small size of the lithium atom makes it more sensitive to the structure of the face even at small coverages. The role of the atomic structure of the surface increases markedly at high adatom concentrations, when we are in fact dealing with two dimensional epitaxial crystals of the adsorbate. The ratio of concentrations of adatoms and surface atoms of tungsten on the different faces at the minimum φ suggests that the occurrence of the minimum φ corresponds to formation of a definite structure of the adsorbed film, addition to which of new adsorbate atoms leads to the beginning of "metallization" of the film, i.e., to a loss by the adsorbed atoms of their specific properties. A knowledge of the structure of the films is evidently just as important for a correct understanding of the mechanism of adsorption processes as a knowledge of the structure of the substrate.

---

[1] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

[2] L. W. Swanson, R. W. Strayer, F. M. Charbonnier, and E. C. Cooper, Electric Propulsion Development, Acad. Press, N. Y., 1963, p. 165.

[3] L. D. Schmidt and R. Gomer, J. Chem. Phys. **43**, 2055 (1965).

[4] R. D. Young and E. W. Müller, J. Appl. Phys. **33**, 91 (1962).

[5] V. M. Gavrilyuk and V. K. Medvedev, FTT **8**, 1811 (1966), Soviet Phys. Solid State **8**, 1439 (1966).

[6] J. B. Taylor, Z. Physik **57**, 242 (1929).

[7] S. A. Vekshinskiĭ, Novyĭ metod metallograficheskogo issledovaniya splavov (A New Method for the Metallographic Study of Alloys), Gostekhizdat, 1944, p. 28.

[8] V. N. Shrednik and E. V. Snezhko, FTT **6**, 1501 (1964), Soviet Phys. Solid State **6**, 1173 (1964).

[9] L. Schmidt and R. Gomer, J. Chem. Phys. **42**, 3573 (1965).

[10] U. V. Azizov and G. N. Shuppe, FTT **7**, 1970 (1965), Soviet Phys. Solid State **7**, 1591 (1965).

[11] F. L. Reynolds, J. Chem. Phys. **39**, 1107 (1963).

[12] O. A. Panchenko and Yu. G. Ptushinskiĭ, Izv. AN SSSR, ser. fiz. **28**, 1466 (1964).

[13] Yu. S. Vedula and V. M. Gavrilyuk, FTT **7**, 2547 (1965), Soviet Phys. Solid State **7**, 2056 (1966).

[14] A. G. Naumovets, FTT **5**, 2294 (1963), Soviet Phys. Solid State **5**, 1668 (1964).

[15] Collection of articles, Cesium, edited by V. E. Plyushchev, IIL, 1963, p. 23.

[16] V. N. Shrednik, Radiotekhn. i élektron. **5**, 1203 (1960).

[17] V. M. Gavrilyuk, Ukr. fiz. zh. **4**, 734 (1959).

[18] G. Bliznakov, in: Rost kristallov (Crystal Growth) **3**, AN SSSR, 1961, p. 37.

[19] A. G. Naumovets, FTT **6**, 2088 (1964), Soviet Phys. Solid State **6**, 1647 (1965).

Translated by C. S. Robinson
159