FEM AND FIM STUDY OF THE WORK FUNCTION OF STEPPED METAL SURFACES

Zlatko KNOR

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2

Received 26th March, 1979

Dedicated to Professor E. Hála on the occasion of his 60th birthday.

A comparison between FEM and FIM images of the tungsten surface shows that stepped (high-index) planes influence emitted electrons in two ways: *a*) if monoatomic steps whose edges form the crystal face under question are wider than about three atoms, the surface behaves as a "patchy surface" formed by flat areas of the steps; *b*) if steps are narrower than the above mentioned limit, the emitted electrons "feel" the field of the crystal plane determined by step edges (the work function acquires low values corresponding to atomically rough surface).

The distribution of the electric charge (of electron densities) in a complex of particles under study (molecule–crystal surface) is a quantity of general importance for the chemical reactivity of the system. The chemical reactivity of transition metal surfaces is determined both by partly localized *d*-electrons and by nearly free *s*- (*s*, *p*-) electrons[1,2]. Incompletely occupied *d*-orbitals on transition metal surfaces are presumably responsible for trapping of gaseous molecules[1–3], nearly free electrons contribute by dynamical screening to weakening of bonds in the trapped molecules[2–4]. Experimental information on the electron density distribution in surfaces of metals and in surface complexes can be obtained indirectly from studies of the anisotropy of such phenomena as, *e.g.*, photoemission, electron stimulated desorption, work function, and ionization in the electric field near the surface[1,2].

In this contribution attention is paid to the latter two phenomena. The work function of metals depends strongly on the electron density distribution. This was shown as early as in the classical paper of Smoluchowski[5] whose physical model of metals has been successfully used until now[6]. This model explains the work function anisotropy of various crystalographic planes using the assumption that the free electron density "smooths out" the anisotropy of the ion core potential in the surface layer of the crystal lattice ("smoothing effect") (Fig. 1) (ref.[2–5]). In this way an additional dipole moment originates on the surface of atomically rough crystal faces (planes of a low density of surface atoms) which lowers – in agreement with experiments – the work function of these crystal planes. The model can be conveniently used in the discussion of the work function of the crystal planes of low Miller indices; however, it fails for high-index planes[2].

Metal surfaces, as encountered in practice in various disciplines (heterogeneous catalysis, corrosion etc.) are not ideally smooth; the model of so called stepped surfaces approximates them reasonably well. The stepped surfaces are in fact high-index planes of a step type, where the width of a particular step is several times larger than its height. These surfaces exhibit a high chemical reactivity (an ability of dissociative chemisorption of gases)[7]. Samples in the form of single-crystal tips used in field electron emission microscope (FEM) and field ion microscope[8] (FIM) represent a typical example of stepped surfaces[8]. Therefore, the problem of the work function of surfaces of this type can be studied by comparing the anisotropy distribution of the work function on the tip surface, as found in FEM, with the atomic structure of this surface, as obtained by FIM.

In FEM electrons are emitted from the apex of the tip under the influence of a high electric field ($1-5 \cdot 10^{10}$ Vm^{-1}) and they project onto the fluorescent screen an image of the surface enlarged about 10^6 times[8]. As the electron emission is exponentially dependent on the work function[8], a system of bright and dark spots appears on the screen (Fig. 2) representing the projection of the particular crystallographic planes of a low and high work function, respectively. In FIM the experimental arrangement is practically identical with the preceding set-up, only the field polarity is reversed (positively charged tip), and instead of the ultra-high vaccuum between the tip and the screen there is about $10^{-1}-10^{-3}$ Pa pressure of an inert gas (*e.g.*, of helium)[8]. Because of the electric field (in this case $5-20 \cdot 10^{10}$ Vm^{-1}) atoms of the inert gas are ionized in the vicinity of the surface metal atoms, and their point of origin is projected onto the screen[8-10]. Edges of the atomic layers which approximate the apex surface (a flat pyramide) show up as bright concentric circles (Fig. 3). The optimum resolving power of FIM (image gas helium, tip temperature $T = 21$ K) is 0·2—0·3 nm so that on atomically rough planes (*e.g.*, the plane (334) in Fig. 3) projections of single atoms can be resolved. Of low-index, atomically smooth planes only edges are visible (closed circles in Fig. 3, *e.g.*, the (011) plane).

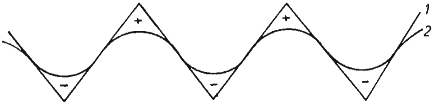


FIG. 1

Simulation of an Atomically Rough Surface Model of Metal-Jellium Showing the "Smoothing Effect" of Nearly Free Electrons

1 The contour of jellium positive charge distribution, *2* the contour of electron density distribution.

EXPERIMENTAL

In this study of the work function distribution over the sample surface a field electron emission microscope was used working in the ultra-high vacuum region (pressures lower than $1 . 10^{-7}$ Pa)[9]. The surface structure was studied by an ion emission microscope performing in the pressure region $10^{-2}-10^{-5}$ Pa[8,10]. The samples measured had the shape of a tip of the tip radius $10-10^2$ nm; they were obtained by electrochemical etching of a tungsten wire[10]. Besides the pure tungsten surface a layer of palladium — an example of a special adsorbate — could be prepared by vacuum evaporation of the metal onto the tungsten tip.

RESULTS AND DISCUSSION

In the image of the tungsten tip apex (a metal with the body centered cubic lattice) in FEM the dark central region is designated as the projection of the (011) plane (Fig. 2). From the comparison with the atomic structure of this tungsten surface region in FIM (Fig. 3)* it is evident that the real atomically smooth plane (011) has a much smaller dimension than the high work function region in FEM (the dark area[11] (011)) (Fig. 4).* Though the equilibrium shapes of the tips in the electron and ion microscope are somewhat different (Fig. 5), the above mentioned work function effect cannot be explained by a subsequent enlargement of the central plane due to a different distribution of the electric field intensity resulting from different curvature radii of both surfaces. This conclusion follows from the comparison of the electron and ion image after a thermal treatment of the tips and from the comparison of both surface images after the field evaporation (obtained *in situ*)[12]. A similar disagreement in the size of the electron and ion projection of the central plane of a high work function and the size of the actual atomically smooth plane on the tip apex was observed

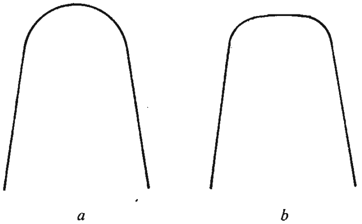


FIG. 5

The Equilibrium Tip Shape after a Thermal Treatment *a* and after the Evaporation in a High Electric Field *b*

---

* See insert facing page 3440.

not only for tungsten, but also for other metals, *e.g.*, for rhodium in the (001)plane[13] (a metal with the face centered cubic lattice). It is evident from the schematic picture of the tip profile (Fig. 6*a*) that in discussing the work function of the central plane vicinity on the apex surface (stepped surface) one has to take into consideration, if an electron in passing through its terraces "feels" the field of the crystallographic plane (hkl) or the $(h'k'l')$ plane field (Fig. 6*a*). The comparison of Figs 2*, 3*, and 4*, together with the measurement of the atomic step dimensions[14] shows that the work function of an electron for the atomically rough plane (hkl) has a physically meaningful definition only if the steps are narrower than about three atoms. If the surface is formed by wider steps, the entire region behaves – from the point of view of the work function – as a "patchy surface" formed by $(h'k'l')$ areas. In another words, with wide steps the perturbation of the electron density distribution at a step edge

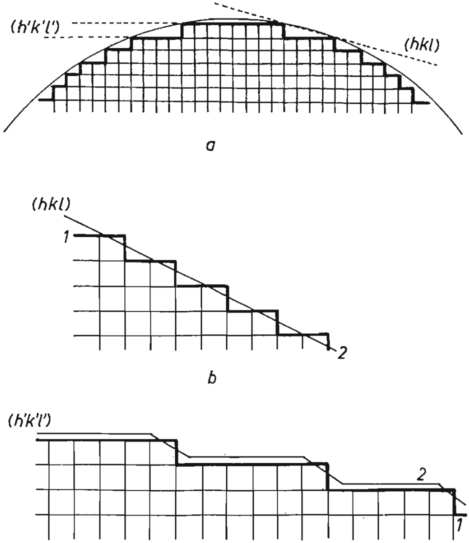


FIG. 6

A Schematic View of the Stepped Surface: *a* the Tip Apex Contour (for tungsten $(h'k'l') =$ $= (011)$); *b* Examples of Steps of Various Width

1 Contours of atomic terraces, 2 free electron density distribution.

---

* See insert facing page 3440.

is negligible in comparison with the step flat area (it manifests itself in the dependence of the work function on the step width[15,16]), and a low work function – corresponding to an atomically rough plane of the (hkl) type – is observed only with monoatomic steps narrower than about three atoms (Fig. 6*b*). An analogous conclusion could be made on the basis of photoemission experiments, too: the simple Smoluchowski correlation between the work function and the atom surface density[5] of different crystal planes is applicable only to low-index planes[17].

The above described interpretation of the image of the central apex region of the FEM tip is supported by the results of studies concerning the effect of adsorption on the work function of this region (in the case of tungsten the vicinity of the (011) plane). The work function of atomically smooth planes (of a high surface atom density) can be lowered as a result of: *a*) roughening of the surface during the deposition of metal atoms (or even atoms of the same kind as the atoms of the crystal lattice[18,19]); *b*) roughening of the surface during its reconstruction resulting from adsorption, thermal or other treatment (ion bombardment); *c*) a suitable oriented dipole layer of the adsorbate. The most active sites for trapping particles from the gaseous phase are just edges of atomic layers[2,7]. Therefore, it may be expected that in the process under consideration (deposited layer growth, adsorption) which lowers the work function, the dark area will be only the region of the projection of the central atomically smooth plane (for tungsten the (011) plane), as shown in Fig. 7*. The following Fig. 8* gives for a comparison the ion image of the clean tungsten surface in the vicinity of the (011) plane and the image of the same surface covered by palladium at T ~ 1000 K. The comparison shows a "roughening" of the surface in the vicinity of the (011) plane (which manifests itself in the electron projection as the work function decrease – *cf.* Fig. 7*), while the (011) plane proper remained smooth (in the electron projection the dark area of a high work function – *cf.* Fig. 7*). A similar effect (*i.e.* a pronounced imaging of the central atomically smooth surface) was observed both in various stages of the surface coverage and during the deposition of a variety of other adsorbates on tungsten: Ni (ref.[20]), Cu (ref.[21]), Ag (ref.[22-24]), Au (ref.[24]), Cd (ref.[25]), Ti (ref.[26]), U (ref.[27]), Si (refs[28-30]), Ge (refs[30,31]), Se (ref.[32]), Te (ref.[32]), H_2 (ref.[33]), N_2 (ref.[34]), CH_4 (ref.[35]).

The results of this study show that in theoretical modelling of interactions on stepped surfaces of transition metals it is useful to distinguish two limiting cases: narrow steps on the one hand and wide steps on the other hand. The division between these two cases represents the step width of about three atoms. The characteristic property of the wide steps from the point of view of chemical reactivity of surface complexes is, besides the "denuded character" of atoms on step edges (the atoms expose into the gaseous phase localized "atomic-like" *d*-orbitals[36] which make the trapping of gaseous particles possible[1,2]), also a further activation of trapped particles due to

---

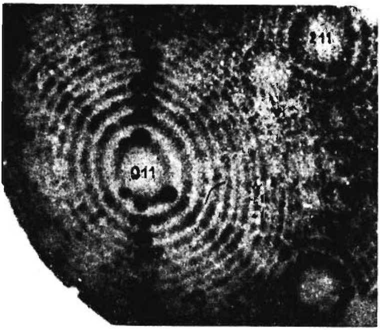
* See insert facing page 3440.

Fig. 2

The FEM Image of the Tungsten Surface (image voltage 4·9 kV, $T_{\mathrm{tip}} = 78$ K)

Fig. 3

The FIM Image of the Tungsten Surface (image gas: He — $1{\cdot}6 . 10^{-1}$ Pa, Ne — $1{\cdot}5 . 10^{-2}$ Pa; image voltage BIV = 12 kV, $T_{\mathrm{tip}} = 21$ K)



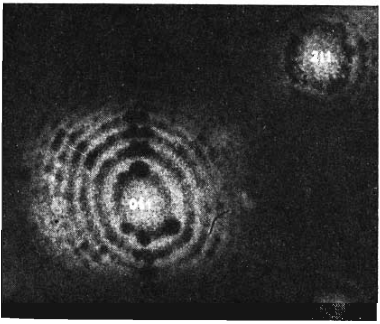


FIG. 4

The Negative FIM Image of the Tungsten Surface *a* and the Superposition of the Negative FIM and FEM Images of the Tunsten Surface *b* (the high work function region in FEM shows here as the bright area)

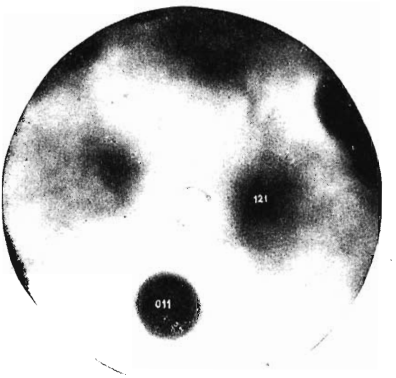


FIG. 7

The FEM Image of the Tungsten Surface Covered by a Palladium Layer (Pd deposited onto the tungsten surface at $T_{\mathrm{tip}} \sim 1100$ K) (image voltage 4·9 eV. $T_{\mathrm{tip}} = 78$ K)

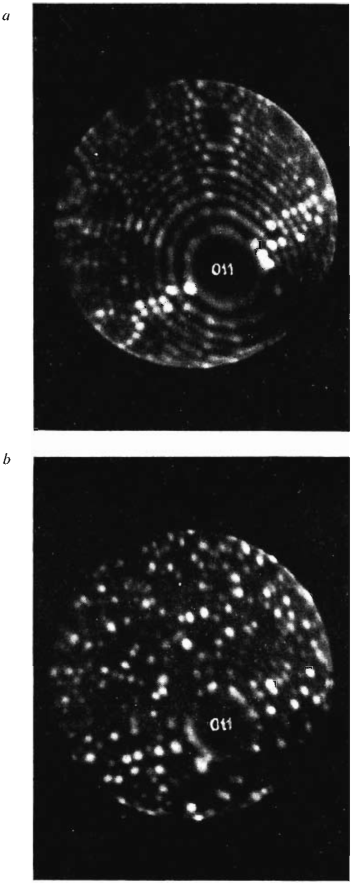


FIG. 8

The FIM Image of the Clean Tungsten Surface *a* and the Surface Covered by Palladium (at $T_{\text{tip}} \sim 1000$ K). *b* (image gas: He — $4{\cdot}5 \,.\, 10^{-3}$ Pa, image voltage BIV = 8·5 kV, image intensity enhanced by a channel plate) their immersion into the Fermi sea of free *s*- (*s*, *p*-) electrons close to the edge of the atom layer. This is because due to the screening both internal bonds of the trapped molecule and its bonds to the surface may be weakened. This may lead to a migration of particles over the atomically smooth terrace and thus occasionally even to a liberation of localized orbitals for a further interaction with gaseous particles[2,37].

REFERENCES

1. Knor Z.: Surface Sci. *70*, 286 (1978).
2. Knor Z.: *Surface and Defect Properties of Solids.* (M. W. Roberts, J. M. Thomas Eds), Vol. 6, p. 139. The Chemical Society, London 1977.
3. Gorodetskii V. V., Sobyanin V. A., Bulgakov N. N., Knor Z.: Surface Sci. *82*, 120 (1979).
4. Shirley D. A.: J. Vac. Sci. Technol. *12*, 280 (1975).
5. Smoluchowski R : Phys. Rev. *60*, 661 (1941).
6. Smith J. R.: Phys. Rev. Lett. *25*, 1023 (1970).
   Boudreaux D. S., Juretschke H. J.: *Structure and Properties of Metal Surface* (Honda Memorial Series on Material Science No 1). Maruzen Co., Tokyo, 1973.
7. Somorjai G. A.: Surface Sci. *34*, 1202 (1973; Advan. Catal. Relat. Subj. *26*, 1 (1977).
8. Knor Z.: Československ. Čas. Fys. *A 27*, 460 (1977).
9. Knor Z., Lazarov D.: Czech. J. Phys. *B 16*, 333 (1966).
10. Müller E. W., Tsong T. T.: *Field Ion Microscopy.* American Elsevier, New York 1969.
11. Oostrom A. van: J. Chem. Phys. *47*, 761 (1967).
12. Feldman U., Gomer R.: J. Appl. Phys. *37*, 2380 (1966).
    Holscher A. A.: *Thesis.* University, Leiden, 1967.
13. Ehrlich G., Heyne H., Kirk C. F.: *The Structure and Chemistry of Solid Surfaces* (G. A. Somorjai, Ed.), Paper 49—1. Wiley, New York 1969.
14. Drechsler M., Wolf P.: *Proc. 4th Internatl. Conf. Electron Microscopy, Berlin, 1958* (W. Bergmann, G. Möllenstedt, H. Niers, D. Peters, E. Ruska, C. Wolpers, Eds). Vol. 1, p. 835. Springer, Berlin 1960.
15. Krahl-Urban B., Niekisch E. A., Wagner H.: Surface Sci. *64*, 52 (1977).
16. Besocke K., Krahl-Urban B., Wagner H.: Surface Sci. *68*, 39 (1977).
17. Berge S., Gartland P. O., Slagsvold B. J.: Surface Sci. *43*, 275 (1974).
18. Plummer J., Rhodin T. N.: Appl. Phys. Lett. *11*, 194 (1967).
19. Besocke K., Wagner H.: Phys. Rev. *B 8*, 4597 (1973). Surface Sci. *53*, 351 (1975).
20. Jones J. P., Martin A. D.: Surface Sci. *41*, 559 (1974).
21. Melmed A. J.: J. Appl. Phys. *36*, 3585 (1965); J. Chem. Phys. *43*, 3057 (1965).
22. Sugata E., Takeda K.: Phys. Status Solidi *38*, 549 (1970).
23. Gretz R. D.: Rev. Sci. Instr. *38*, 112 (1967).
24. Centronio A., Jones J. P.: Surface Sci. *44*, 109 (1974).
25. Sokolskaya I. L.: Fiz. Tverd. Tela *3*, 790 (1961).
26. Anderson J. R., Thompson N.: Surface Sci. *26*, 397 (1971).
27. Collins. R. A., Blott. B. H.: Surface Sci. *9*, 1 (1968).
28. Collins R. A.: Surface Sci. *26*, 624 (1971).
29. Swenson O. F., Sinha M. K.: J. Vac. Sci. Technol. *9*, 942 (1972).
30. Janssen A. P., Jones J. P.: Surface Sci. *41*, 257 (1974).
31. Nikliborc J., Radon T., Zbrowski J.: Acta Phys. Pol. *23*, 53 (1963).
32. Köster H., Schütt W.: Phys. Status Solidi (*a*) *4*, 265 (1971).

33. Ustinov Yu. K.: Fiz. Tverd. Tela *13*, 558 (1971).
34. Ehrlich G., Hudda F. G.: J. Chem. Phys. *35*, 1421 (1961).
35. Hellwig S., Block J. H.: Surface Sci. *29*, 523 (1972).
36. Tsang Y. W., Falicov L. M.: J. Phys. *C 9*, 51 (1976).
37. Melius C. F.: Chem. Phys. Lett. *39*, 287 (1976).

Translated by Z. Herman.