A FIELD EMISSION STUDY OF CARBON ON TUNGSTEN

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The adsorption of carbon on tungsten was investigated using the field emission microscopy technique. The slopes of the Fowler-Nordheim plots were determined and the average work function was calculated as a function of the time of carbon evaporation. It was assumed that an increase in the average work function at small coverages is a result of an increase in the surface concentration of uniformly spread carbon. The average work function of one monolayer to 4.7 ± 0.05 eV. A distinct decrease in work function observed for thick layers seems to be apparent and connected with an enhancement of the strength of the electric field caused by the adsorbate roughness. An explanation of the observed phenomena is proposed.

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1. Introduction

The properties of carbon layers adsorbed on the metal surface are of technological importance. Carbon is an impurity of many metals and significantly influences the self-diffusion [1, 2] which is essential in metallurgy. Refractory-metal carbides can be used as effective catalytic agents [3]. Recently, interesting investigations of carbides were made by means of the field emission and field ion microscopes [4, 5].

The present work is a continuation of our previous investigations concerning the adsorption of carbon on tungsten [6] and a completion of studies of the fourth group elements adsorption [6–8]. Recent work function measurements of the C/W system [1] differ from the previous results obtained in our work [6], where an increase in the work function was observed with an increasing amount of deposited carbon. However, a decrease in work function was found in [1]. It seemed to be interesting to complete the measurements [6] and to explain the discrepancy.

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2. Experimental

The measurements were done using an all-glass field emission microscope (FEM). The ultra-high vacuum was obtained using diffusion mercury pumps and after sealing off the tube it was improved by a titanium pump. A piece of graphite heated by electron bombardment was used as a carbon source. For proper out-gassing, the graphite was heated for many hours at temperatures exceeding 2500 K. Flashing at temperatures above 3000 K was also used. The apparatus was immersed in liquid nitrogen while doing the measurements. The residual gas pressure did not exceed 3×10^{-10} torr during the carbon deposition. It was even lower while performing the measurements. The direction of the carbon atom beam was approximately normal to the emitter axis. Thus, the emitter was covered on one side. Raising the emitter temperature to 900–1200 K caused the surface diffusion of carbon to be on its other side. It was assumed that the amount of deposited adsorbate was proportional to the deposition time. Assuming also that the average work function of tungsten $\varphi_0 = 4.52$ eV from the current-voltage characteristics the average work function of the carbon-tungsten system was determined using formula [9] $\varphi = \varphi_0(\alpha/\alpha_0)^{2/3}$, where φ_0 and φ are the average work functions of clean and carbon covered tungsten respectively, and α_0 and α are the relevant Fowler-Nordheim slopes (F–N). The adsorbate was spread at temperatures exceeding 900 K determined by means of optical pyrometry. The carbon was removed from the emitter surface by heating for some minutes at a temperature 2400 K. The experiment was carried-out with very blunt tungsten emitter tips.

3. Results and discussion

The dependence of the average work function on the time of carbon deposition onto a tungsten field emitter is shown in Fig. 1. Each point of the curve was obtained by the evaporation of increasing carbon doses onto clean emitters and their thermal spreading over the entire tip surface. The spreading of small amounts of adsorbate occured at tem-

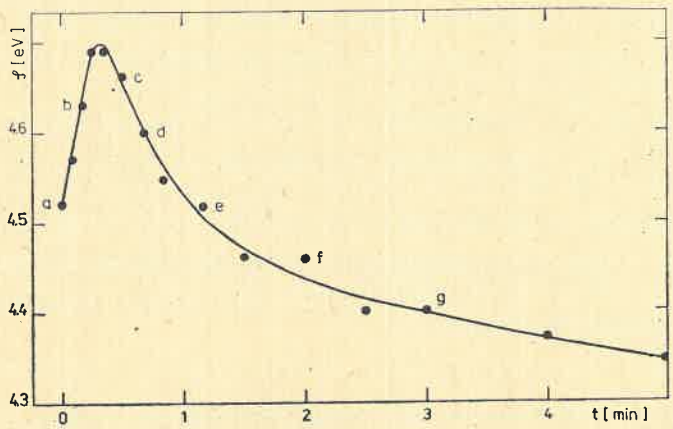

Fig. 1. The dependence of the work function change on the time of carbon deposition

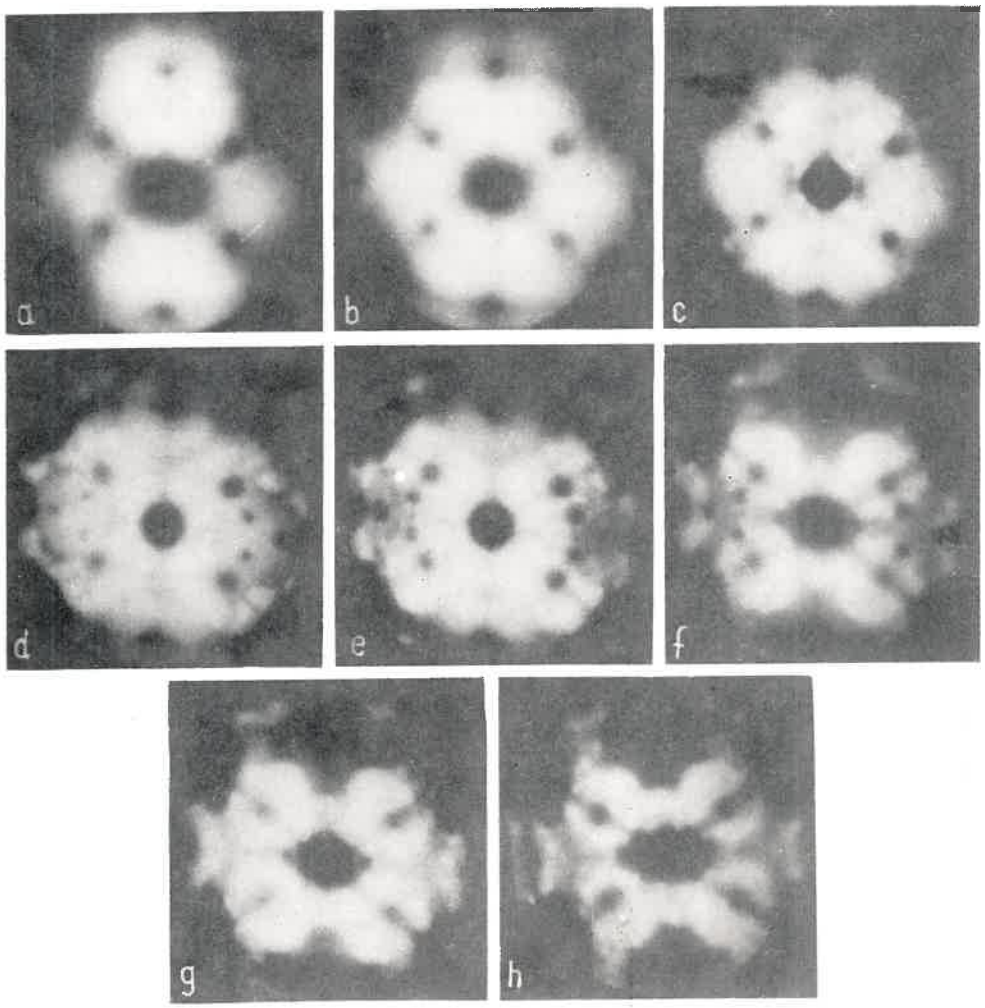

Fig. 2. Field emission patterns of the clean tungsten emitter (a) and covered with uniformly spread carbon after carbon deposition during: 10 s (b), 30 s (c), 40 s (d), 70 s (e), 120 s (f), 180 s (g), 360 s (h)

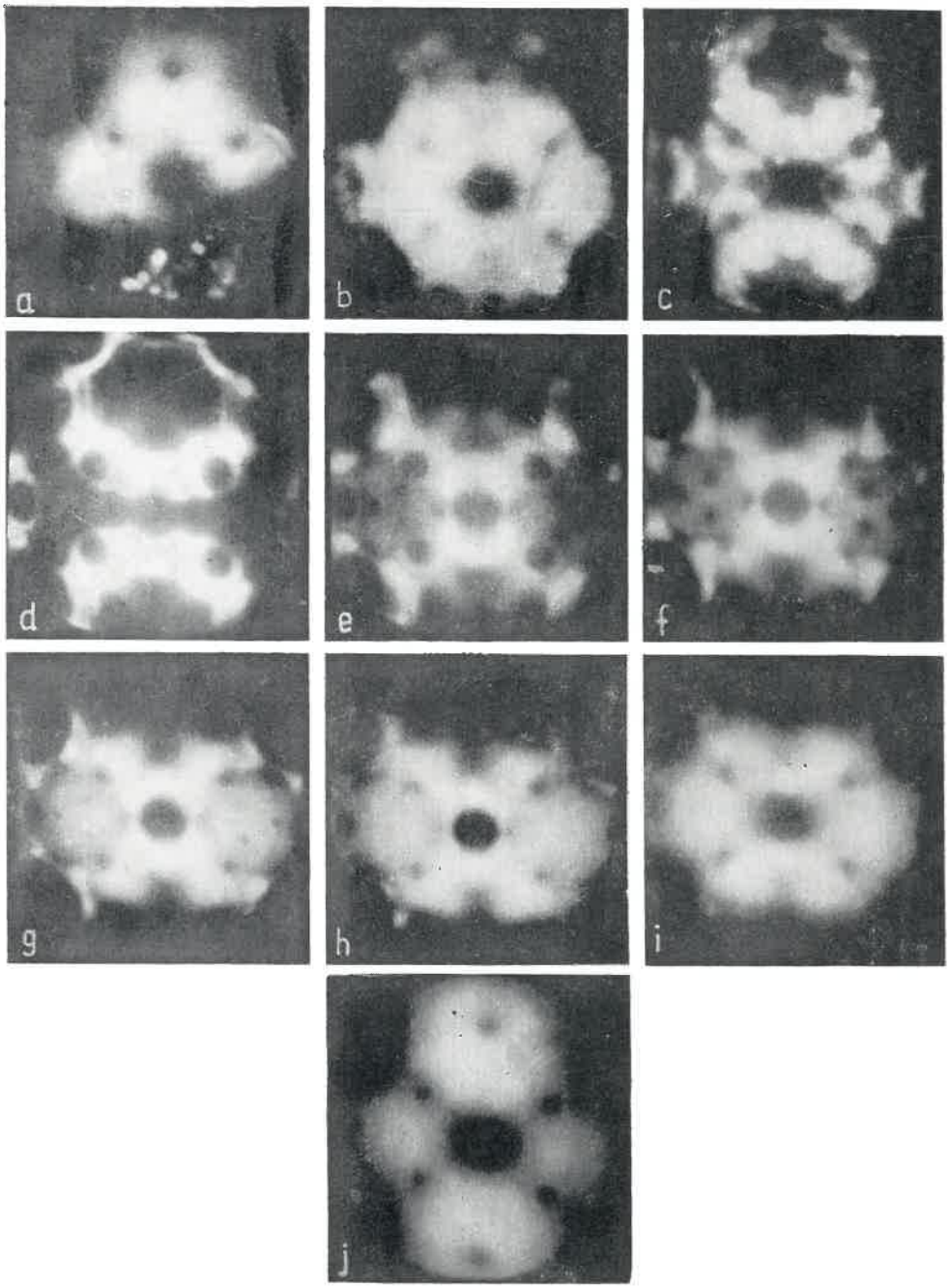

Fig. 3. Field emission patterns of a tungsten emitter covered with a thick carbon layer: (a) carbon deposited from below at 80 K, (b) carbon uniformly spread at about 1230 K, (c) carbon heated at 1400 K, (d) 1640 K, (e) 1700 K, (f) 1770 K, (g) 1810 K, (h) 1850 K, (i) 2100 K, (j) 2370 K

peratures in the 900 to 1000 K range [10, 11]. Large amounts of adsorbate were spread at higher temperatures up to 1200 K. Field emission currents were measured at a temperature close to that of liquid nitrogen. The field emission patterns (Fig. 2b) corresponding to the ascending part of the curve in Fig. 1. i.e., before the work function maximum of 4.7 eV is reached, are "smooth". The descending part of the curve observed for the increasing thickness of the adsorbate layers seems to be associated with changes in emitter surface geometry caused by an agglomeration of carbon atoms in preferential sites. This results "roughness" of the FEM patterns in Fig. 2 c-h. The increase of the amount of adsorbate on the emitter is accompanied by an increase in the image brightness and the extend of the built-ups around the {112} and {011} crystal faces of tungsten. The last photograph in Fig. 2 shows a large difference in electron emission between the "collars" created around these faces and the remaining part of the emitter surface. Müller [12] and Klein [10] attributed the increase observed in field emission from the "collars" to the enhancement of the electric field. However, this phenomenon has not been explained until now. The change in shape of a previously rounded tungsten emitter caused by carbon adsorption was found by Okuyama [13], Fig. 2b, using electron microscopy photographs of the emitter. Consequently, one should treat the decrease in the work function for thick carbon layers as an apparent although it is relatively large (Fig. 1). The apparent drop in the work function value for thick layers from 4.7 eV up to 4.35 eV nearly twice as large as the real increase due to the adsorption from 4.52 eV up to 4.7 eV. It is likely that the work function remains constant, with a value of 4.7 eV, for coverages higher than one monolayer, similar to that of silicon [6] and germanium [8]. Since the carbides are formed above 1500 K [13,5], it seems improbable that at a temperature of 1200 K used for the spreading of adsorbed carbon in this study they could appear in amounts affecting the work function. Thus, the observed work function decrease is mainly a consequence of an increase of the geometrical factor in the F-N equation [9]. The discrepancies in the character of the work function vs the coverage curves reported in [6, 1] can be now better understood. Taking into account that in [1] where only large doses of carbon have been used, it can be stated that the increasing part of the curve was not mentioned, although it was observed previously [6]. In this study, both an increasing part for small doses and a decreasing one for larger doses was observed, Fig. 1. The agreement with the result of paper [1] is qualitative. The shape of the curve in Fig. 1 indicates that the work function value of 4 eV could hardly be obtained for a very thick carbon layer, which is still much more than the value of 2.5 eV found in [1]. The very low work function was found in the present study either, Fig. 5, when the thick carbon layer was heated at 1600 K.

The magnitude of the apparent reduction of the work function depends not only on the amount of deposited carbon but also on the temperature at which it was spread over the emitter surface. Accordingly, for a given thick carbon layer different changes in work function can be observed depending on the temperature at which the layer was heated. Changes in the emitter surface caused by the heating of a carbon layer at a higher temperatures occur in two stages. In the first stage in the temperature range of 1200 to 1600 K, the agglomeration of carbon atoms occurs first in the {112} and {011} vicinity (Fig. 3 b-d). These patterns show that the agglomeration of carbon with increasing temper-

ature takes place on smaller areas of the emitter surface. An increase in the image contrast and an enhancement of field emission current at constant voltage is also observed. This indicates that the hight of the "collars" surrounding the {112} and {011} planes increases and this is the reason for the work functions apparent decrease. The points on the curve in Fig. 4 were determined after heating o the same deposit at increasing temperatures

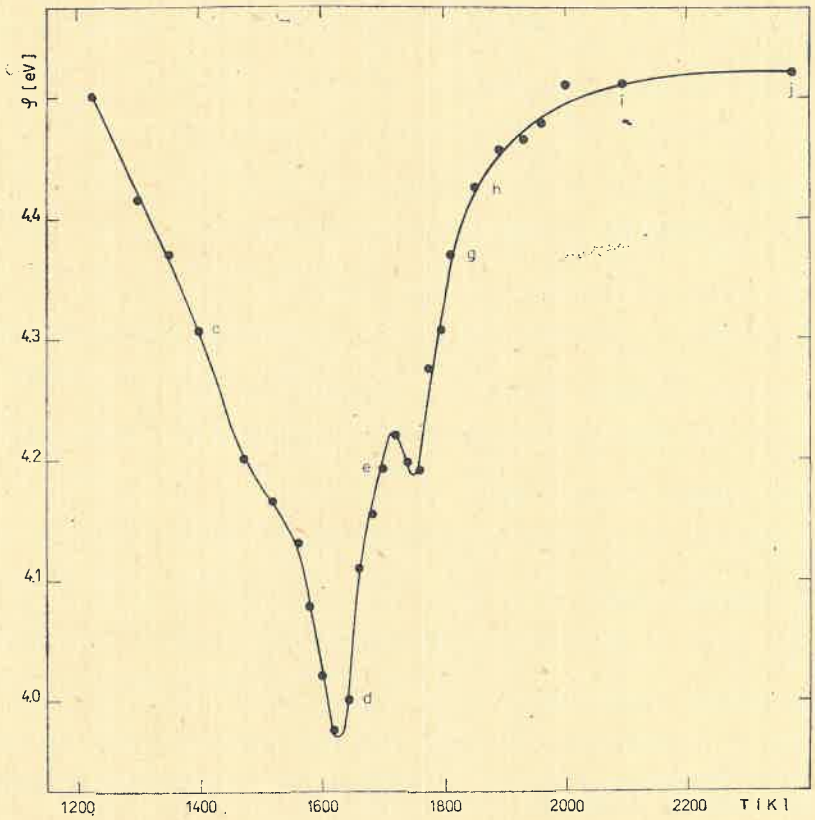

Fig. 4. The effect of heating of the thick carbon layer on the apparent work function change. The layer was heated for 5 minutes at indicated temperatures. The letters b-j correspond to the patterns of Fig. 3

for 5 minutes with no electric field applied. In the second stage, beginning at a temperature of ca. 1625 K, the image contrast between "collars" surrounding the {112} and {011} faces and remaining parts of the emitter surface diminishes (Fig. 3e-i). This is probably caused mainly by the evaporation of carbon. The progressive diminishing of the "collars" and their vanishing is obtained at increasing temperatures in a pattern (i). A clean surface of the tungsten emitter (j) was obtained by heating at a temperature of ca. 2400 K for some minutes. Characteristic crystal faces {334} [1, 10, 12, 14] in the {111} vicinity are very well visible in photographs (f) and (g). Their size decreases with increasing temperature and they vanished after heating the tungsten emitter to a temperature of about 1800 K. The increase in work function observed in this stage is also apparent. In fact, the geometri-

cal factor, β, is reduced due to the disappearence of carbon protrusions formed on the even surface of the tungsten emitter. The changes of work function instead of those of β are shown in Fig. 4 for the purpose of a convenient comparison with previous data [1, 6].

Larger apparent changes of the work function and the more complicated shape of the curve, Fig. 5, were obtained by heating smaller amounts of carbon. Corresponding FEM patterns, Fig. 6, show a decrease in the diameters of rings surrounding the {112} crystal faces and a disappearing of the three divided "collars" around the {011} crystal

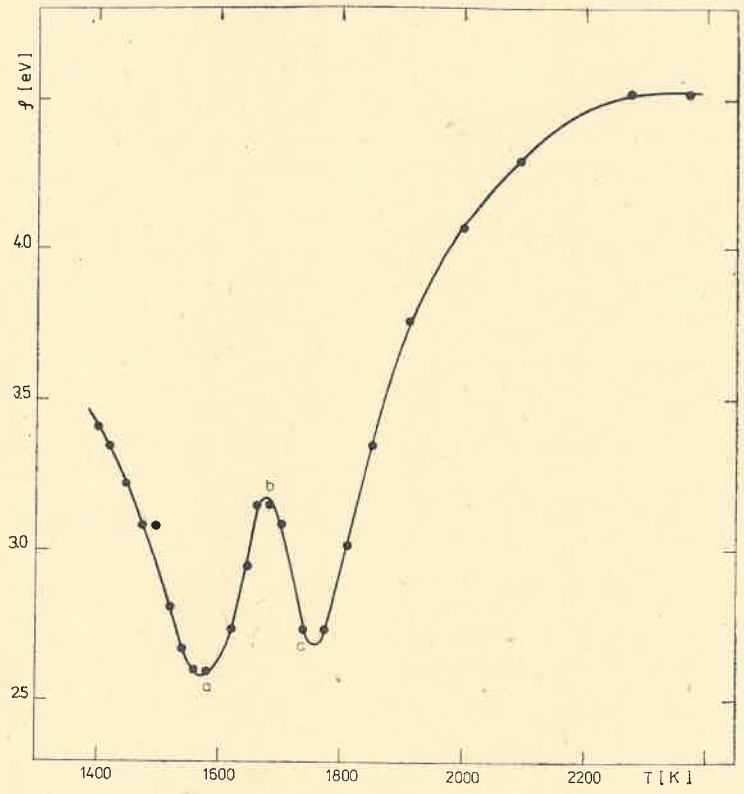

Fig. 5. The effect of heating of the thin carbon layer on the apparent work function change. The layer was heated for 5 minutes at the indicated temperatures. The letters a-c correspond to the patterns of Fig. 6

face of tungsten. In other words, the "smoothing" of the ribbed pattern structure and the image contrast become visible. After further evaporation of the adsorbate and the rearrangement of carbon atoms at higher temperatures, the thin and well resolved single "collars", which surround the {011} crystal face, were observed, Fig. 6c. This resulted in another apparent, appreciable decrease in the work function. The shapes of the curves in Fig. 4 and 5 are most probably to some extent connected with the penetration of the carbon into the bulk substrate [4, 14] upon the heating of the carbon layer at lower temperatures and on the segregation of the carbon at higher temperatures [14]. Thus, the details of the

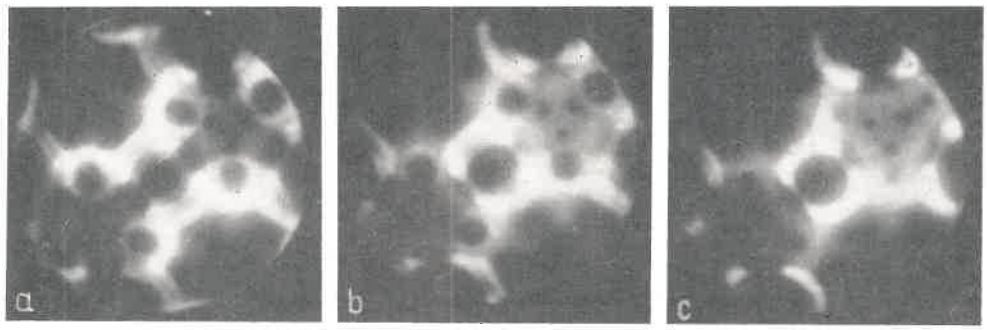

Fig. 6. Field emission patterns of a thick carbon layer heated for 5 minutes at temperatures of (a) about 1590 K, (b) 1690 K and (c) 1730 K

work function vs the coverage curve can be related with the changes in the geometry of the emitter clearly visible in the emission patterns. The carbonisation apparently plays a smaller role. The formation of carbides was not observed.

4. Conclusions

The carbon doses, forming a coverage not larger than one or two monolayers, can be "uniformly" spread at 1000 K over a tungsten emitter surface. For these layers the true change of work function is measured, which increases monotonically up to a value of 4.7 ± 0.05 eV with increasing coverage. Larger carbon doses do not form uniform layers. Carbon is agglomerating in preferential sites forming protrusions and leads to a considerable apparent decrease in work function which indicates that the protrusions are relatively high. Raising the temperature up to about 1600 K results in a progressive enhancement of these protrusions. The size of carbon protrusions decreases at heating at temperatures exceeding 1600 K. Heating at a temperature of 2400 K for some minutes leads to the complete cleaning of the emitter.

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