ADSORPTION OF SILICON AND CARBON ON TUNGSTEN

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The adsorption of silicon and carbon on tungsten has been investigated by means of the electron field-emission microscope. It was found that for small degree of coverage the work function increases continuously with increasing amount of adsorbate; for higher coverages the work function approaches a constant value which is close to the values of the work function for bulk silicon and carbon (graphite), respectively.

For the thicker layers $\varphi_{W-Si} = 5.0 \pm 0.1$ eV and $\varphi_{W-C} = 4.7 \pm 0.05$ eV.

1. Introduction

During the past few years several papers have appeared in which the adsorption of the semiconductors on tungsten was investigated. The results obtained by different authors differ essentially. These differences can be observed first of all in the dependence of the work function on the thickness of the adsorbed semiconductor layer. In Ref. [4] the dependence of the work function on the coverage was measured using the method of the Fowler-Nordheim (F-N) plot. In two groups of the F-N plots obtained in case of low coverages the F-N plots are parallel to those for clean tungsten what means that the work function does not change in this coverages range, *i.e.*, it remains the same as the work function for clean tungsten. For higher coverages the slope of the plots increases which corresponds to the increase of the work function from 4.5 to 5.1 eV. In Ref. [8] it was shown that if one increases the coverage the slope of the F-N plots and thus the work function increases starting from very low coverages, then passes through a maximum and reaches the value of $\varphi = 4.7$ eV for higher coverages.

Similar differences in the dependence of the work function on the coverage have been observed for the adsorption of germanium on tungsten [1, 3, 7].

This discrepancy of results shows the necessity of further experimental investigation of the properties of adsorption systems metal-semiconductor. The present paper is devoted to the tungsten-silicon and tungsten-carbon systems. In particular the measurements of the dependence of the work function on the degree of coverage has been performed. This dependence for the tungsten-carbon system has not been measured so far [11, 12]. Since

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carbon is in the same group of the periodic table as silicon and germanium the study of such system may contribute to the explanation of the dependences obtained in case of the latter elements.

2. *Apparatus and method*

The observation and the measurements were carried out using the electron field-emission microscope sealed off from the vacuum line. Zone-refined silicon was deposited by evaporation from a crucible made of tungsten wire covered with aluminium oxide. During the deposition of silicon on the emitter the pressure of the residual gas did not exceed $5 \cdot 10^{-10}$ Tr. The deposition of carbon has been achieved by the bombardment of graphite by high energy electrons. The lump of graphite was supported by tungsten wire. Close to it there was a tungsten wire spiral which served as the source of the thermoelectrons. The whole set-up was surrounded by tungsten or tantalum cylinder in order to minimize the heat losses. In the last stage of outgassing the graphite was heated up to the temperature of 2600 K at which a detectable evaporation of carbon takes place. In order to achieve good vacuum the electron field-emission microscope together with the carbon source were immersed in liquid nitrogen. During the deposition of carbon on the emitter the pressure of the residual gas did not exceed $3 \cdot 10^{-10}$ Tr.

Silicon and carbon were deposited on the tip kept at room temperature. The silicon and carbon sources were located in a separate bulb connected with the main part of the microscope so that the atomic beam falls from side (perpendicularly to the emitter axis) and covers a part of the emitter surface. Deposition of the adsorbate on one side only permits the check whether the remaining part of the emitter is or is not covered by residual gas. The adsorbed portion of the adsorbate was spread over the tip surface by heating it up. Silicon was heated to the temperature of 900 K, carbon — up to about 1000 K. It was assumed that the number of the adsorbed atoms is proportional to the deposition time. Absolute determination of the atomic concentration is very difficult. In order to make the F-N plot the emission currents were measured in the range from 10^{-8} to 10^{-6}A. Assuming the average work function for tungsten as equal to $\varphi = 4.5$ eV the work function for the tungsten-adsorbate system has been determined from the well-known formula [13]:

$$\varphi_* = \varphi \left(\frac{\alpha_*}{\alpha} \right)^{2/3}$$

where φ_* and φ are the average work function values for the substrate covered with adsorbate and clean substrate, respectively α_* and α the corresponding slopes of F-N plots. The measurements discussed in this paper have been carried out using several emitters.

3. *Results*

Deposition of a silicon portion on the tungsten emitter causes a decrease in the emission current. In Fig. 1a the F-N plots are presented for the adsorption layers of silicon of different thickness.

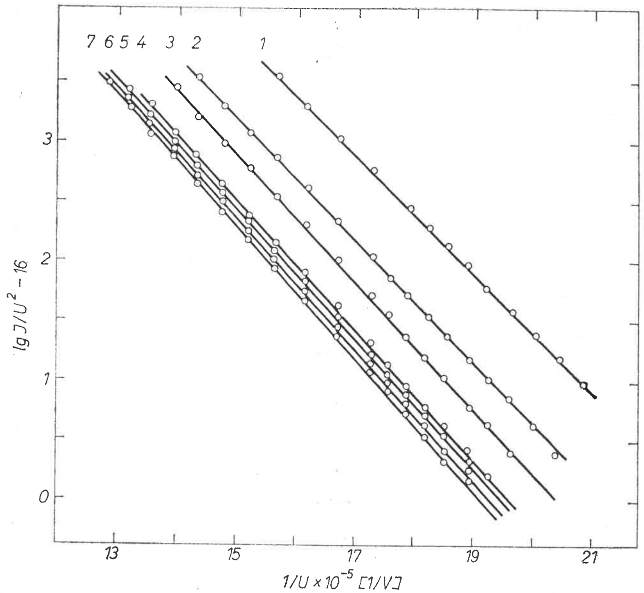

Fig. 1a

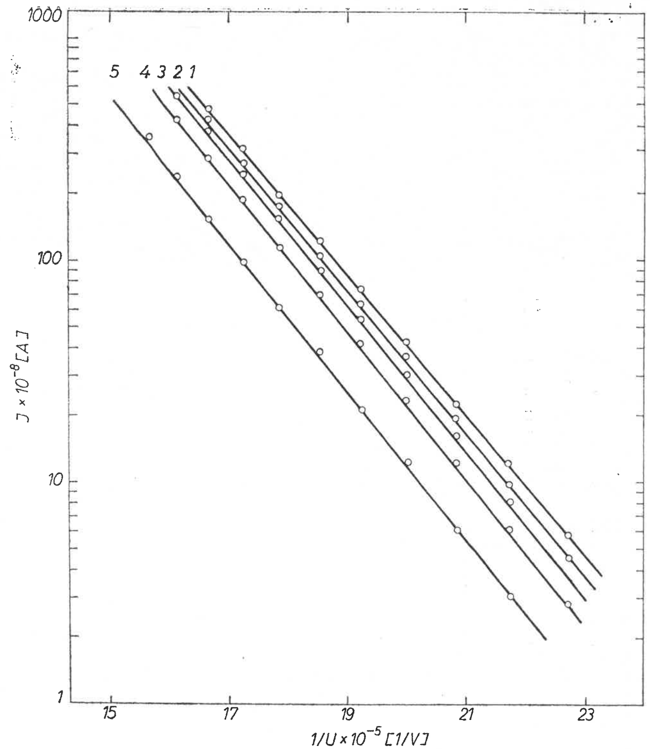

Fig. 1b

Fig. 1a. The F–N characteristics for tungsten covered with various portions of silicon: *1* — clean tungsten, *2* — 1 minute of evaporation, *3* — 2 minutes of evaporation, *4* — 4 minutes of evaporation, *5* — 6 minutes of evaporation, *6* — 10 minutes of evaporation, *7* — 20 minutes of evaporation
Fig. 1b. The F–N characteristics for tungsten covered with various portions of carbon: *1* — clean tungsten, *2* — 0.5 minutes of evaporation, *3* — 1 minutes of evaporation, *4* — 1.5 minutes of evaporation, *5* — 2 minutes of evaporation

The F-N plots systematically increase their slope as the amount of silicon increases. For large partions they remain parallel to one another within the limits of errors. Using the slope values the average work function values were calculated for the tungsten-silicon system. The results thus obtained are presented in Fig. 2a. For low coverages the work

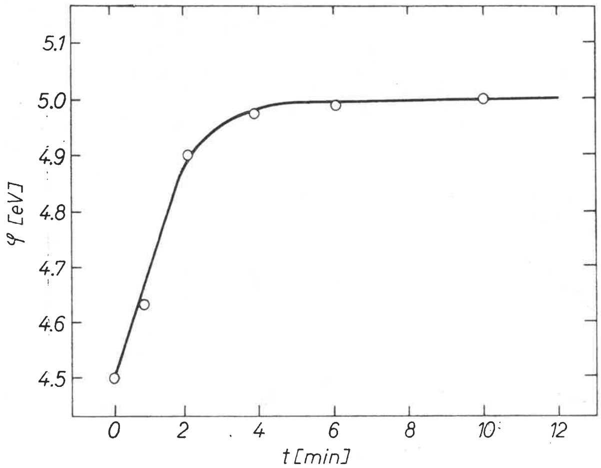

Fig. 2a. Dependence of the work function of tungsten on silicon evaporation time

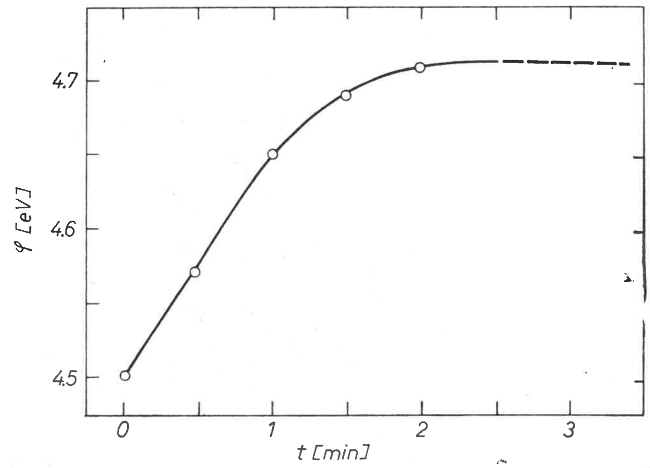

Fig. 2b. Dependence of work function on carbon evaporation time

function significantly increases, for higher ones it becomes constant and reaches the value of $\varphi_{W-Si} = 5.0 \pm 0.1$ eV.

Similar measurements have been carried out for the tungsten-carbon adsorption system. Carbon diminishes the tungsten emission very little. In connection with this the shift of the plots and the change in their slope are very small. A typical family of plots is presented in Fig. 1b. Similarly as for silicon the average work function systematically increases with the time of carbon deposition, for the thicker layer it approaches a constant value (Fig. 2b). From the measurements carried out on several emitters it follows that the average work function for the thick carbon layer reaches the value of $\varphi_{W-C} = 4.7 \pm 0.05$ eV.

4. *Discussion*

The thickness of the silicon and carbon layers obtained by adsorption is not precisely known. The density of the adsorbed atoms can, however, be estimated from the character of the diffusion of adsorbate deposited on one side of the tip. Such estimation has been made, *e.g.* in case of oxygen [14] and germanium [1]. It is also possible to state basing on observations of the diffusion of silicon [15] and carbon [16] that the smallest portion of both of these elements for which the diffusion process occurs with a sharp boundary through the whole surface of the emitter, covers the emitter with one to two monolayers. In case of silicon and carbon such a layer has been obtained after 6 and 2 minutes of evaporation (Figs 2a and 2b), respectively. Thus the results obtained indicate that small portions of silicon, probably several times smaller than that necessary for the formation of monolayer, cause a considerable increase of the slope of the F-N plots (lines *2* and *3* in Fig. 1a), while the work function increases approximately proportional to the degree of coverage (Fig. 2a). A similar character of changes of the work function has been observed in Ref. [8]. The systematic increase of the slope of the F-N plot appears to be present also for tungsten covered with very small amount of carbon (lines *2* and *3* in Fig. 1b) in spite of the small difference in the work function values for tungsten and carbon (Fig. 2b). Among the many measurements carried out for the different emitters one did not observe the F-N plots parallel to those of clean tungsten and also the broken lines which were observed for silicon [4] and for germanium [1, 3].

Starting from the smallest portion of silicon, for which the diffusion occurs with a sharp boundary over the whole emitter surface, *i.e.*, for the silicon layer estimated as 1 or 2-atomic, the work function attains the constant values of $\varphi_{W-Si} = 5.0 \pm 0.1$ eV. This value agrees within the errors with the value of 5.1 eV, obtained in Ref. [4] and is reasonably consistent with the data found for bulk silicon [17].

The value of the work function of 4.7 eV, obtained in [8] is substantially lower. This result was probably influenced by the increased electric field, caused by granulation of the thick silicon layer, which was also noticed by the author himself. Similar effect has been observed in Ref. [18].

The character of the changes of the work function with the increase of the coverage of carbon is similar to that of silicon (Fig. 2b). The curve approaches asymptotically the value of $\varphi_{W-C} = 4.7 \pm 0.05$ eV which agrees exactly with the value 4.7 eV proposed for graphite [10]. The measurements were not carried out for thick carbon layers because of the difficulties in spreading out the large amount of carbon. The F-N plots and the changes of the value of the work function obtained in this work do not require the assumption of the semiconductive character of the thin silicon and carbon film on tungsten. According to the Dobretsov idea [19] it is unlikely that the one or two monolayers of silicon or carbon has semiconductive properties, as it was suggested in order to explain the peculiar results obtained for silicon [4, 5] and germanium [1, 3]. The systematic increase of the work function observed for the thir layers is probably induced by the electronegative character of silicon and carbon with respect to tungsten.

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