COADSORPTION OF NICKEL AND POTASSIUM ON TUNGSTEN PART I: AVERAGE WORK FUNCTION CHANGE*

By M. Błaszczyszyn and R. Błaszczyszyn

Institute of Experimental Physics, Wrocław University**

(Received October 6, 1977; revised version received May 6, 1978)

Field emission microscopy was used for a preliminary study of the adsorption of potassium atoms on nickel-covered tungsten. For various nickel coverages, θ_{Ni}, over the interval, $0 < \theta_{Ni} < 2$, the general form of the dependence of the average work function on potassium coverage ($\phi_{K/Ni/W}$ vs θ_K) does not vary; $\phi_{K/Ni/W}$ first decreases and then passes through a minimum (ϕ_{min}). It finally attains a constant value, (ϕ_s), with the amount of potassium. The adsorption of nickel on tungsten leads to an increase of ϕ_{min} for $\theta_{Ni} \approx 1$. The adsorption of nickel on tungsten also causes an increase in ϕ_s over the interval $0 < \theta_{Ni} < 2$. Our results suggest that in the potassium high coverage region the potassium adlayer has specific metallic properties which depend on the atomic structure of the substrate.

1. Introduction

In the last decades, the adsorption of alkali metals on the surface of various metals was intensively investigated for fundamental studies of the adsorption. The main objective of both the experimental and theoretical studies has been to investigate dependence of the work function, ϕ, on alkali metal coverage, θ. The chief characteristic of this dependence is the occurrence of a minimum in the curve $\phi = f(\theta)$ and, with a further increase in θ up to 1, there is a saturation of the work function value. $\theta = 1$ is usually ascribed to the saturation of the work function. According to Wojciechowski's considerations [2], for larger coverages than about 0.8, the alkali metal adlayer has properties similar to the bulk alkali metal. Data for potassium adsorption on Ta, Mo [3], W [4] and Re [16] indicate that the average work function minimum, (ϕ_{min}), corresponding to a coverage in the range of 0.64 to 0.76, exhibits no distinct dependence on the type of substrate. Similarly, results for these adsorption system suggest that, within the high coverage limit, the average work function of the potassium layer, (ϕ_s), is essentially identical to that of the bulk potassium metal (Table I).

* This work was supported by the Polish Academy of Sciences within the research project MR.I.-9.

** Address: Instytut Fizyki Doświadczalnej, Uniwersytet Wrocławski, Cybulskiego 36, 50-205 Wrocław, Poland.

Since the data for potassium adsorption refer to substrates with approximately similar structures, we have investigated the influence of the variation of this structure on the adsorption process of potassium. In this study the structure of tungsten substrate was varied

TABLE I

Experimental data (see Ref. [3]) for potassium adsorption illustrating that ϕ_{min} and ϕ_s are not strongly dependent on the work function of the substrate, ϕ_{sub}

Substrate	ϕ_{sub} (eV)	ϕ_{min} (eV)	ϕ_s (eV)
W	4.50	1.65±0.05	2.20
		1.78±0.02	—
Ta	4.12	1.73±0.05	2.26
Mo	4.20	1.76±0.05	2.14
Re	4.85	1.72 (Ref. [16])	2.18 (Ref. [16])
K	2.20	—	—

by the adsorption of nickel on tungsten. We used nickel because nickel adatoms with their smaller atomic radius "feel" the roughness of the tungsten substrate, the atomic radii are 1.24 Å and 1.41 Å for nickel and tungsten, respectively. Furthermore, some basic data are available for the systems of K/W [4, 5] and Ni/W [6, 8].

2. Experimental apparatus and procedures

The majority of experiments were made using a very simple field emission Müller-type tube equipped with potassium and nickel sources, the Bayard-Alpert gauge and an ion getter pump. The tube was evacuated and baked out before being sealed-off. After several hours of pumping with the ion getter pump the vacuum reached about 1×10^{-10} Torr. Potassium was deposited onto the tip from a glass ampoule. The temperature of the ampoule was maintained constant by a thermostat operated on a glycerine bath. The nickel source was composed of two pieces of nickel wire spot-welded to two crossed tungsten loops.

Additional experiments were performed using a field emission tube with an emitter rotating about its center. This tube was used to investigate the coadsorption of nickel and potassium on single planes of tungsten. This tube was similar in construction to that used by Błaszczyszyn et al. [4]. During the measurements the entire field emission tube was immersed in liquid nitrogen. The residual gas pressure was less than 1×10^{-11} Torr.

Nickel was deposited onto the tungsten tip held at 300 K. After heating to 860 K (or 450 K for some measurements) to produce an equilibrated nickel layer, a dose of potassium was condensed on the tip held at 350 K.

Work function changes were evaluated from field emission current-voltage data using the Fowler-Nordheim equation and assuming the average work function of clean tungsten to be 4.5 eV.

3. Experimental results

In Fig. 1 the average work function of the thermally cleaned tungsten substrate versus the time of nickel evaporation, t/t_{max} is shown. If we assume that the maximum of the curve corresponds to a coverage, $\theta_{Ni} = 1$ [6], then a non-dimensional unit of t/t_{max} represents the average coverage, θ_{Ni}. The value of θ_{Ni} was determined by Jones and

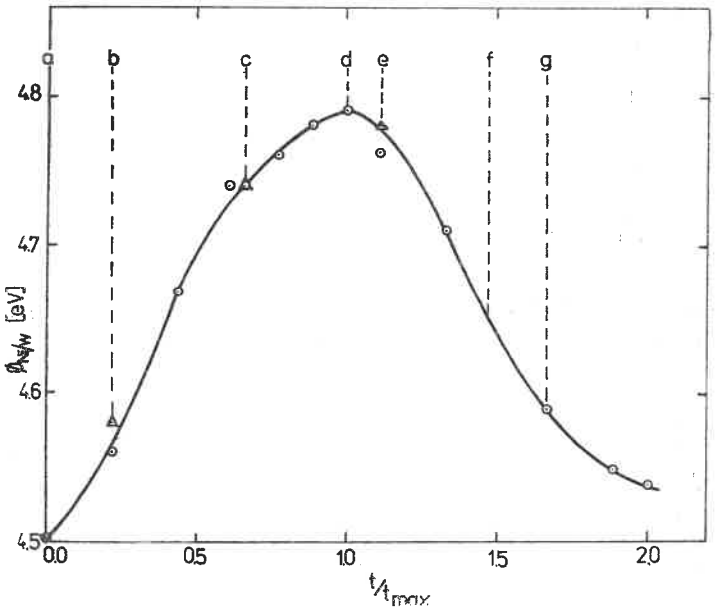

Fig. 1. Work function, $\phi_{Ni/W}$, of the thermally cleaned tungsten tip versus time of nickel evaporation t, where t_{max} is the time corresponding to the maximum of the average work function for the Ni/W system. The symbols ○ and Δ represent the data calculated from slopes of the Fowler-Nordhein plots and from the formula $\phi = \phi_0(U/U_0)^{2/3}$, respectively

Martin [6] as the ratio of the mean density of surface nickel atoms to that of surface tungsten atoms. The first row of field emission images (Fig. 3) illustrates the patterns which correspond to the points designated as a, b, c, etc. in Fig. 1.

Our measurements indicate that for various nickel coverage the general form of the dependence of the average work function, $\phi_{K/Ni/W}$, on potassium coverage, (θ_K) does not vary. For example, as shown in Fig. 2, the curve for the change of work function, $\Delta\phi_{K/Ni/W}$, for $\theta_{Ni} = 1$ has the characteristic shape for potassium metal deposited on clean tungsten [4]. $\Delta\phi_{K/Ni/W}$ is the difference between the average work function of the nickel-covered tungsten and the average work function corresponding to a coverage of θ_K of this nickel-covered tungsten surface. With an increase in the potassium coverage, the average work function decreases rapidly from its initially high value, then it reaches a minimum and finally rises to an approximately constant value. The points marked d, d_l, d_{min}, d_s in Fig. 2. correspond to the column d of the field emission patterns shown in Fig. 3. The symbols l, min, s, are equivalent to a low potassium coverage, ($\theta_K \approx 0.24$), to a maximum work function change, ($\theta_K \approx 0.70$), and to the high potassium coverage

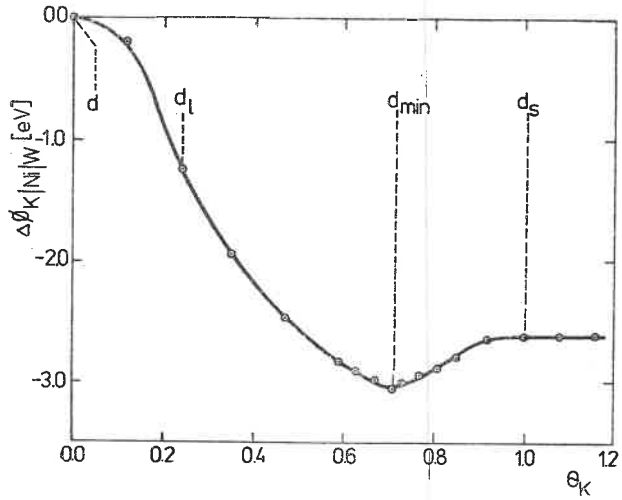

Fig. 2. Work function change, $\Delta\phi_{K/Ni/W}$, versus potassium coverage, θ_K for nickel covered tungsten at $\theta_{Ni} = 1$. The marked points (d, d_l, d_{min} and d_s) correspond to the fourth column of Fig. 3

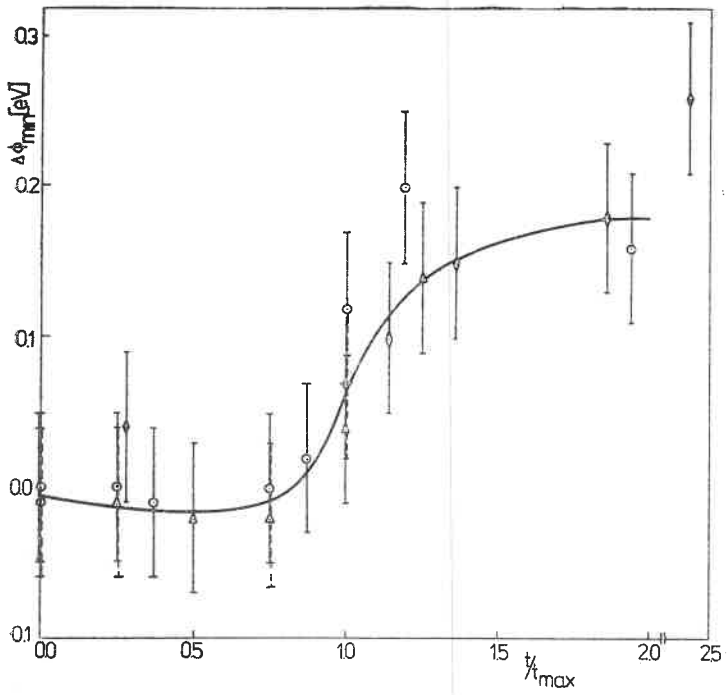

Fig. 4. Variation in the average work function minimum of potassium on nickel-covered tungsten with nickel deposition time at a constant flux. The change in the work function, $\Delta\phi_{min}$, is the difference between the values of the average work function minimum for clean tungsten and nickel-covered tungsten. The error bars represent uncertainties in the calculated results. The symbols ○ and Δ correspond to potassium adsorption after heating the nickel-covered tungsten emitter to 860 K and 450 K, respectively. The symbol ◊ represents data from another emitter at 860 K

limit, ($\theta_K = 1$), respectively, for the K/Ni/W system. The rest of the columns in Fig. 3 show the sequence of field emission patterns observed during the deposition of potassium on the nickel-covered tungsten for other amounts of preadsorbed nickel. The first column of Fig. 3 shows the field emission patterns for potassium adsorbed on the clean tungsten substrates. The field emission patterns observed for potassium adsorbed on a nickel layer are shown in a manner similar to column d for a low potassium coverage (about $\theta_K = 0.25$), an intermediate potassium coverage (about $\theta_K = 0.67$) and a high potassium coverage limit (about $\theta_K = 1$) in the second, third and fourth rows of Fig. 3, respectively.

To simplify the following discussion we concentrated on two characteristic points of the $\Delta\phi_{K/Ni/W}$ vs θ_K relationship. These are a minimum and a constant value at high potassium coverage in each of the work function versus potassium coverage curves. The effect of nickel coverage on the change of the work function minimum, $\Delta\phi_{min}$, is shown in Fig. 4. The $\Delta\phi_{min}$ is the difference between the values of the work function minimum for clean tungsten and nickel covered tungsten. Similarly, the changes of the work function

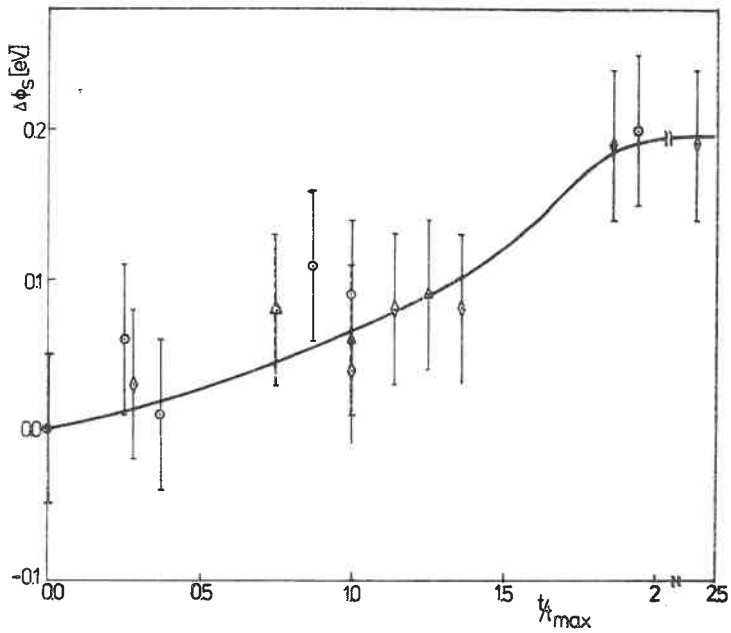

Fig. 5. Variation in the average work function at saturation coverage of potassium on nickel-covered tungsten with nickel deposition time at constant flux. The work function change, $\Delta\phi_s$, is the difference between the values of the average work function at saturation for clean tungsten and nickel-covered tungsten. The error bars represent uncertainties in the calculated results. The symbols ○ and Δ correspond to potas sium adsorption after heating the nickel-covered tungsten emitter to 860 K and 450 K, respectively. The symbol ◊ represents data from another emitter at 860 K

for the potassium high coverage limit, $\Delta\phi_s$, with nickel coverage are shown in Fig. 5. Here, $\Delta\phi_s$ is the difference between the constant value of the work function that corresponds to the potassium high coverage limit for clean tungsten and that for nickel-covered tungsten.

4. Discussion

Although measurements of changes in the average work function do not give a complete knowledge for single planes, the field emission patterns do yield some useful information. In this paper we will also analyse the changes in the average work function during adsorption as the field emission patterns.

The results obtained during the adsorption of nickel on thermally cleaned tungsten agree with those reported by Pichaud and Drechsler [8] and Jones and Martin [6]. As shown in Fig. 1, the $\phi_{Ni/W}$ vs t/t_{max} curve reaches a maximum where the change in $\phi_{Ni/W}$ is about 0.3 eV and the maximum error is less than 0.05 eV. The sequence of field emission patterns associated with this curve is shown in the first row of Fig. 3. The deposition of nickel on tungsten does not cause an essential change in the field emission patterns. It is very probable that the behaviour observed for $\theta_{Ni} < 1$ could be explained in terms of an accumulation of nickel on a region having a lower work function. This will be discussed in a subsequent paper. Although applied field emission microscopy does not give any structural information, the substantial change in $\phi_{Ni/W}$ that occurs at $\theta_{Ni} = 1$ (about 0.3 eV), indicates that the structure of the nickel deposited on the tungsten surface differs from that of the clean tungsten surface. A comparison of results from potassium and nickel coadsorbed on tungsten with results from potassium on tungsten adsorption may give a better understanding of the behaviour of potassium on a tungsten surface.

The fourth row of Fig. 3 shows field emission patterns which correspond to high potassium coverage in each curve of the $\Delta\phi_{K/Ni/W}$ vs θ_K relationship. These patterns were observed when $\Delta\phi_{K/Ni/W}$ approached a constant value. The change of this limiting value with nickel coverage is shown in Fig. 5. These data represent cases at which a potassium adlayer can be treated as surface with nearly the same properties as a surface layer of bulk potassium. This conception was proposed previously [2, 5, 11, 12]. For example, according to Wojciechowski's considerations [2], for coverages greater than about 0.8, the alkali adlayer should have properties similar to the bulk alkali metal. A thorough analysis of the field emission patterns (a_s) to (g_s) in Fig. 3 indicates that the preadsorbed nickel layer causes significant variations in the emission of high index tungsten faces with a further increase of their coverage induced by potassium. Thus, for $0 < \theta_{Ni} < 1$, the continuation of the deposition of nickel atoms first extends the relatively dark vicinity of the (100) and (110) planes. An addition of further nickel atoms causes a progressive decrease of these dark regions (for $\theta_{Ni} > 1$). These observations indicate that the work function in the vicinity of the (100) and (110) planes rises initially and then decreases. Similarly, from the patterns (a_l) to (g_l) of Fig. 3, it is seen that the greatest changes in field emission appear for high index tungsten faces for a low potassium coverage. An explanation of this is to be given below. Comparing this observation with the change of the work function, $\Delta\phi_s$ (Fig. 5), we may conclude that in the potassium high coverage limit, the potassium layer has specific metallic properties that depend on the atomic structure of the substrate.

The third row in Fig. 3 shows field emission patterns which correspond to a minimum in each curve of the $\Delta\phi_{K/Ni/W}$ vs θ_K relationship. The change of the work function minimum with nickel coverage is shown in Fig. 4. Patterns (a_{min}) to (d_{min}) in Fig. 3 for $0 < \theta_{Ni} < 1$

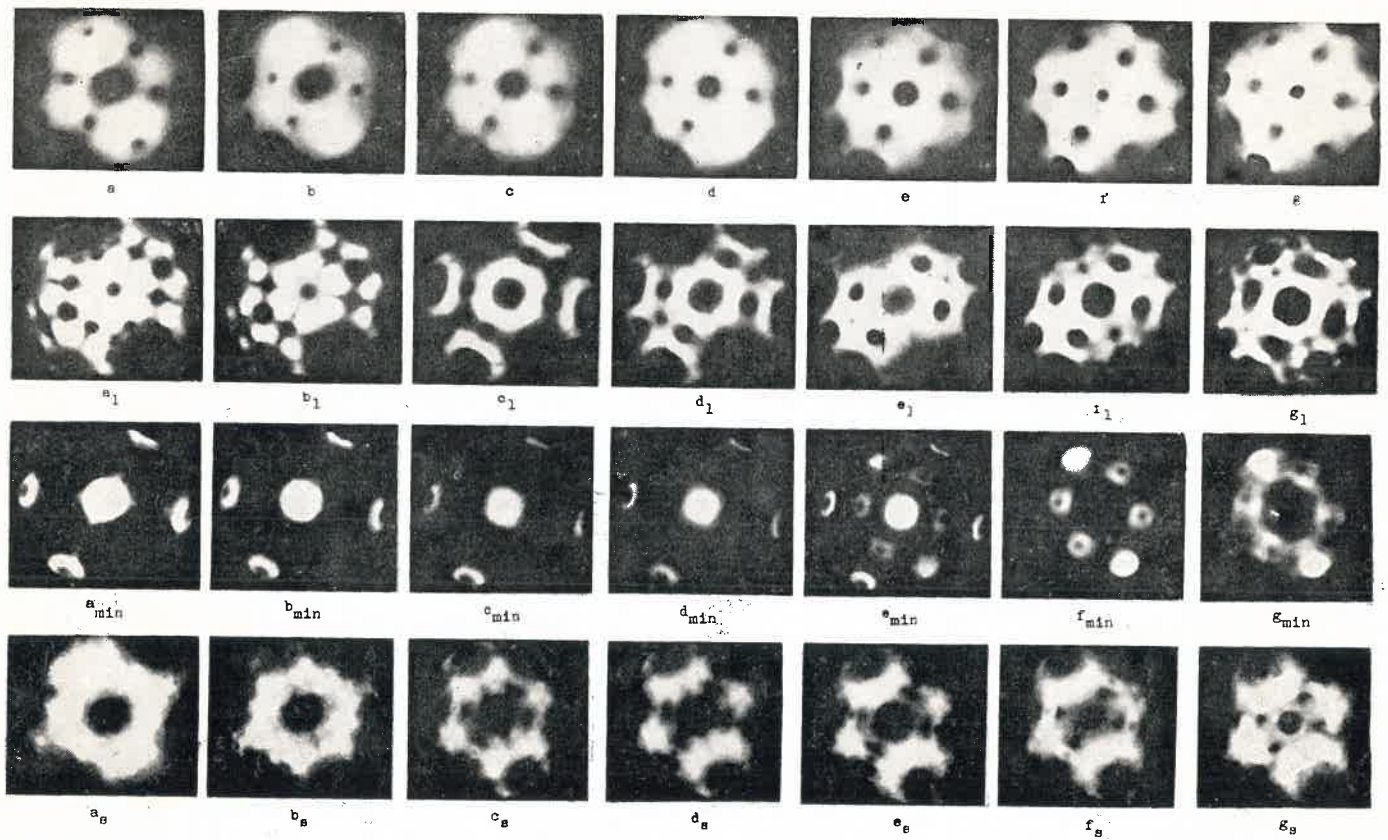

Fig. 3. Field emission patterns of potassium on nickel-covered tungsten. Patterns a, b, c, d, e, f and g — nickel on thermally cleaned tungsten: a — clean tungsten, b — $\theta_{Ni} = 0.22$, c — $\theta_{Ni} = 0.67$, d — $\theta_{Ni} = 1$, e — $\theta_{Ni} = 1.11$, f — $\theta_{Ni} = 1.47$, g — $\theta_{Ni} = 1.67$. Patterns (a_l), (a_{min}) and (a_s) — potassium on the thermally cleaned tungsten: (a_l) $\theta_K = 0.25$, (a_{min}) $\theta_K = 0.67$, (a_s) $\theta_K = 1$. The successive columns show the field emission patterns of potassium on nickel-covered tungsten. The symbols l, min, s, correspond to a low potassium coverage (about $\theta_K = 0.25$), to a maximum work function change (about $\theta_K^* = 0.67$) and to the high potassium coverage limit ($\theta_K = 1$), respectively, for the K/Ni/W system

indicate that the emission occurs only from the (110) tungsten planes. Therefore, on the basis of Fig. 4 where $\Delta\phi_{min}$ for $\theta_{Ni} < 1$ has a constant value, we conclude that the work function minima for the (110) tungsten planes remain constant in this nickel coverage range. Further nickel doses generally reduce the emission from the (110) planes and progressively increase the emission from the (100) and (112) planes (patterns (f_{min}) and (g_{min}) of Fig. 3), raise the values of the average work function minimum about 0.2 eV, Fig. 3(b). The increase in the average work function minimum is associated with the rise of the work function minimum for the (110) planes. A possible explanation for this observation is that the addition of extra nickel atoms leads to the formation of a rough nickel adlayer on the (110) tungsten crystal planes, where in the case of potassium adsorption, the value of the work function minimum is greater than that for the smooth, clean (110) tungsten plane. On the other hand, for $0 < \theta_{Ni} < 1$, the nickel adatoms omit the (110) planes and occupy the rough high index tungsten faces. This would also explain the invariable work function minimum for the (110) planes for this nickel coverage range (Fig. 4). This observation is in agreement with our preliminary results of studies for the (110) tungsten planes with adsorbed, thermally equilibrated nickel, where work funcion persists essentially unchanged for the small nickel coverage.

It seems that the adsorption of nickel on the rough tungsten planes smooths them and decreases the values of the work function minimum for these planes for the K/Ni/W system. This interpretation is illustrated by the pattern, (f_{min}), of Fig. 3. Thus, a similar intensity of the emission from the (100) and (112) planes corresponds to either reduction of the work function minimum for the (112) planes (the smoothing process) or increase in that for the (100) planes (the roughing process) or else one and the other. The work function minimum for the clean tungsten (112) and (100) planes covered with the potassium adsorbate is 1.95 eV and 1.75 eV, respectively. Data for the adsorption of potassium on the pure single crystal planes of Ta, Mo and W show a similar dependence. That is the work function minimum is determined by the atomic structure of a single plane [3, 4].

The above observations concerning the variations in emission of high index tungsten faces shown in patterns (a_1) to (g_1) in Fig. 3 appear to be explained by the process of smoothing the faces. The adsorption of nickel on the rough tungsten planes that results in smoothing them, raises the values of the work function which correspond to the potassium high coverage limit. For a careful consideration of this problem further studies of the potassium and nickel coadsorption for single tungsten crystal planes are needed. Nevertheless some general suggestions may be formulated.

It has been often suggested that in high alkali coverage regions some properties, e.g., work function and heat of evaporation of the alkali adsorbate layer are similar to those of the surface of an alkali metal crystal. Our results tend to indicate that these properties are specific for an alkali metal layer which has a nearly free electron gas. However, the atomic structure of the layer is modulated by the atomic substrate. Therefore, the alkali monolayer which is adsorbed on a metal substrate can have an atomic structure different from that of the bulk alkali metals. For example, an incoherent hexagonal, closely packed surface structure with Cs on W(110) [14] and also with Na on Ni(111) and Ni(110) at high coverages [15] were observed.

Jones [7] suggested that the increase in work function for the adsorption of nickel on tungsten is caused by forming nickel-tungsten dipoles with the nickel adatoms negatively charged. It seems that another explanation can be given. That is, nickel atoms occupy the "valley" sites in the rough tungsten planes and cause an increase in the work function [9]. On the smooth, densely packed planes the increase in the nickel coverage lowers the extent for smoothness thereby decreasing the work function. Polański and Sidorski [10] proposed this model as an explanation of the work function variation caused by deposition of copper with an atomic radius of 1.27 Å on tungsten.

The authors would like to thank their scientific guide, Professor Dr. habil. R. Męclewski. We also thank Mr. S. Surma for critical reading of the manuscript.

REFERENCES

[1] N. D. Lang, *Phys. Rev.* **B4**, 4234, (1971).
[2] K. F. Wojciechowski, *Surf. Sci.* **55**, 246 (1976).
[3] M. Błaszczyszyn, *Surf. Sci.* **59**, 533 (1976).
[4] R. Błaszczyszyn, M. Błaszczyszyn, R. Męclewski, *Surf. Sci.* **51**, 396 (1975).
[5] L. Schmidt, R. Gomer, *J. Chem. Phys.* **42**, 3573 (1965); L. Schmidt, R. Gomer, *J. Chem. Phys.* **45**, 1905 (1966).
[6] J. P. Jones, A. D. Martin, *Surf. Sci.* **41**, 559 (1974).
[7] J. P. Jones, *Surf. Sci.* **32**, 29 (1972).
[8] M. Pichaud, M. Drechsler, *Surf. Sci.* **36**, 813 (1973).
[9] R. Smoluchowski, *Phys. Rev.* **60**, 661 (1941).
[10] J. Polański, Z. Sidorski, *Surf. Sci.* **40**, 282 (1973).
[11] N. D. Lang, W. Kohn, *Phys. Rev.* **B3**, 1215 (1971).
[12] Z. Sidorski, K. F. Wojciechowski, *Acta Phys. Pol.* **A40**, 661 (1971).
[13] Z. Sidorski, *Acta Phys. Pol.* **A42**, 437 (1972).
[14] A. C. Fedorus, A. G. Naumovets, *Surf. Sci.* **21**, 426 (1970).
[15] R. L. Gerlach, T. N. Rhodin, *Surf. Sci.* **17**, 32 (1969).
[16] A. Dąbrowski, *Acta Phys. Pol.* **A52**, 55 (1977).