

**TPD STUDY OF CARBON MONOXIDE INTERACTION
WITH Pd/Nb BIMETALLIC SYSTEM**

Tomas JIRSAK, Vladimir NIKOLAJENKO and Zlatko KNOR

*The J. Heyrovsky Institute of Physical Chemistry,**Academy of Sciences of the Czech Republic, 182 23 Prague 8, The Czech Republic*

Received January 19, 1994

Accepted March 23, 1994

Chemisorption properties of thin films of Pd evaporated onto Nb recrystallized-foil surface have been studied by temperature-programmed desorption (TPD) and by measurement of the work function changes (WFC) at room temperature. TPD results indicate two states of CO adsorbed in dependence on the thickness of the palladium layer. The low temperature state (330 K) occurs at low Pd coverages (about one monolayer). Second state, occurring at slightly higher temperature (370 K), is attributed to bulk Pd. WFC data show negligible change of the work function after deposition of small amounts of Pd onto a clean Nb surface. With increasing amount of Pd, $\Delta\phi$ rises and reaches a saturation value. Adsorption of CO onto Pd/Nb surface caused the work function increase at all coverages of Pd deposited.

During the last decade large attention has been focused on ultrathin metal overlayers on metal substrate. Deposition of one metal onto a surface of a second one can dramatically change physical, chemical and catalytic properties of both constituents. Up to about one monolayer coverage the properties of the deposited metal differ from those of its bulk. A large effect has been found in the case of Pd overlayers on refractory metals Nb (refs¹⁻¹⁰), Ta (refs⁸⁻¹⁸), W (refs^{10,18-28}) and Mo (refs^{10,29-33}).

In general, but not always, the first monolayer of the admetal adopts a lattice constant which differs from its bulk crystal structure and matches coherently the lattice of underlying substrate (pseudomorphic growth). Subsequent layers tend to form the lattice that is closer to the crystal structure of the admetal. This behaviour was also found in the case of the Pd-layer growth on Nb(110). Two phases of Pd deposited onto Nb were observed by LEED technique⁹. First, commensurate (1 × 1) Pd(110) phase occurred up to about a monolayer ($\theta_{\text{Pd}} = 1$). Second phase, incommensurate one, characteristic of bulk (111) Pd was found above 1 monolayer Pd coverage. The commensurate (1 × 1) monolayer of Pd on a Nb(110) surface undergoes a first order structural phase transition to an incommensurate layer Pd(111) structure when the Pd coverage is increased at $\theta_{\text{Pd}} = 1$ by $\Delta\theta_{\text{Pd}} = 0.18$ only³.

Electronic properties of the admetal are perturbed in submonolayer region too. It is generally believed that formation of heteronuclear metal-metal bond induces large

changes in the electron density of both metals. These modifications in electronic structure affect the cohesive energy of the metal-metal bond and the chemical properties of the metal. El-Batanouny et al.⁶ found discrepancy between photoemission energy-distribution curves of two phases of Pd overlayers on (110) Nb surface. In the commensurate (110) phase the Pd 4d band has the high energy edge at about 1.5 eV below the Fermi level E_F similarly as observed with noble metals. In the incommensurate Pd(111) phase the Pd 4d band broadens and its edge shifts to the Fermi level. It can be expected that the perturbation of the electronic structure would modify the chemical properties of the metal overlayers. On transition metals the CO molecule desorbs at temperatures in the range between 300 and 600 K (ref.¹⁰). In contrast, molecular desorption of CO from noble metals occurs at much lower temperatures: for Cu $T_{\text{des}} \approx 200$ K, for Ag and Au $T_{\text{des}} < 100$ K. Therefore in the case of bimetallic systems with the electronic structure similar to that of the noble metals, the desorption temperature is expected to be lower than on transition metals. Several studies have shown that it is indeed so. Weakening of CO adsorption bond has been found on Pd layers deposited onto Mo, W and Ta substrates. TPD data show the decrease of the desorption temperature at monolayer coverage of Pd layers on Mo(100) $T_{\text{des}} \approx 180$ K (ref.³⁰), W(110) $T_{\text{des}} \approx 155$ K (ref.²⁴) and on Ta(110) $T_{\text{des}} \approx 200$ K (ref.¹¹), ≈ 210 K (ref.¹³).

Our paper deals with CO adsorption on Pd/Nb system with different thicknesses of deposited Pd layers. The amount of the desorbed CO and the desorption temperature have been followed by TPD technique. Work function measurements have been applied to monitor Pd deposition, CO adsorption and thermal desorption.

EXPERIMENTAL

Apparatus

Experiments were performed in an UHV stainless steel apparatus with a background pressure of about $5 \cdot 10^{-10}$ Torr (1 Torr = 133.32 Pa). Its block scheme is shown in Fig. 1. The vacuum chamber of the volume ≈ 65 l has been pumped down by a mechanical pump (pumping speed $2 \text{ m}^3 \text{ h}^{-1}$) with liquid nitrogen cooling trap, by a sorption pump and an ion getter pump. The chamber has been baked for 8–10 h. Cooling procedure to the room temperature (after baking) took about 12–14 h. Total pressure was measured in individual ranges by means of a Pirani gauge (10^{-4} –760 Torr) and by a nude Bayard-Alpert gauge (10^{-4} – 10^{-11} Torr). Partial pressures were monitored by a quadrupole mass spectrometer Finnigan 400 equipped with a tungsten cathode. The method of diode characteristics has been used to measure the WFCs after modification of the sample surface due to Pd deposition, carbon monoxide adsorption and thermal desorption. Tungsten wire (diameter 0.11 mm) has been used as a cathode (working temperature ≈ 1500 K) and the sample represented an anode. Their mutual distance was about 2 mm. A schematic top view of the experimental chamber is shown in Fig. 2. X-Y-Z manipulator, enabling also the rotation, makes possible to move the sample to different positions: facing gas dosing system, QMS head for thermal desorption measurement, Pd evaporation source and the tungsten cathode for WFCs measurements.

Sample Preparation

Nb ribbon (12.7×3.15 mm), having the thickness of 0.115 mm, has been used as a sample. It was mounted to the holder by means of two leads at each end of the ribbon. The leads consisted of three Ta wires (each one having diameter of 0.2 mm) spot-welded to the back of the sample (Fig. 2). This allowed resistive heating of the sample to 2 500 K. W-Ta thermocouple^{34,35} has been used to measure the sample temperature in the range of 300 – 2 500 K. The thermocouple was spot-welded to one side of the sample and was calibrated by means of an optical pyrometer. Initially the sample was annealed in vacuum at 2 000 K for 8 h. This procedure had to lower the bulk contamination. A series of short flashes up to 2 500 K has followed to obtain a clean sample surface. The sample was then exposed to oxygen for half an hour at 1 200 K (oxygen pressure of $1 \cdot 10^{-7}$ Torr) to lower the content of carbon dissolved in the bulk of the sample. After the oxygen treatment the sample was repeatedly flashed to 2 500 K again. Such a procedure is described in literature^{1,6-8,36-40} to result in clean niobium surface. Before each experiment the sample was heated twice to 2 400 K for 1 min in order to remove Pd from the previous experiment and to prepare the clean surface. We found that two flashes to 2 400 K after Pd deposition or carbon monoxide dosing are necessary. Subsequent flashing exhibited within the experimental error no further change in the work function of the sample. Recrystallization of Nb foil of thickness 0.025 – 0.127 mm with (110) orientation has been achieved after heating of sample to the temperature 2 200 – 2 500 K (refs.^{1,2,6-9,37}). Sagurton et al.³ have prepared 5 mm-wide-region on a 0.025 mm thick foil even at temperature 1 900 K. It can be assumed on the basis of these experiments that the (110) planes represent the prevailing part of our sample surface. Domains of sizes between 2 and 3 mm were readily observed on the surface by the authors when the sample was removed from the apparatus.

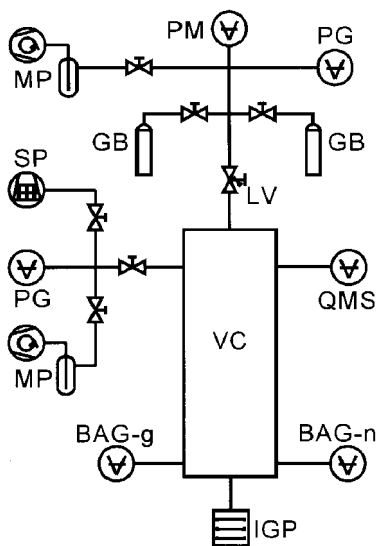


FIG. 1

Block scheme of the apparatus (BAG-g all-glass Bayard–Alpert gauge, BAG-n nude Bayard–Alpert gauge, GB gas bottle, IGP ion getter pump 400 l s^{-1} , LV leak valve, MP mechanical pump ($2 \text{ m}^3 \text{ h}^{-1}$) with liquid nitrogen trap, PG Pirani gauge, PM precision manometer 0 – 2 000 mbar, QMS quadrupole mass spectrometer, SP sorption pump, VC vacuum chamber of volume 65 l)

Deposition of Pd and CO Dosing

Palladium evaporation source (a Pd spiral prepared from a rope, consisting of 4 Pd wires, each one having the diameter of 0.2 mm) has been used for deposition of Pd onto Nb. A glass cone around Pd spiral served as a shield against the evaporation of the metal into the undesired directions. Deposition of Pd has been carried out at the temperature of the sample 320 – 360 K. Total pressure never exceeded $8 \cdot 10^{-10}$ Torr during the Pd deposition. Palladium has been resistively heated for 5 h, using the current $0.6 I_{\text{evap}}$ (where I_{evap} was the electrical current needed for evaporation). Then the current was step by step increased up to deposition value $I_{\text{evap}} \approx 5.5$ A. During oxygen exposure, used for cleaning the surface of the Nb sample, Pd has been kept at room temperature. Carbon monoxide (LINDE, Germany; purity 99.97 %) was introduced into the vacuum chamber through a metal leak valve and the gas was focused onto the sample by a stainless steel capillary (internal diameter ≈ 3 mm) the end of which was at about 20 mm above the sample surface. Saturation exposures 30 L (1 L = 1 langmuir = $1 \cdot 10^{-6}$ Torr s) were used in all our experiments. During carbon monoxide dosing the chamber was filled by CO for 1 min to a pressure of $5 \cdot 10^{-7}$ Torr at the sample temperature of 310 K. Our experiments were performed under dynamic conditions, i.e. ion getter pump has worked continuously. A memory effect of the ion getter pump have been observed during carbon monoxide dosing when the pressure in the chamber rose to $5 \cdot 10^{-7}$ Torr. Main contributions to the total pressure were in this case besides CO the inert gases He and Ne. Both these gases do not influence the results of room temperature experiments described in this paper.

TPD Experiments

After initial flashing the sample was cooled down and Pd was deposited. The deposition time at standardized conditions is used as a measure of the thickness of palladium layers throughout this paper. The temperature of the sample at the end of the Pd deposition has been always 320 K. Subsequently the sample has been exposed to carbon monoxide for 1 min at a pressure of $5 \cdot 10^{-7}$ Torr

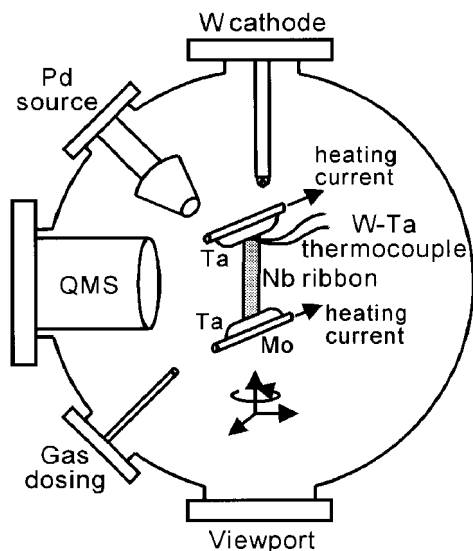


FIG. 2
Schematic view of the vacuum chamber

what corresponds to the exposure of about 30 L. After few minutes, when the pressure returned to the level before the CO dosing, TPD has been carried out. Linear heating rate 6 K s^{-1} has been used in all experiments. The sample has been moved to the position for the work function measurement before and after each step described and the diode characteristics has been recorded.

RESULTS AND DISCUSSION

Temperature-Programmed Desorption

TPD spectra of carbon monoxide obtained on Pd/Nb system as a function of Pd coverage are shown in Fig. 3. Pd has been deposited at a sample temperature of 320 – 360 K and CO has been adsorbed at the sample temperature 310 K. Subsequently, TPD has been carried out. Single desorption state, characterized by the desorption maximum at 335 K, appears when small amounts of Pd are deposited. Its temperature slightly decreases to $\approx 330 \text{ K}$ for the deposition time 1.5 min and it is constant for layers obtained after 1.5 and 3.5 min of deposition. The height and the area of the desorption peak increase with increasing amount of deposited Pd. A high temperature shoulder appears at deposition time longer than 6 min. It rises with the increasing thickness of the palladium layer and becomes dominant at long deposition times, when the initial state appears as a shoulder on the low temperature side of the desorption peak. The dependence of the position of the TPD maximum on deposited amount of Pd is shown in detail in Fig. 4 where the above mentioned two features can be seen.

Adsorption of CO on Pd(111) has been extensively studied by various methods^{41–50}. TPD data show that CO desorbs in range 450 – 500 K with a low temperature shoulder

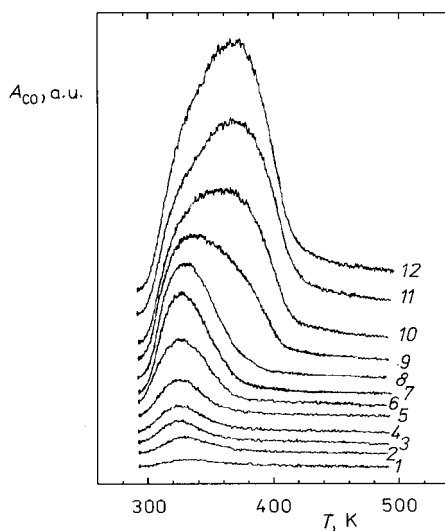


FIG. 3

CO TPD spectra (mass 28) as a function of Pd amount deposited on Nb. Pd deposited at 320 – 360 K, without annealing. CO adsorbed at 310 K (exposure 30 L). Rate of TPD was 6 K s^{-1} . Time of Pd deposition: 1 20 s, 2 40 s, 3 1 min, 4 1 min 40 s, 5 2 min 20 s, 6 3 min 20 s, 7 5 min, 8 6 min 40 s, 9 8 min 20 s, 10 11 min 40 s, 11 16 min 40 s, 12 25 min

at high CO coverages^{42–44}. When Pd is deposited on refractory metals two types of behaviour appear in dependence on thickness of Pd adlayer. At monolayer Pd coverage have been observed properties different from Pd(111). At $\theta_{\text{Pd}} = 1$ TPD maximum was shifted to lower temperatures on Ta(110), W(110) and Mo(110) (see Table I) with respect to the value on bulk sample of Pd(111). Electronic properties of Nb(110) resemble those^{8,9} of Ta(110). Consequently lower desorption temperatures at $\theta_{\text{Pd}} = 1$ on Nb as well as on Ta and on other refractory metals can be expected.

TPD properties of thick Pd layer deposited on refractory metals, approach those of the bulk Pd(111). This occurs on individual substrates (Ta, Mo, W) at different thicknesses of the Pd adlayer (Table I). Berlowitz and Goodman²⁴ have found on Pd/W(110) annealed surface that a shoulder (375 K) appears above one monolayer. It grows slowly with Pd coverage and shifts gradually toward higher temperatures. Bulk Pd properties are not fully established even at $\theta_{\text{Pd}} = 19.5$ at their case. They attribute this shoulder to desorption from the three-dimensional Pd islands. Our results resembles these data. We found a shift of TPD maximum at low Pd coverages (about monolayer) and a shoulder of ≈ 370 K started to appear when Pd layer became thicker.

Figure 5 shows the area of CO desorption peak as a function of Pd amount deposited onto a clean Nb surface. The area increases nearly linearly with the deposition time and saturates above ≈ 18 min. We assume that a monolayer coverage is reached at the evaporation time of about 1.5 – 3 min and that (110) orientation prevails on the Nb substrate. Comparison of deposition times at the saturation value of TPD maxima with that corresponding to one-monolayer region shows that 6 – 10 monolayers are needed to reach the saturation of the temperature maximum. When these data are analyzed, the annealing process has to be considered as well. At room temperature and below it Pd layers are growing on (110) planes of the refractory metals according to the Frank–van der Merwe (FM) growth mode i.e. layer-by-layer (Pd/Ta(110) (ref.¹²), Pd/W(110) (ref.²⁸) and Pd/Mo(110) (ref.³²)). Pseudomorphic monolayers are stable to very high temperatures 1 350 – 1 600 K (refs^{12,13,19,24,28}). On the other hand, agglomer-

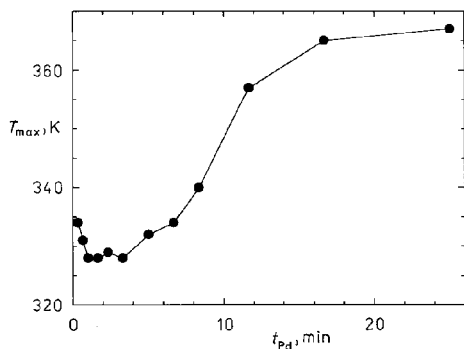


FIG. 4
Temperature maximum (T_{max}) of CO TPD peak (mass 28) as a function of Pd amount deposited on Nb (expressed in deposition time, t_{Pd}). Pd deposited at 320 – 360 K, without annealing. CO adsorbed at 310 K (exposure 30 L). Rate of TPD was 6 K s^{-1} . The data are taken from curves in Fig. 3

ation of Pd into 3D crystallites occurs upon mild heating of the thicker Pd layers (already at 370 – 700 K). Annealing causes the agglomeration of Pd layers into 3D islands on top of the first layer. The first-pseudomorphic layer is partially shielded by thus created palladium 3D clusters and the patches of the first-Pd layer are still accessible for gas CO molecules. It can be seen in Fig. 5 that the area under the desorption peak increases linearly up to about 6 – 10 monolayers. This fact gives evidence that the surface of deposited Pd layer is rough and that its growth does not follow exactly the FM mode. Two factors can influence this departure from FM mode: (i) the exposed surface of the sample does not consist of solely (110) planes and (ii) Stranski–Krastanov (SK) growth mode occurs on this substrate rather than FM mode.

The first factor will be discussed in the following paragraph. Concerning the second factor, agglomeration of thicker Pd layer ($\theta_{\text{Pd}} > 1$) has been observed at very low temperature 370 K (ref.¹²). This value is comparable with the temperature of our sample during the Pd deposition. Therefore the SK growth mode can be expected particularly at longer time of deposition. On the basis of these results we suggest that both described phenomena contribute to the surface roughness at longer deposition time of Pd. We can conclude that high temperature state of adsorbed CO strongly resembles that on bulk Pd samples.

Desorption curves enable to evaluate desorption energies. In the case of the first-order desorption, the relation between the activation energy of desorption E and temperature T_{max} , corresponding to the maximum rate, is given by the following equation^{51,52}

TABLE I
TPD maxima of carbon monoxide on bimetallic systems

System ^a	TPD maximum, K	Ref.
Pd _{1,0} /Ta(110)	≈245	11, 13
Pd _{1,0} /W(110)	300	22
	285	24
Pd _{1,0} /Mo(100)	319	30
Pd _{3,0} /Ta(110)	430	11
Pd _{3,0} /Ta(110)	458	13
Pd ₄₃ /Ta(110)	458	13
Pd _{19,5} /W(110)	≈410	24
Pd ₆ /Mo(110)	435	33
Pd ₂₀ /Mo(100)	483	30

^a Subscript at palladium symbol denotes approximate value of the surface coverage by Pd.

$$\frac{E}{T_{\max}} = R \left(\ln \frac{v_1}{\beta} - \ln \frac{E}{RT_{\max}^2} \right), \quad (1)$$

where R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), v_1 is the preexponential factor (s^{-1}) and β is the linear heating rate of the sample (K s^{-1}). Second-order desorption is described at maximum desorption rate in analogy^{51, 52} with Eq. (1)

$$\frac{E}{T_{\max}} = R \left(\ln \frac{2v_2\theta_m}{\beta} - \ln \frac{E}{RT_{\max}^2} \right), \quad (2)$$

where θ_m is the coverage of particular desorption state at the temperature T_{\max} . It has been empirically shown that the E/T_{\max} ratio is nearly constant and independent of both the metal substrate and the gas adsorbed⁵³. If v_2 does not differ too much from v_1 , Eq. (2) is practically identical with Eq. (1). As an acceptable approximation of the desorption energy one can take $E = cT_{\max}$ ($c = 241 \text{ J K}^{-1} \text{ mol}^{-1}$). In view of these results the activation energy of desorption can be estimated, namely $E = 80 \text{ kJ mol}^{-1}$ and 89 kJ mol^{-1} for the low temperature state ($T_{\max} = 330 \text{ K}$) and the high temperature state ($T_{\max} = 370 \text{ K}$), respectively. The latter value corresponds to data obtained on a Pd(111) surface. Kok et al.⁴³ have obtained activation energy of CO desorption from Pd(111) $E = 112 \text{ kJ mol}^{-1}$ at high CO coverages. This is slightly higher than the value obtained on our polycrystalline samples.

Measurement of the Work Function Changes (WFC)

Figure 6 shows the work function changes ($\Delta\phi$) plotted versus the amount of Pd deposited. Curve 1 represents $\Delta\phi$ measured after the deposition of different amounts of Pd onto a clean Nb surface. Small amounts (corresponding to evaporation times up to about 2 min) cause negligible changes of the work function. WFC ($\Delta\phi$) rises with in-

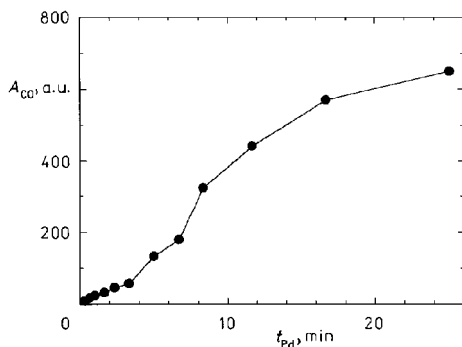


FIG. 5
Area of CO TPD peaks (mass 28) A_{CO} in arbitrary units as a function of Pd amount deposited on Nb (expressed in deposition time t_{Pd}). Pd deposited at 320 – 360 K, without annealing. CO adsorbed at 310 K (exposure 30 L). Rate of TPD was 6 K s^{-1} . The data are taken from curves in Fig. 3

creasing amount of Pd and reaches the limiting value of the evaporation time above ≈ 7 min. This course of $\Delta\phi$ corresponds to the WF values of Nb(110) and Pd(111) ($\phi_{\text{Nb}(110)} = 4.87$ eV and $\phi_{\text{Pd}(111)} = 5.6$ eV (refs^{54,55})). Shang-Li Weng and El-Batanouny⁷ have observed a similar behaviour of $\Delta\phi$ after Pd deposition on Nb(110) foil. They found a slightly negative $\Delta\phi$ up to 0.9 monolayer ($\Delta\phi(\text{Pd}_{0.9}/\text{Nb}) = -0.2$ eV). Above $\text{Pd}_{0.9}$ $\Delta\phi$ increased almost linearly and then reached a saturation value above 3 monolayers⁷.

The method of the WFC measurement used in our experiment yields an average value of $\Delta\phi$ over all surface planes exposed to the gas phase. If one assumes that the WF value at the saturation limit corresponds to the value of Pd(111) plane^{54,55}, the WF of our Nb sample can be estimated to be $\phi \approx 4.55$ eV. The (110) plane of the *bcc* lattice is the most densely packed plane and it exhibits the highest value of ϕ in the case of Nb $\phi = 4.87$ eV (refs^{54,55}). The obtained WF of our Nb substrate $\phi \approx 4.55$ eV suggests that other planes with lower ϕ are also present there.

As it was already mentioned above, one monolayer Pd coverage on refractory metals exhibits different properties from those of the thicker layers (it behaves as a noble metal). Since the work function values of Ag, Cu and Au are all within the range between WF values of Nb and Pd no further conclusions from our measured value of $\phi(\text{Pd}_{1.0}/\text{Nb})$ can be made. However, $\Delta\phi$ caused by CO adsorption on early transition metals differs from that on the noble metals. Carbon monoxide increases ϕ on the former metals, whereas it decreases the WF values on the latter ones. Curve 2 in Fig. 6 shows the WF (compared to WF of clean Nb surface) after CO adsorption on the Nb substrate covered by different Pd amounts. Difference between first and second curve yields the WFCs induced by CO adsorption. Two rough features can be distinguished when this pair of curves is considered. WFC up to about 5 min is about 0.15 eV (difference between the curves) and for longer time of Pd deposition CO causes the $\Delta\phi > 0.3$ eV. It can be seen in Fig. 6 that at low Pd coverages the WFC is lower than

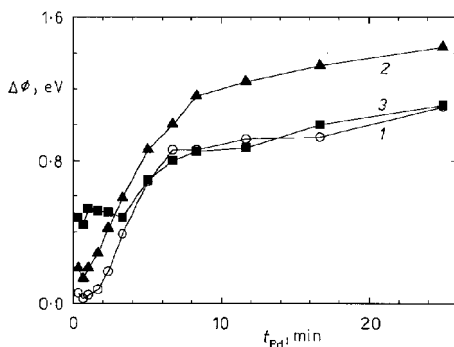


FIG. 6

Work function changes $\Delta\phi$ (reference level: clean Nb surface $\Delta\phi = 0.0$) after Pd deposition on a clean Nb (1), after CO dosing on Pd/Nb (2), after CO TPD from Pd/Nb system (3) as a function of Pd amount deposited (expressed in deposition time t_{Pd}). Pd deposited at 320 – 360 K, without annealing. CO adsorbed at 310 K (exposure 30 L). Rate of TPD was 6 K s^{-1}

on thicker layers. This qualitatively agrees with the $\Delta\phi$ caused by CO adsorption on bulk noble metals (the behaviour of a Pd monolayer corresponds to that of noble metals) and on bulk Pd. However, the absolute value of $\Delta\phi$ at saturation CO coverage on bulk Pd(111) is higher ($\Delta\phi \approx 1$ eV) (refs.^{56,57}) than in our case.

Curve 3 in Fig. 6 shows the work function after TPD of CO from bimetallic system Pd/Nb at different deposition times corresponding to different thicknesses of the Pd layers. Difference between the second and the third curve gives the WFC induced by the desorption of CO. Up to about 2.5 min of Pd deposition the desorption causes positive change of the WF. At longer deposition times $\Delta\phi$ becomes smaller and above 5 min deposition, the desorption causes a negative change of the WF. The value of the work function ϕ returns to that measured before CO adsorption. This behaviour can be explained in terms of different types of CO adsorption on Nb and Pd. Carbon monoxide is dissociatively chemisorbed on Nb surfaces at room temperature and weakly bound on Pd (without dissociation). In submonolayer Pd coverage on Nb ($\theta_{\text{Pd}} < 1$) patches of the bare Nb substrate are accessible to CO and dissociative chemisorption can occur. CO species are not completely removed from the surface after TPD to 500 – 600 K. It has been observed that repeated CO adsorption on this structure leads to lowering of CO TPD peak and saturation value of TPD area has been achieved after 4 – 5 repetitions⁵⁸. CO adspecies increase the value of ϕ for a clean surface of Nb (ref.⁵⁹). Thus performing TPD at submonolayer Pd coverage leads to the increase of the work function. As Pd layer becomes thicker, bulk Pd properties prevail. Carbon monoxide is molecularly bound at bulk Pd(111) surface and both adsorption and desorption of CO after TPD to 500 – 600 K cause reversible changes of the work function.

CONCLUSIONS

Carbon monoxide interaction with palladium layers deposited on a niobium foil has been investigated. The low-temperature desorption state of CO, characterized by the temperature $T_{\text{max}} \approx 330$ K, has been observed already at low coverages of deposited Pd. Therefore it is attributed to desorption from palladium in the region of its submonolayer coverage ($\theta_{\text{Pd}} \leq 1$). Second desorption state characterized by the temperature $T_{\text{max}} \approx 370$ K has appeared after longer deposition times of Pd and its behaviour strongly resembles that of bulk palladium. Roughness of the surface and growth mode of the palladium layer were discussed on the basis of measurements of CO peak area and WF changes. It has been concluded that Stranski–Krastanov mode governs the growth of palladium in our case. Rough estimation of the activation energy of desorption yields $E_1 = 80$ kJ mol⁻¹ and $E_2 = 89$ kJ mol⁻¹ for a monolayer Pd coverage and for a thick (bulk-like) Pd layer, respectively.

Small amounts of palladium cause negligible changes of the work function. Layers resulting from longer deposition times, i.e. thicker palladium layers, exhibit the saturation value of work function. The changes of the work function induced by CO adsorp-

tion on Pd/Nb qualitatively correspond to the literature data. Thermal desorption of carbon monoxide from bimetallic surfaces causes different work function changes of samples with Pd layers of different thicknesses, namely, the WF increases after the desorption of CO from thin Pd layers whereas on thick Pd layers it decreases and attains the initial value.

The support of this work by the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. 44012) and by the Grant Agency of the Czech Republic (grant No. 203/93/0245) is gratefully acknowledged.

REFERENCES

1. Pan X., Johnson P. D., Weinert M., Watson R. E., Davenport J. W., Fernando G. W., Hulbert S. L.: *Phys. Rev.*, B 38, 7850 (1988).
2. El-Batanouny M., Strongin M., Williams G. P.: *Phys. Rev.*, B 27, 4580 (1983).
3. Sagurton M., Strongin M., Jona F., Colbert J.: *Phys. Rev.*, B 28, 4075 (1983).
4. El-Batanouny M., Hamann D. R., Chubb S. R., Davenport J. W.: *Phys. Rev.*, B 27, 2575 (1983).
5. Williams G. P., El-Batanouny M., Colbert J., Jensen E., Rhodin T. N.: *Phys. Rev.*, B 25, 3658 (1982).
6. El-Batanouny M., Strongin M., Williams G. P., Colbert J.: *Phys. Rev. Lett.* 46, 269 (1981).
7. Shang-Li Weng, El-Batanouny M.: *Phys. Rev. Lett.* 44, 612 (1980).
8. Ruckman M. W., Strongin M.: *Phys. Rev.*, B 29, 7105 (1984).
9. Strongin M., El-Batanouny M., Pick M. A.: *Phys. Rev.*, B 22, 3126 (1980).
10. Rodriguez J. A., Goodman D. W.: *J. Phys. Chem.* 95, 4196 (1991).
11. Sellidj A., Koel B. E.: *Surf. Sci.* 284, 139 (1993).
12. Sellidj A., Koel B. E.: *Surf. Sci.* 281, 223 (1993).
13. Koel B. E., Smith R. J., Berlowitz P. J.: *Surf. Sci.* 231, 325 (1990).
14. Schwoebel P. R., Kellogg G. L.: *Phys. Rev.*, B 38, 5326 (1988).
15. Ruckman M. W., Strongin M.: *Phys. Rev.*, B 35, 487 (1987).
16. Ruckman M. W., Murgai V., Strongin M.: *Phys. Rev.*, B 34, 6759 (1986).
17. Ruckman M. W., Johnson P. D., Strongin M.: *Phys. Rev.*, B 31, 3405 (1985).
18. Rodriguez J. A., Goodman D. W.: *Science* 257, 897 (1992).
19. Yang Y.-W., Lin J. C., Engel T.: *Surf. Sci.* 289, 267 (1993).
20. Song K. J., Dong C. Z., Madey T. E.: *Langmuir* 7, 3019 (1991).
21. Campbell R. A., Rodriguez J. A., Goodman D. W.: *Surf. Sci.* 240, 71 (1990).
22. Zhao Y. B., Gomer R.: *Surf. Sci.* 239, 189 (1990).
23. Rodriguez J. A., Campbell R. A., Goodman D. W.: *J. Phys. Chem.* 94, 6936 (1990).
24. Berlowitz P. J., Goodman D. W.: *Langmuir* 4, 1091 (1988).
25. Graham G. W.: *J. Vac. Sci. Technol.*, A 4, 760 (1986).
26. Prigge D., Schlenk W., Bauer E.: *Surf. Sci.* 123, L698 (1982).
27. Fink H. W., Ehrlich G.: *Surf. Sci.* 110, L611 (1981).
28. Schlenk W., Bauer E.: *Surf. Sci.* 93, 9 (1980).
29. Heitzinger J. M., Gebhard S. C., Koel B. E.: *Chem. Phys. Lett.* 200, 65 (1992).
30. Heitzinger J. M., Gebhard S. C., Koel B. E.: *Surf. Sci.* 275, 209 (1992).
31. Rodriguez J. A., Campbell R. A., Goodman D. W.: *J. Phys. Chem.* 95, 5716 (1991).
32. Park Ch., Bauer E., Poppa H.: *Surf. Sci.* 154, 371 (1985).

33. Park Ch., Soria F., Poppa H.: *Thin Solids Films* 116, 23 (1984).
34. Mroz S., Chrzanovski E.: *Prib. Tekh. Eksp.* 4, 176 (1968).
35. Morgan F. M., Danford W. E.: *J. Appl. Phys.* 21, 112 (1950).
36. Colera I., Segovia J. L., Wincott P. L., Casanova R., Thornton G.: *Surf. Sci.* 292, 61 (1993).
37. Smith R. J.: *Phys. Rev.*, B 31, 3131 (1980).
38. Davis P. R., Donaldson E. E., Sandstrom D. R.: *Surf. Sci.* 34, 177 (1973).
39. Dooley G. J., Haas T. W.: *J. Vac. Sci. Technol.* 7, S90 (1970).
40. Haas T. W., Grant J. T., Dooley G. J.: *J. Vac. Sci. Technol.* 7, 43 (1970).
41. Szanyi J., Kevin Kuhn W., Goodman D. W.: *J. Vac. Sci. Technol.*, A 11, 1969 (1993).
42. Guo X., Yates J. T.: *J. Chem. Phys.* 90, 6761 (1989).
43. Kok G. A., Noordermeer A., Nieuwenhuys B. E.: *Surf. Sci.* 152, 505 (1985).
44. Kiskinova M. P., Bliznakov G. M.: *Surf. Sci.* 123, 61 (1982).
45. Conrad H., Ertl G., Kupperts J.: *Surf. Sci.* 76, 323 (1978).
46. Bradshaw A. M., Hoffmann F. M.: *Surf. Sci.* 72, 513 (1978).
47. Engel T.: *J. Phys. Chem.* 69, 373 (1978).
48. Conrad H., Ertl G., Koch J.: *Surf. Sci.* 43, 462 (1974).
49. Ertl G., Koch J. in: *Adsorption-Desorption Phenomena* (F. Ricca, Ed.), p. 345. Academic Press, New York 1972.
50. Ertl G., Koch J.: *Z. Naturforsch.*, A 25, 1906 (1970).
51. Redhead P. A.: *Vacuum* 12, 203 (1962).
52. Lord F. M., Kittelberger J. S.: *Surf. Sci.* 43, 173 (1974).
53. Knor Z.: *Surf. Sci.* 154, L233 (1985).
54. Michaelson H. B.: *J. Appl. Phys.* 48, 4729 (1977).
55. Holz J., Schulte F. K.: *Solid Surf. Phys.* 85, 1 (1979).
56. Ishi S., Ohno Y., Viswanathan B.: *J. Sci. Ind. Res.* 46, 541 (1987).
57. Ishi S., Ohno Y., Viswanathan B.: *Surf. Sci.* 161, 349 (1985).
58. Jirsak T., Nikolajenko V.: Unpublished results.
59. Yates J. T., Madey T. E., Campuzano J. C. in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* (D. A. King and D. P. Woodruff, Eds), p. 389. Elsevier, Amsterdam 1983.

Translated by the author (T. J.).