

ADSORPTION OF CARBON MONOXIDE ON Pd/SiO₂/Si(111) STUDIED BY CORE-LEVEL PHOTOEMISSIONZdenek BASTL¹ and Tomas SARAPATKA²

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X-Ray photoelectron spectroscopy (XPS) has been used to study the adsorption of carbon monoxide on Pd dispersed on oxidized Si(111) surface. A fraction of the deposited Pd diffusing at room temperature to the SiO₂/Si interface increases with decreasing SiO₂ thickness. For oxide layers thinner than ≈1 nm, almost all deposited Pd diffuses to SiO₂/Si interface forming there Si silicide. Consequently, the amount of adsorbed CO is dependent on the thickness of the thermally grown SiO₂ layer. Two different chemical states of adsorbed carbon atoms, the population of which depends on the amount of the Pd deposited, are observed in the C (1s) spectra of adsorbed CO. Adsorption activity of Pd clusters does not depend on whether n- or p-type Si is used. Comparison of the experimental Pd/CO concentration ratios with those calculated assuming several different modes of the Pd growth on SiO₂/Si points to the pseudo-Stranski–Krastanow mode (flat clusters with incomplete condensation of the first layer) at 300 K. Changes in charge balance across the Pd/SiO₂/Si interface caused by CO adsorption are discussed in terms of the surface photovoltage effect and work function variation.

Key words: X-Ray photoelectron spectroscopy; Pd/SiO₂/Si(111); Pd-Clusters; Palladium; CO Adsorption.

The understanding of the size-dependent changes in electronic structure and chemical properties of metals and semiconductors is of particular importance in heterogeneous catalysis. Small metal particles deposited onto various substrates are widely used as catalysts and their catalytic properties are known to depend on metal cluster size. Group VIII metals deposited on SiO₂/Si substrate have received interest recently due to the observed possibility of influencing electronic properties and adsorption activity towards carbon monoxide^{6,7} of a metal by interaction with the support^{1–3} as well as its surface potential by illumination^{4,5}. While the interaction of Pd with Si and various silica substrates has been extensively studied^{8–11}, the studies of the well characterized Pd/SiO₂/Si systems are rather rare^{12,13}. The detailed investigation of the influence of the oxide thickness and preparation conditions on its interaction with deposited Pd is still missing. Possibility of incorporation of the deposited metal atoms within the thin oxide layer is also an open problem^{2,12,14}. Many other questions concerning the relation of the growth mode, cluster shape and adsorption properties of the deposited metals to the

structure and chemical composition of insulating support surface are not well understood yet^{3,12-19}.

In this contribution, we have used X-ray photoelectron spectroscopy (XPS) to study adsorption of carbon monoxide on Pd particles deposited on the SiO₂/Si(111) surface. The adsorption data are used to estimate the influence of the oxide layer thickness on adsorption properties and growth mode of Pd and to characterize the changes in the surface electron structure after adsorption of CO gas.

EXPERIMENTAL

Experiments were performed using a VG ESCA 3 Mk II electron spectrometer operating at the pressure of residual gases $\leq 10^{-8}$ Pa. The XPS measurements were performed using an Al K α ($h\nu = 1\,486.6$ eV) source at a power of 220 W. The spectrometer was operated in the fixed analyzer transmission mode with a pass energy of 20 eV giving a resolution of 1.1 eV on the Au (4f_{7/2}) line. Calibration of the spectrometer was set up to the Au (4f_{7/2}) peak at 84.0 eV. The estimated error in binding energy determination was ± 0.1 eV. High-resolution spectral scans were taken at an angle of 45° (measured from the sample surface) over Si (2p), Pd (3d) and C (1s) regions.

The surface of Si(111) samples doped either by $6 \cdot 10^{18}$ P atoms/cm³ or $3 \cdot 10^{18}$ B atoms/cm³ was cleaned by Ar ion sputtering (4.5 kV, 15 μ A, 15 min) and subsequent annealing under ultrahigh vacuum at 1 000 K. Let us mention that we are unaware of any differential sputtering effects for B and P in Si. The oxide layers were grown at 900 ± 50 K in the preparation chamber of the spectrometer by oxygen exposures ranging from 45 to 90 000 L (langmuir). Heating in oxygen might result in boron segregation into the oxide layer. The thicknesses of the oxide layers, d , ranged from 0.6 to 1.9 nm. A simple method²⁰ based on a uniform oxide layer model was used to estimate the oxide thickness. A more detailed characterization of the SiO₂ layers prepared by the method described has been given elsewhere²¹.

Different amounts of Pd (Aldrich Chem. Co., 99.99%) were deposited in situ from a resistively heated tungsten wire at a pressure lower than $2 \cdot 10^{-8}$ Pa using a commercial (VG) evaporator. The evaporator was calibrated in a separate experiment. Assuming layer-by-layer growth of Pd on the Ta surface¹⁵ cleaned by Ar ion sputtering, the Pd coverage, θ_{Pd} , was calculated from the Pd (3d) and Ta (4d) line intensities and the evaporation rate was adjusted to 0.5 ± 0.1 monolayer/min. The spectra were recorded always 10 min after the sample preparation.

The overlapping spectral features were resolved into individual components of Gaussian-Lorentzian shape using a damped non-linear least squares procedure. In fitting the Pd (3d) spectra obtained for high surface coverage, we used also Doniach-Sunjic line shapes²² to resolve the main line and satellite contributions. Prior to spectra treatment, the AlK $\alpha_{3,4}$ (refs^{3,4}) satellites were removed numerically.

RESULTS AND DISCUSSION

The Si (2p) photoelectron spectra measured before and after Pd deposition on the SiO₂/Si(111) substrates differing in the thickness of the oxide layer, are shown in Fig. 1. With exception of broadening of the oxide Si (2p) peaks, the spectra of the SiO₂/Si supports remain unchanged. The observed broadening is likely due to the effects of variation in the oxide electron structure and/or in the electron relaxation in

SiO₂ below the Pd clusters compared with the free SiO₂ surface. The origin of the decreased separation between Si⁰ (2p) and Si^{x+} (2p) peaks observed for samples with $d < 1$ nm has been discussed in a previous paper²¹.

It has been proposed in the literature¹² that palladium deposited on SiO₂/Si can exist at 300 K in three states with different environment of metal atoms. Namely, Pd₂Si present at SiO₂/Si interface, Pd atomically incorporated within the SiO₂ layer and elemental Pd located on the top of the oxide. Two chemical states of Pd deposited are seen in our Pd 3d spectra (Fig. 2). Their relative population is a function of the oxide layer thickness. The interaction between Pd and Si substrate leading to the formation of Pd silicide dominates for samples with the oxide layers thinner than ≈ 1 nm. The observed thickness-dependent diffusion of the Pd atoms through SiO₂ is similar to that observed previously with the Ni/SiO₂/Si system¹⁴.

The elemental Pd is characterized by the 3d_{5/2} core level binding energies decreasing from 335.6 to 335.2 eV with increasing amount of Pd deposited on the surface. The origin of the observed increase in the binding energy with decreasing amount of the deposited metal is related to the cluster size effects and is still widely discussed in the literature from the point of view of contributions of the initial and final state effects^{19,23–27}. The second peak located at 337.2 eV corresponds to Pd silicide^{5,12}. The binding energy of Pd (3d_{5/2}) electrons in Pd silicide does not change with metal coverage within the experimental error.

The Pd/SiO₂/Si samples were exposed to 100 L of CO (1 L = 1.33 · 10⁻⁴ Pa s). This exposure was found sufficient to achieve saturation surface coverage. For a given amount of Pd deposited, the extent of CO adsorption increases with increasing oxide

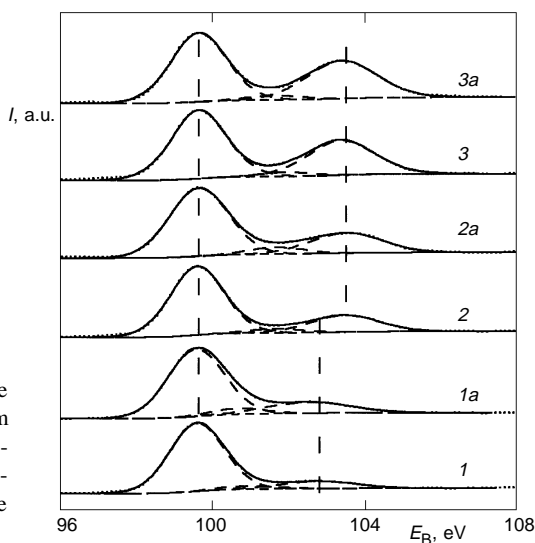


FIG. 1

Fitted Si (2p) core level spectra of the SiO₂/Si(111) substrates with 0.7, 1.2 and 1.9 nm thick oxide layer before (1, 2 and 3, respectively) and after (1a, 2a and 3a, respectively) Pd deposition. The spectra are normalized to the same height

thickness. This finding demonstrates that CO adsorbs only on Pd remaining on the SiO₂ oxide surface.

The C (1s) spectra accumulated for 1 h are shown in Fig. 3. They reveal the presence of two different chemical states of carbon, the relative population of which depends on the amount of the metal deposited. They reflect different local surroundings of the carbon atoms. Two different states of CO adsorbed on Rh(111) and Ni(100) corre-

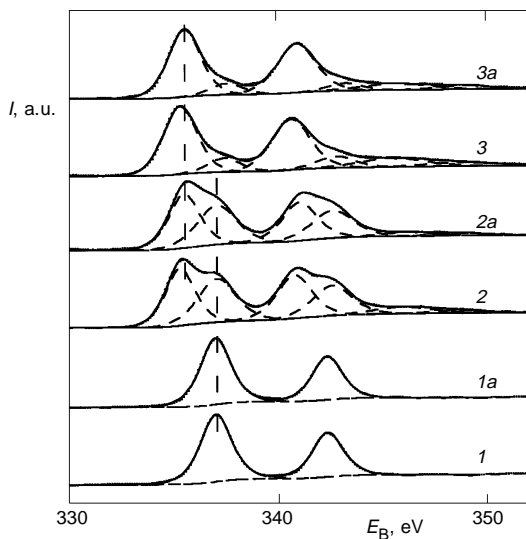


FIG. 2

Fitted Pd (3d) core level spectra recorded after deposition of ≈ 3 monolayers of Pd on the SiO₂/Si(111) substrates specified in Fig. 1 before (1, 2 and 3, respectively) and after (1a, 2a and 3a, respectively) CO adsorption. The spectra are normalized to the same height

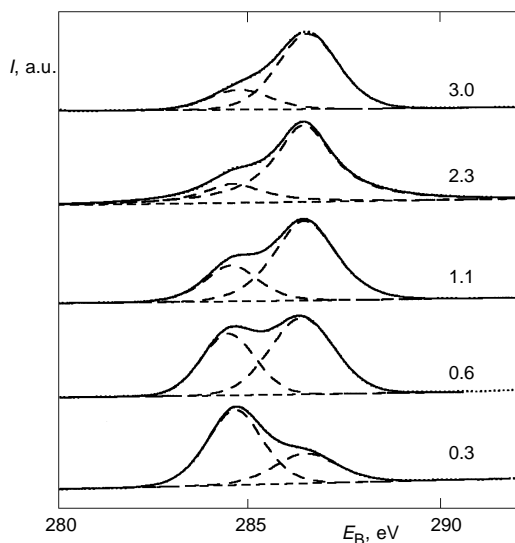


FIG. 3

Fitted C (1s) core level spectra of CO adsorbed on the Pd/SiO₂/Si(111) surface. The amounts of elemental Pd on the SiO₂ surface (in effective monolayers) are shown alongside of the spectra. The spectra are normalized to the same height

sponding to on-top and three-fold hollow adsorption sites were identified in the high resolution C (1s) photoelectron spectra^{28,29}. The separation of C (1s) peaks for these systems was about 0.5 eV, *i.e.* much less than 1.8 eV observed in the present work. Consequently, we assign the first peak located at 284.8 eV rather to carbon atoms produced by dissociation of CO. The possibility of dissociation of CO molecules on specific Pd surface sites present on small Pd particles has already been discussed in the literature³⁰⁻³³. However, it has to be mentioned that long times are necessary to accumulate the C (1s) spectra of rather small amounts of CO adsorbed on small clusters. Adsorption of small amounts of hydrocarbons from the background gases might therefore be at least partly responsible for this peak. Besides, dissociation might be induced by extensive exposure to the X-rays and with bremsstrahlung radiation. In blank experiment, in which no CO was introduced to the sample, we observed that the amount of this carbon increased with time only by 0.05 of monolayer/h. Unfortunately, it is impossible to confirm or exclude the dissociative adsorption of CO by measuring the binding energy of O (1s) electrons. This is due to the overlap of O (1s) photoemission from the adsorbed species with the intense signal of O (1s) electrons arising from the SiO₂ and with the Pd (3p_{3/2}) peak which coincides with the O (1s) spectra.

The second C (1s) peak located at 286.3 eV can undoubtedly be assigned to molecularly adsorbed CO. We also observed the C (1s) signal at the same binding energy after CO adsorption on the clean surface of the bulk Pd, but did not observe it in the blank experiments on the SiO₂/Si and Pd₂Si surfaces. The integral intensity of the peak belonging to molecularly bound CO increased with increasing amount of elemental Pd (see Fig. 3), *i.e.* with increasing average Pd cluster size, and did not change with time.

Upon CO adsorption, the elemental Pd (3d) peaks as well as the Pd Fermi level edges shifted by about 0.3 eV towards higher binding energy, whereas the position of the Pd-silicide peaks remained unchanged (see Fig. 2). We observed similar Pd core level shifts after oxygen adsorption on a Pd/SiO₂/Si sample. An influence of static surface charging can be excluded because the Pd (3d) spectra followed the value of the potential applied to the sample holder. The reason for the observed spectral shift can be the CO-induced increase in the Pd work function³⁴, *i.e.* the effect similar to adsorption of oxygen³⁵. Such potential change at the surface causes an increase in the Pd/SiO₂ barrier height³⁶ and thus enhances an influence of the surface photovoltage effect discussed in^{5,37}. Consequently, the higher E_B shift of the elemental Pd (3d) peaks upon X-ray irradiation can be observed compared with that determined before CO adsorption.

For the purpose of comparison, we have also investigated adsorption of CO on the surface of polycrystalline bulk sample of Pd. We observed no dissociative adsorption in this case. To determine the saturation surface coverage of Pd by adsorbed CO molecules, we used the equation published by Carley and Roberts³⁸. Assuming the average surface density of Pd atoms equal to $1.3 \cdot 10^{15}$ atoms/cm² and using the published values of the photoionization cross-sections³⁹ and electron mean free paths⁴⁰, we ob-

tained Pd^s/CO (number of surface Pd atoms per molecule of CO adsorbed) ratio of 2.2. This value corresponds to an average number of surface Pd atoms per one adsorbed CO molecule and agrees well with the commonly accepted value for the CO/Pd system¹⁸.

Using the adsorption data, we have attempted to elucidate the Pd growth mode on SiO₂/Si substrate. For the series of Pd/SiO₂/Si samples, the Pd/CO ratios were calculated using the C (1s) and elemental Pd (3d) peak intensities (this ratio involves the total amount of elemental Pd). We adopted the published⁴¹ cluster model for our Pd/CO intensity ratios and modified it for three different cluster shapes (see Fig. 4.) including spheres, hemispheres and truncated hemispheres of $v = r/2$ (v is the height and r the radius of the clusters). Assuming roughly the same adsorption capacity of Pd clusters as that of the bulk Pd surface, the model Pd/CO ratios, calculated using Eq. (1), are shown in Fig. 5 together with experimental points. It is implicitly assumed that Pd clusters are regularly distributed on the SiO₂ support^{18,42}. The practical applicability of the model is limited to metal clusters with sizes ranging from 0.2 to 3 λ , where λ is inelastic mean free path of electrons characteristic of the material and electron energy. This will be discussed later together with the effect of the used values of λ and atomic volume, v_{at} , on the results obtained.

$$\text{Pd/CO} = 2.2 \frac{\sigma^C \lambda_M(E_M) [A - \iint (M)] \exp(\text{CO}) dl}{\sigma^M \lambda_c(E_c) [X - (1 - X) \iint (\text{CO}, M)] (1 - \exp(\text{CO})) dl} , \quad (1)$$

where

$$\exp(\text{CO}) = \exp[-d_{\text{CO}}/(\lambda_c(E_c) \sin(\theta))] . \quad (2)$$

Here, σ^C and σ^M are theoretical photoionization cross-sections³⁹ for C (1s) and Pd (3d) electrons, respectively, $A(r, \lambda)$ is the area of integration across the cluster, $X(\theta)$ is the area of the non-shaded fraction of adsorbed CO. $\iint (r, \lambda, \theta)$ is the two-dimensional integral of the intensity of photoelectrons emitted from clusters of radius r in direction θ (measured from the substrate surface) and d_{CO} is the effective thickness of a monolayer

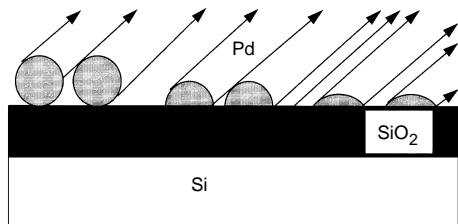


FIG. 4
Schematic drawing of the Pd clusters on a flat support considered in this work. To reach the detector the photoelectrons emitted from different parts of the system must pass through different components depending on their exit angle

of adsorbed CO. Further details of the used method of calculation has been published elsewhere⁴¹.

For a given amount of elemental Pd, the calculated cluster radius r depends on its shape and on the used values^{40,43} of λ , ν_{at} and the areal density of clusters, N_d . The obtained optimized N_d values corresponding to the curves which are close to the experimental data (see Fig. 5) are summarized in Table I. Let us mention that the modification to $\nu = r/4$ in the model of truncated hemispheres leads to the optimized N values of 35 and 59 $\cdot 10^{11} \text{ cm}^{-2}$ for λ_E and λ_T , respectively^{40,43}, but this does not mean any significant change in the submonolayer region of the curve a in Fig. 5.

The calculated Pd/CO dependences in Fig. 5 show that none of the employed Pd morphologies can describe the whole coverage region, regardless of the values of parameters λ and ν_{at} . The same Pd evaporation rate was used in all experiments, so that significant differences in the values of N_d for various amounts of elemental Pd do not seem likely.

We are aware of the fact that many other factors could affect the modeling and conclusions on Pd growth mode; this includes the cluster size distribution, surface roughness, influence of surface impurities and possibility of other shapes of Pd clusters⁴⁴. To use the correct inelastic mean free paths of photoelectrons, λ , is also a problem because the values published differ^{40,43}. In addition, CO adsorption on Pd clusters may be more complicated than implied. One may observe CO-induced reconstruction⁴⁵, different adsorption structures^{46,47}, cluster size effects⁴⁶, *etc.*

Two effects might be responsible for the observed increase in the experimental Pd/CO values compared with the calculated ones in the region of the submonolayer Pd coverage: (i) Dissociative adsorption of CO requires more adsorption sites to accommodate dissociation products. (ii) About 20% of elemental Pd, contributing to the spectral intensity is deactivated in some way, *e.g.* by incorporation in the SiO_2 layer where Pd loses the ability to adsorb carbon monoxide¹². We suppose therefore that during the Pd

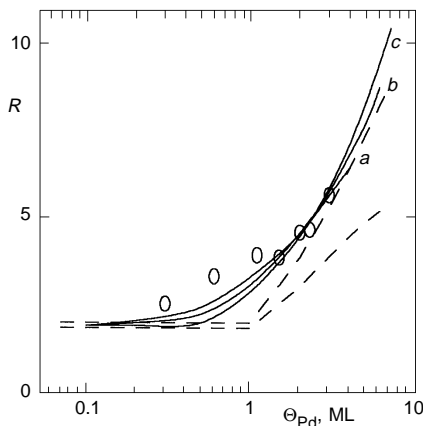


FIG. 5

Dependence of the Pd/CO ratio, R , on the metal coverage, θ_{Pd} , (expressed in equivalent monolayers of Pd) on the $\text{SiO}_2/\text{Si}(111)$ surface. Experimental data (O) are compared with the calculated models of Pd morphologies: truncated hemispheres (a), hemispheres (b) and spheres (c). The dashed lines correspond to layer by layer growth of Pd

diffusion through SiO_2 *via* imperfections and grain boundaries², a certain fraction of elemental Pd remains within the oxide layer. This appears preferably when SiO_2 layer is thinner than about 1.2 nm.

Typical density of Pd clusters on SiO_2 reported in literature^{16,48} and determined by transmission electron microscopy (TEM) is $3 \cdot 10^{12}/\text{cm}^2$. If we compare this value with the data of Table I, the model *a* of truncated hemispheric-like islands seems to be the most probable picture of the Pd/ SiO_2 /Si surface morphology. This growth mode of Pd, estimated from the Pd/CO data, corresponds to the pseudo-Stranski–Krastanov model (flat clusters without completion of the first layer), confirmed by combined XPS and AES–TEM methods with the Pd/ Al_2O_3 , Ni/ SiO_2 /Si and Pt/ SiO_2 systems^{15,16,19}.

Recently, suppression of the CO adsorption has been reported for the Ni/ SiO_2 /n-Si system⁷. The effect has been explained by electron tunneling from Si *via* thin oxide layer to the Ni deposit. In fact, this process has been proposed with neglect of the inward Ni diffusion and without subtraction of the Ni-silicide contribution⁷. However, we observed no influence on whether n- or p-type Si substrate is used on CO adsorption on the Pd/ SiO_2 /Si(111) surface. We suggest, therefore, that the extent and/or the mode of CO adsorption on Pd/ SiO_2 /Si(111) is not influenced by electron transfer from Si to the Pd clusters. Rather a disappearance of elemental Pd (or Ni) from the SiO_2 surface is responsible for suppression of the CO adsorption on the metal/ SiO_2 /Si systems with the ultrathin SiO_2 interlayers.

CONCLUSIONS

Interaction of Pd with the SiO_2 /Si(111) substrate and subsequent CO adsorption have been studied by the XPS method. It was observed that the thickness of the thermally grown SiO_2 determined the amount of Pd which diffused to the SiO_2 /Si interface and, consequently, the adsorption capacity towards CO. Two different chemical states of

TABLE I

The optimized values of surface cluster densities, N_d , which correspond to the particular models of Pd morphology truncated hemispheres (*a*), hemispheres (*b*), spheres (*c*) obtained by using the inelastic electron mean free path values published by Ebel⁴⁰ (λ_E) and Tanuma⁴³ (λ_T) (*c*). The scatter of N_d values characterizes the effect of variations in the λ value of 14.7 \AA^3 within $\pm 20\%$

Cluster shape	N_d ($\cdot 10^{11}$ clusters/ cm^2)		
	<i>a</i>	<i>b</i>	<i>c</i>
λ_E	39 ± 7	19 ± 4	1.3 ± 0.3
λ_T	24 ± 5	9 ± 3	0.6 ± 0.2

adsorbed carbon atoms probably corresponding to dissociative and molecular adsorption of CO were identified in the C (1s) spectra.

The observed shift of the elemental Pd (3d) spectra after CO adsorption is attributed to the enhanced surface photovoltage effect. This is caused by the increase in the Pd/SiO₂ barrier height due to the increased work function of Pd caused by adsorption of CO.

A comparison of experimental Pd/CO ratios with those calculated using different models suggests that the growth of Pd on our SiO₂/Si supports at room temperature follows the pseudo-Stranski–Krastanov mechanism with incomplete condensation of the first metal layer and truncated hemispheric-like clusters. The results seem to agree with results of the TEM observations.

The results indicate that for SiO₂ layers thinner than about 1.2 nm, the amount of 0.1–0.2 effective monolayer of elemental Pd is incorporated within the oxide layer. No influence of the type of the Si conductance on the adsorption activity of Pd towards CO was observed.

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