PHYSICAL REVIEW B VOLUME 27, NUMBER 8 15 APRIL 1983

Drastic reduction of adsorption of CO and H_2 on (111)-type Pd layers

H. Poppa and F. Soria*
Stanford NASA Joint Institute for Surface and Microstructure Research,
NASA Ames Research Center, Moffett Field, California 94035

(Received 18 November 1982; revised manuscript received 31 January 1983)

Clean surfaces of (111)-type Pd layers, grown from the vapor phase on Mo(110) at room temperature, were used to study the adsorption of CO and H_2 by temperature-programmed desorption, Auger electron spectroscopy, and low-energy electron diffraction. Mild annealing of the as-grown layers during a single desorption cycle (to about 600 K) drastically reduces the adsorption for both adsorbates. Low-dose argon-ion bombardment introduces surface imperfections which restore a high adsorption probability. The results are interpreted in terms of particular (111)-type surface structures that persist to layer thicknesses of about four monolayers; the results raise questions with respect to the surface structure of supported thin epitaxial islands and particles of Pd and possibly also with respect to conventional methods of preparing bulk surfaces of Pd for adsorption studies.

The feasibility of using temperature-programmed desorption (TPD) to characterize adsorption on Pd particles grown from the vapor phase onto oxide-type substrates has been demonstrated in a series of recent publications.[1,2] For one type of oxide substrates [stable two-dimensional oxides of W(110) and Mo(110)] significantly reduced adsorption was found after a heat treatment at about 600 K. These results were tentatively attributed to oxygen deactivation of the Pd island surfaces.[3] This communication discusses the results of subsequent adsorption studies on thick, continuous films of Pd grown on oxygen-free single-crystal metal substrates, Mo(110) or W(110); they suggest unusual (111)-oriented surface structures as another reason for the observed reduction of CO adsorption and show, furthermore, that intentionally introduced surface defects can restore the adsorption in a dramatic way. These results are considered important because of their controversial nature, and because of their implications for adsorption studies with small particles or islands of Pd and conceivably also for conventional adsorption studies on bulk single-crystal surfaces of Pd prepared by extended sputter and anneal cleaning cycles.

Recognizing the important role played in adsorption studies by surface impurities,[4,5] every effort was made to insure surface cleanliness throughout this work. Films of Pd were grown by evaporation from a thoroughly outgassed sublimation source onto an atomically clean Mo(110) substrate. The background pressure was between 5×10^{-11} and 8×10^{-11} Torr, and the pressure during evaporation never exceeded 3×10^{-10} Torr. All nonmetallic impurities, either on the Mo substrate or on the Pd films, such as O, S, and P, were each lower than 0.5% of a monolayer (ML) as judged by Auger electron spectroscopy (AES). Carbon was monitored with particular care because of Auger peak overlap with Pd (279 eV); Auger peak ratio of

$$[\mathrm{C}(272\text{ eV})] + [\mathrm{Pd}(279\text{ eV}]]/[\mathrm{Pd}(330)\text{ eV})]$$

was always smaller than 0.16, which is 10% to 50% lower than any previous value reported for clean bulk Pd.[6,7] The search for any conceivable nonmetallic impurity was negative, even after annealing of the films, which indicates no surface segregation of impurities. The thickness of the as-deposited Pd films ranged from 2–10 ML (1 ML = 0.224 nm) as calibrated from the [Pd][Mo] Auger peak ratio. The substrate temperature during film growth was either room temperature (RT) or 600 K. For some of the measurements the films were ion bombarded at grazing incidence and 5×10^{-5} Torr of Ar with 2-kV ions for periods of up to 15 min. This procedure did not change measurably the amount of all monitored impurities. Low energy electron diffraction (LEED), AES, and TPD were used in an instrumental arrangement described previously.[8] The heating rate was kept constant at 11 K/s in all TPD measurements.

At RT Pd grows in a metastable layer-by-layer mode on Mo(110) forming about six continuous monolayers which occupy roughly 80% of the total film surface area (for a nominal total deposit thickness of about 10 ML), as judged from [Pd][Mo] Auger peak ratio measurements.[9] The corresponding LEED pattern is a slightly diffused (1×1) structure with increased background. If a saturation dose (6 L) of CO is adsorbed at RT on a fresh Pd film more than 2 ML thick, TPD produces the CO spectrum shown in curve 1 of Fig. 1. Redosing the film with 6 L of CO produces a drastically reduced subsequent TPD spectrum, curve 2 of Fig. 1. (A similarly reduced TDP peak is obtained for CO adsorbed onto Pd films grown at 600 K instead of at RT.[9]) After

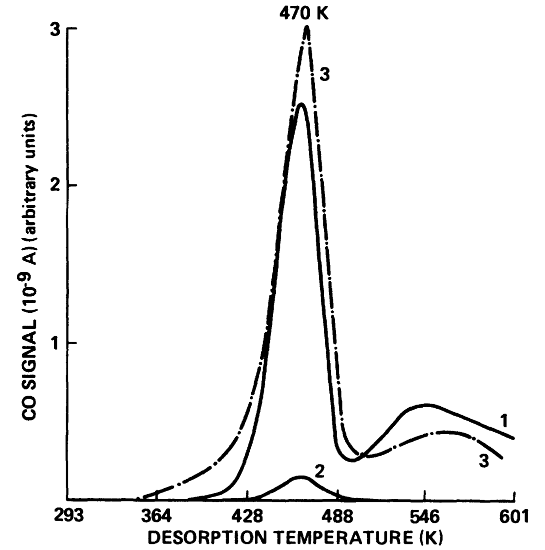

FIG. 1 Carbon monoxide thermal desorption spectra from different Pd(111) surfaces after saturation of CO (6 L): (1) first TPD cycle (600 K) on RT grown surfaces; (2) subsequent TPD cycles (600 K) on RT grown surfaces or first TPD (600 K) on surfaces grown at 600 K; (3) after 2-min ion bombardment of the surfaces which produce curve 2.

the first desorption, a reduced continuous layer thickness of about 4 ML is measured by AES for a Pd deposit that originally was about 6 ML thick indicating further island growth in the top layers of the deposit during TPD. The LEED pattern of the annealed and coalesced film shows a slightly distorted (111)-oriented surface structure rotated by about 2° out of the Nishijama-Wassermann orientation—$[1\bar{1}0]_{fcc} \parallel [001]_{bcc}$—which was previously found and analyzed by Schlenk and Bauer[10] for Pd layers on W(110) when the film thickness exceeded 1.4 ML and the annealing temperature exceeded 530 K. [The surface structure of about 4-ML-thick Pd films grown at 600 K is an almost perfect (111) structure in equilibrium relationship with the substrate—$[1\bar{1}0]_{fcc} \parallel [1\bar{1}1]_{bcc}$—which is the Kurdjumov-Sachs relationship also seen by Schlenk and Bauer.[10]]

The desorption peak at 470 K indicates the presence of molecularly adsorbed CO with $E_{des} = 32$ Kcal/mol (for $\nu = 2.5 \times 10^{14}$ s^{-1}, Ref. 11). The much smaller peak at 546 K is presently ascribed to either the associative desorption of CO on a substrate with high adsorbate mobility or to a sparsely populated higher-energy adsorption state of molecular CO.[12] When the TPD-annealed or epitaxially grown (600 K) films, curve 2 of Fig. 1, are subjected to 2 min of ion bombardment, the subsequent TPD of CO (6 L)

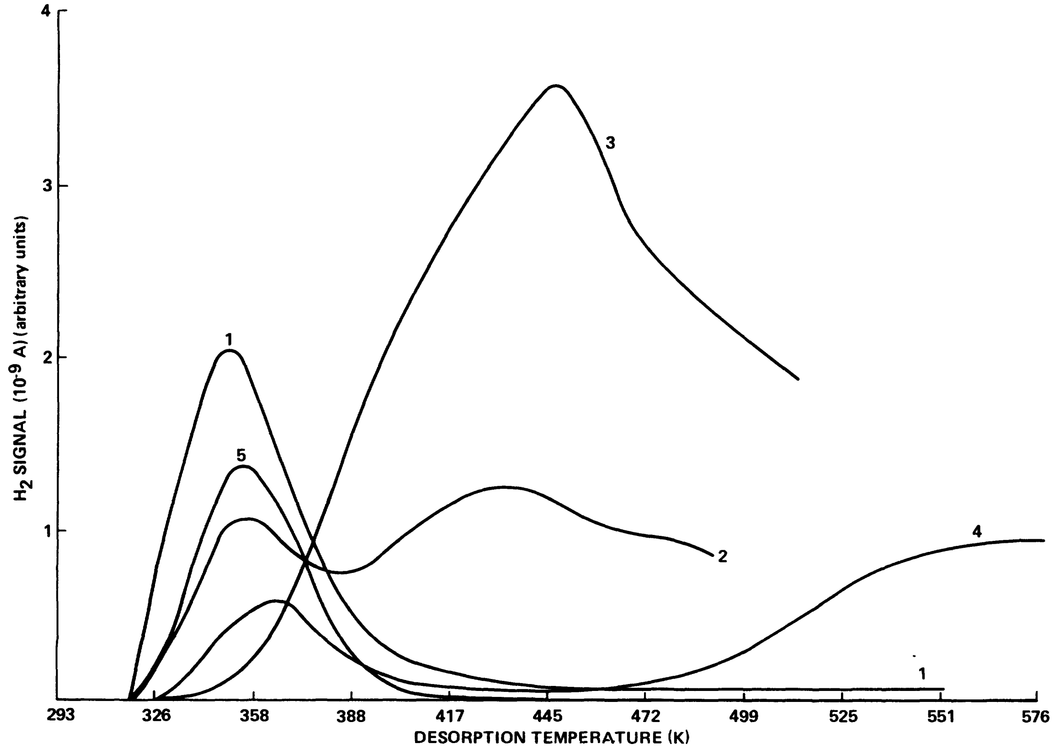

FIG. 2. Molecular hydrogen thermal desorption spectra from different Pd(111) surfaces after saturation with 0.6 L of H_2: (1) first TPD cycle (550 K) on RT grown surfaces; (2) first TPD (490 K) after 5-min ion bombardment of RT grown surfaces; (3) first TPD (500 K) after 15-min ion bombardment; (4) second TPD (580 K) after (3); (5) third TPD (445 K) after (4).

results in curve 3 of Fig. 1. The ion bombardment more than restores the original adsorption in curve 1.

We conclude from the results of Fig. 1 that adsorption of CO on the imperfect surface of the RT films is reduced sharply by annealing during the TPD of CO to 600 K because well-ordered (111)-type surface structures with strongly reduced adsorption probability for CO are formed over approximately 80% of the deposit surface area. The continuous layer base has a thickness of about 4 ML, and roughly 20% of the deposit area is occupied by thick islands on top of the continuous base.

Similarly structured (111)-type film surfaces grown epitaxially on Mo(110) at 600 K exhibit the same reduced adsorption of CO after cooling to RT. Short-duration ion bombardment reintroduces surface defects or roughness with the concomitant increase in adsorption. These disordered surfaces can be easily perfected again by subsequent annealing, which reduces CO adsorption as expected.

The effect of surface structure and perfection of vapor-grown Pd layers on the adsorption of H_2 is slightly different from the adsorption of CO because of the lower adsorption energy for H_2 on Pd and the ability of H to diffuse easily below the film surface. Figure 2, curve 1, shows the usual dissociative adsorption TPD peak at about 355 K, but without the presence of higher desorption peaks, as observed in the case of H_2 on Pd(110).[13] These higher-energy TPD peaks appear with the Pd films only after ion bombardment, which induces higher-energy adsorption sites (545 K) at the expense of the 350-K sites (curves 2 and 3 of Fig. 2). The subsequent adsorption-desorption cycle (up to 600 K) restores some of the low-energy adsorption sites, by annealing, and drives most of the remaining surface H into the bulk of the Pd film leading to the 580-K back-diffusion peak of curve 4. A further TPD cycle restores the original low-temperature desorption peak, curve 5, which is reduced in amplitude because of the high-temperature TPD cycle employed (600 K). This peak is always regained without decay if the TPD temperature does not exceed 400 K. Several TPD cycles to 600 K, however, will reduce the peak area by as much as 60%.

We conclude for the H_2-Pd(111)-Mo(110) system that (1) desorption temperatures in excess of 400 K reduce the subsequent adsorption of H_2; (2) surface defects and roughness produced by ion bombardment increase the amount and the desorption energy for adsorbed H_2; and (3) annealing during subsequent TPD cycles first drives some surface H into the bulk of the film but eventually removes the bombardment damage and causes the formation of (111)-type Pd film surfaces with a lower adsorption probability for H_2.

---

[*] Permanent address: Instituto de Física de Materiales, Consejo Superior de Investigaciones Cientisicas, Serrano 144, Madrid-6, Spain.

[1] D. L. Doering, H. Poppa, and J. T. Dickinson, J. Catal. 73, 104 (1982).

[2] S. Ladas, H. Poppa, and M. Boudart, Surf. Sci. 102, 151 (1980).

[3] H. Poppa and F. Soria, Surf. Sci. 115, L105 (1982).

[4] R. J. Behm, K. Christmann, G. Ertl, and M. A. Van Hove, J. Chem. Phys. 73, 2984 (1980).

[5] V. S. Sundaram, S. P. da Cunha, and R. Landers, Surf. Sci. 119, L383 (1982).

[6] L. D. Davis, N. C. Mac Donald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, Inc., Minnesota, 1976).

[7] J. C. Hamilton and J. M. Blakely, Surf. Sci. 91, 199 (1980).

[8] E. Bauer, H. Poppa, G. Todd, and F. Bonczek, J. Appl. Phys. 45, 5164 (1974).

[9] H. Poppa and F. Soria (unpublished).

[10] W. Schlenk and E. Bauer, Surf. Sci. 93, 9 (1980).

[11] T. Engel, J. Chem. Phys. 69, 373 (1978).

[12] W. Erley and H. Wagner, Surf. Sci. 74, 333 (1978).

[13] H. Conrad, G. Ertl, and E. E. Latta, Surf. Sci. 41, 435 (1974).