ELSEVIER

Journal of Alloys and Compounds 404–406 (2005) 284–287

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Chemical and structural components of work function changes in the process of palladium hydride formation within thin Pd film

R. Duś*, R. Nowakowski, E. Nowicka

Institute of Physical Chemistry, PAS, 01-224 Warszawa, ul. Kasprzaka 44/52, Poland

Received 7 September 2004; received in revised form 2 December 2004; accepted 9 December 2004

Abstract

Surface phenomena which occur in the process of palladium hydride PdH_x formation during H_2 interaction "in situ" with thin palladium films were studied by means of two methods: (i) measurements of work function changes $\Delta\Phi$, and (ii) determination of topographical images using atomic force microscopy (AFM). A very strong decrease of the work function up to $\sim$2 V was registered in the course of the reaction at 78 K when thin Pd films deposited on Pyrex glass were applied. However a small $\Delta\Phi$ was noticed when using Pd films deposited on glass precovered with a thick platinum film. AFM topography exhibited a net of distinct protrusions in the first case, but the topography was almost unchanged in the second. We suggest that the above unusually high decrease of the work function in the process of PdH_x formation within a Pd/glass system is caused by the change of thin Pd film topography, and not by very strong polarization of hydrogen adspecies on PdH_x surface.

Keywords: Thin palladium hydride films; Chemical and structural components of work function; AFM studies of palladium hydride formation

1. Introduction

Hydrogen interaction at low temperatures with thin films of many transition metals deposited under ultra-high vacuum (UHV) conditions (1–2) × 10^{-8} Pa, thus having a clean surface, can form hydrides MeH_x at H_2 pressure below 1 Pa. This allows studies of surface phenomena occurring "in situ" in the course of this reaction. Determination of the electron work function Φ, one of the most important surface properties of metals, provides information concerning the electric charge of the hydrogen adspecies at every selected step of the process. The change of electron work function $\Delta\Phi$ caused by adsorption or surface reaction is often called surface potential (SP). By definition $SP = -\Delta\Phi$. The SP is an additive property of the adsorbent–adsorbate system and depends on the change of the electric charge density distribution induced by adsorption or chemical reaction on the surface. Hence SP is a function of chemical composition and structure of the surface. According to the well-known Smoluchowski's model [1] the increase of surface roughness increases SP (decreases Φ). This theoretical prediction was confirmed by numerous experimental findings [2]. On the other hand the negatively charged adspecies arising on the outer surface in the course of adsorption or a chemical reaction decrease SP (increase work function), and those positively charged increase SP (decrease Φ). It has been found from measuring SP at low temperature (e.g. 78 K) in the process of hydride formation within thin films of several transition metals deposited on Pyrex glass, that two distinct forms of hydrogen adsorbate exist on the surface [3–6]. These are: (i) β^- atomic form arising at the beginning of the reaction, negatively polarized (negative pole of the dipole pointing away from the surface), stable on the outer surface, and (ii) β^+ atomic form induced by an increase of coverage, positively polarized. The β^+ adspecies are not stable on the surface as are β^-, but quickly incorporate into the bulk. This leads to transition metal hydride formation. The formation of a positively charged hydrogen adspecies on the surface of a transition metal precovered with an amount of hydrogen adatoms was predicted theoretically by Grimley [7]. According to his model the increase of the hydrogen population on the metal surface also increases the magnitude of

---

* Corresponding author. Tel.: +48 22 632 32 21; fax: +48 22 632 52 76.
E-mail address: dus@ichf.edu.pl (R. Duś).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.165

the splitting between even and odd induced localized states. There is a critical value of the population above which the lower state merges into the metal conduction band. Then donation of electrons from hydrogen adatoms into unoccupied states of the conduction band occurs. This leads to the β^+ adspecies creation.

It has been well established that in the case of hydrides of several transition metals (e.g. PdH_x, VH_y) hydrogen in their bulk exhibits protonic character [8]. Thus the nature of the β^+ adspecies is similar to that characteristic of hydrogen in the bulk of these hydrides, and incorporation below the surface can be driven just by the concentration gradient. It has been found that hydrides formation within thin films of several transition metals (Pd, Ti, V, Nb) deposited on glass very strongly increases SP [3–6]. This would suggest that on surfaces of these hydrides strongly polarized hydrogen adspecies exist.

Studies of AFM topographical images of thin palladium film deposited on microscope glass (Menzel, Glaser) carried out "ex situ", after moving the samples from the UHV apparatus into the atomic force microscope cell, showed that their interaction with hydrogen at 298 K under H_2 pressure ∼101 kPa (far above $P_{eq} \sim 1$ kPa, which is the H_2 equilibrium pressure for palladium hydride formation at 298 K) leads to the formation of a net of protrusions [9]. The protrusions disappeared completely when hydrogen in the cell was changed to argon. This process was well reversible. It could be expected that the net of protrusions arising on thin PdH_x film on glass is caused by the stress accompanying the hydride formation (the lattice constant of palladium hydride is higher than that characteristic of palladium), which is too large to be compensated by the adhesive force between the metal film and glass support. Thus on some local sites the film was losing its contact with the glass support, forming protrusions. This contact was restored when PdH_x was decomposed, changing the H_2 gas phase above the sample for argon.

If our interpretation is valid, then the hydride formation within thin Pd film deposited on glass precovered with a thick layer of a metal which exhibits a strong cohesion against palladium and which does not form hydrides, should result in the absence of protrusions. The absence of protrusions should also influence the electric charge density distribution over the surface, leading to a decrease of SP. Thus mentioned above strong increase of SP in the course of PdH_x formation within thin Pd film deposited on glass could be a superposition of structural and chemical changes. To answer this question, experiments with SP measurements, and AFM topography studies were performed using thin Pd films deposited on glass and on glass precovered with thick platinum film.

2. Experimental

The Pyrex glass UHV system capable of routinely reaching $(2–3) \times 10^{-8}$ Pa during palladium and platinum film deposition, and which also allows to work at H_2 pressure up to 10 Pa in the course of PdH_x formation, was used. SP measurements were performed by means of the static capacitor method [3,10,11]. The static capacitor circuit of short response time (10^{-3} s), high sensitivity (1 mV) and high stability (1 mV/10 min), allowing for work within a large interval of pressure (10^{-8} to 10 Pa) and temperature (78–500 K), was applied for SP measurements. Thin films of known mass were obtained by complete evaporation of a fine Pd wire, of precisely determined weight, wound around a tungsten heater. Spectroscopically pure hydrogen additionally purified in the course of the experiments was introduced into the static capacitor (disconnected from pumps) in successive calibrated doses. H_2 pressure was recorded continuously by means of an ultra-sensitive Pirani-type gauge capable of working within the interval 2×10^{-4} to 10 Pa. The volume of the static capacitor cell was previously determined, thus knowing the mass of the Pd film and H_2 pressure, the atomic ratio H/Pd at every step of the process could be calculated and correlated with SP. Surface potential studies in the course of PdH_x formation within Pd/Pt/glass system were performed having thick (100 nm) Pt film deposited on glass before thin Pd film (40 nm) was obtained.

For the AFM studies, thin films were deposited on glass microscopic plates under UHV conditions. Application of a proper mask allows to cover part of the glass plate with Pd film, while the other part was precovered with a thick Pt film and next with Pd film. Next, the samples were transported through the air into the AFM cell (Topometrix, Discoverer). The topography of the film in the course of PdH_x formation or its decomposition was monitored by video camera and AFM during H_2 or Ar flow at pressure ∼100 kPa through the cell maintained at 298 K. XPS experiments showed that only small traces of platinum were present within thin palladium film ($Pt/Pd < 10^{-3}$) when Pd/Pt/glass system was examined.

3. Results

The course of surface potential in the process of PdH_x ($0.01 < x < 0.95$) formation at 78 K within thin Pd film on glass and on glass precovered with Pt film is shown in Fig. 1, while the dependence of SP on the H/Pd atomic ratio is presented in Fig. 2. The response of the surface potential to H_2 doses introduction is clearly visible. When the critical coverage is reached, a rapid increase of SP due to the β^+ adspecies creation is followed by a slow decay of the signal. Examination showed that the rate of the SP decay fits the first order kinetic equation, as should be expected for incorporation below the surface. It was observed that these transients of positive SP signals registered as a result of successive hydrogen doses were not complete within the concentration of hydrogen in PdH_x ($0.2 < x < 0.8$) (Fig. 2). Hence the total increase of the surface potential during the whole process of hydride formation was strongly positive. At higher concen-

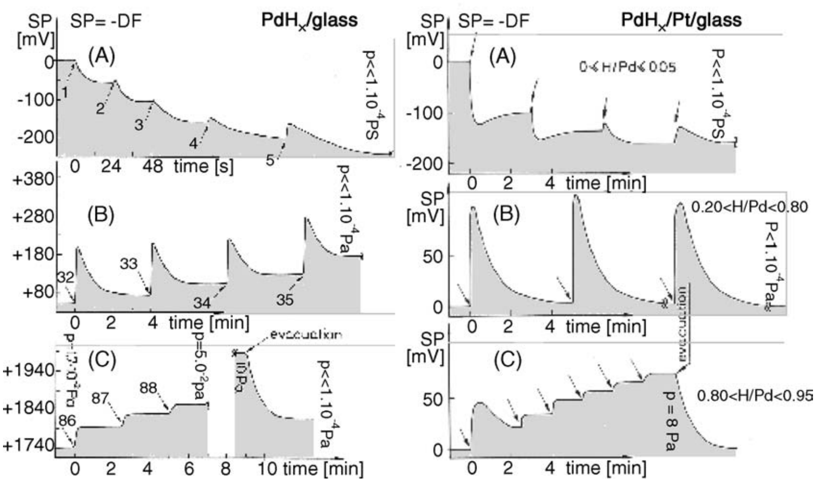

Fig. 1. Surface potential changes in the course of PdH$_x$ ($0 < x < 0.95$) formation at 78 K within thin Pd films deposited on Pyrex glass (Pd/glass) and on Pyrex glass precovered with thick Pt film (Pd/Pt/glass). Sections (A), (B), (C) correspond to the successive steps of the process described by the H/Pd atomic ratio. Arrows indicate successive H_2 doses introduction. Creation of β^- and β^+ adspecies is observed within both systems. A weakly bound hydrogen deposit on PdH$_x$ ($x > 0.8$), desorbing during evacuation of the static capacitor is also clearly seen.

tration H/Pd successive H_2 doses caused monotonic increase of SP. The increase of SP for PdH$_{0.95}$ under H_2 pressure 2.5 Pa was reaching as much as ∼2 V. This would mean a strong polarization of hydrogen adatoms on the surface of PdH$_x$, or a strong roughening of the film. Isothermal evacuation of the system caused decrease of SP by ∼120 mV due to desorption of some weakly adsorbed adspecies on PdH$_{0.95}$ surface.

In contrast with the strong increase of SP in the case of Pd/glass system, a plateau of the surface potential characterizes PdH$_x$ ($0.2 < x < 0.82$) formation within Pd/Pt/glass. Other features like β^- and β^+ forms of the adsorbate, as well as the presence of the weakly bound deposit on the surface of PdH$_x$ ($x > 0.82$) are the same.

Figs. 3 and 4 show the AFM topographic images for the PdH$_x$/glass and PdH$_x$/Pt/glass systems, and the corresponding video camera response. Protrusions are created only within PdH$_x$/glass system. The part of the sample, with the surface roughened by protrusions, is seen by the video camera as darkened because of the dispersion of light, in contrast to the light-reflecting unchanged topography of the PdH$_x$/Pt/glass system.

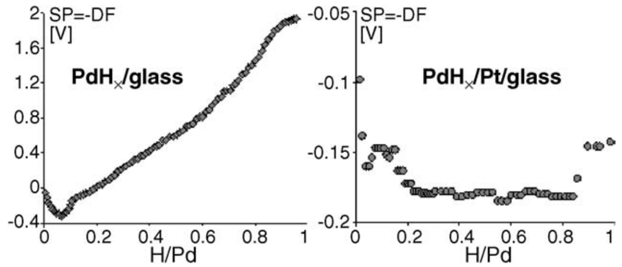

Fig. 2. SP dependence on the H/Pd ratio in the process of PdH$_x$ ($0 < x < 0.95$) formation at 78 K within thin Pd film deposited on Pyrex glass and within thin Pd film deposited on Pyrex glass precovered with thick platinum film.

It should be emphasized that in the course of this work $\Delta\Phi$ and AFM studies were carried out under different thermodynamic conditions. Hence AFM data collected at 78 K under UHV conditions (unavailable in our laboratory) would be very useful to confirm the presented results.

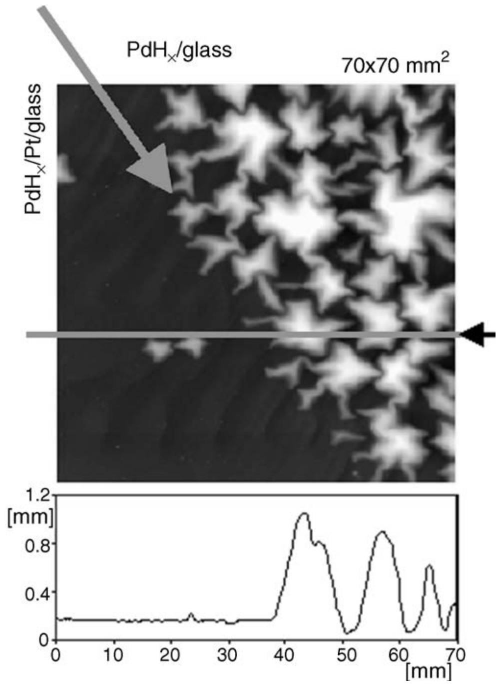

Fig. 3. AFM topographical image and profile of PdH$_x$ formed at 298 K within thin Pd film deposited on glass and on glass precovered with thick platinum film. Protrusions formed within the PdH$_x$/glass system are clearly seen, as well as their absence in the PdH$_x$/Pt/glass system.

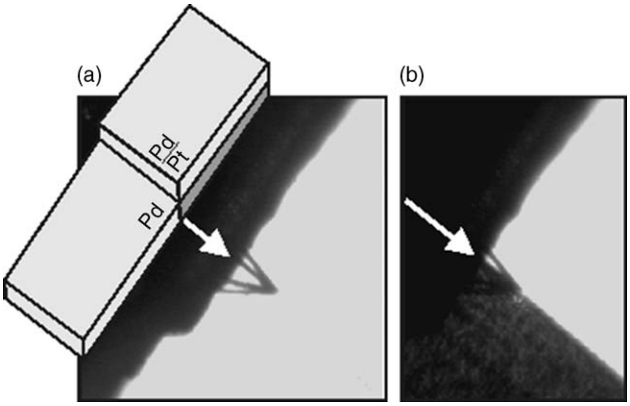

Fig. 4. Video camera images: (a) The films Pd/glass and Pd/Pt/glass in Ar atmosphere. The arrow indicates the boundary between the two films. (b) The films PdH_x/glass and PdH_x/Pt/glass in H atmosphere. The arrow indicates the boundary between the films. Darken image caused by dispersion of light on protrusions can be noticed for PdH_x/glass system, while light image corresponds to unchanged topography of PdH_x/Pt/glass system. Black part of the picture in the left upper corner corresponds to the shadow of the AFM cantilever.

4. Conclusion

We suggest that the decrease of SP registered at the beginning of the process of PdH_x formation within thin Pd film due to arising of the β^- adspecies, plateau of SP within PdH_x composition ($0.1 < x < 0.80$), and the presence of the weakly adsorbed β^+ adspecies on the surface of PdH_x ($x > 0.8$) are features corresponding to the chemical component of SP. On the other hand the strong increase of SP (decrease of the work function) registered in the process of PdH_x ($0.1 < x < 0.8$) formation at 78 K within a Pd/glass system is caused by roughening of the film, and not by a high polarization of hydrogen adspecies on the palladium hydride surface.

References

[1] R. Smoluchowski, Phys. Rev. 60 (1941) 661.
[2] F.C. Tompkins, Chemisorption of Gases on Metals, Academic Press, London, 1978.
[3] R. Duś, Surf. Sci. 5 (1975) 440.
[4] R. Duś, E. Nowicka, Langmuir 16 (2000) 584.
[5] R. Duś, E. Nowicka, Langmuir 14 (1998) 5487.
[6] E. Nowicka, Vacuum 47 (1996) 193.
[7] T.B. Grimley, in: W.E. Garner (Ed.), Chemisorption, Butterworths, London, 1957.
[8] B.C. Brouer, R. Griessen, Phys. Rev. Lett. 62 (1989) 176010.
[9] R. Nowakowski, P. Grzeszczak, R. Duś, Surf. Sci. 507/510 (2002) 813.
[10] T. Delchar, A. Eberhagen, F.C. Tompkins, J. Sci. Instrum. 40 (1963) 105.
[11] A. Bachtin, Vacuum 12 (1985) 519.