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ATOMIC DEUTERIUM EMISSION FROM PALLADIUM DEUTERIDE PdD_y SURFACE

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Deuterium desorption from the surface of decomposing palladium deuteride was studied by monitoring the atomic component of the desorbing gas using an adsorption method. A thin gold film was applied as an adsorbent active for D adsorption, but inert to D_2 adsorption. The deuterium deposit thereby collected on the Au surface was analysed by means of the thermal desorption mass spectrometry (TDMS). The atomic component of deuterium, arising by desorption from decomposing PdD_y was clearly detected. The experimental results obtained for PdD_y, are compared with those observed during the decomposition of PdH_x.

1. Introduction

Surface phenomena associated with the formation of transition metal hydrides MeH_x (deuterides MeD_y) are poorly understood in spite of their importance in many applications [1]. It has been reported [2-8] that interaction of H_2 (D_2) with thin films of some of transition metals leads to hydride (deuteride) formation over the pressure range 10^{-6}–10^{-2} Torr, (Torr = 133.3 Pa), even at temperatures as low as 78 K.

Several specific adsorption states of hydrogen (deuterium) adspecies, have been identified in the course of low temperature MeH_x (MeD_y) production. These adsorption states are similar for all examined metals capable to form hydrides (deuterides), e.g. Pd [2-4], Ni [5], Nb [6], Ti [7] and V [8]. The adsorption states occur as follows:

(i) At the beginning of adsorption, negatively polarized (i.e. the negative pole of the dipole protruding out from the surface) atomic, surface stable form of the adsorbate is created. This form of the adsorbate is referred to as β^-.

(ii) With increasing coverage an entirely different form of hydrogen (deuterium) adsorbate arises. It is the positively polarized, atomic form, referred to as β^+. The β^+ adspecies are not stable on the surface, but are rather quickly incorporated into the bulk. Transition metal hydrides (deuterides) are thus formed, thereby storing a large amount of hydrogen (deuterium). The β^+ adspecies which are quickly incorporated below the surface have never been observed during the course of hydrogen (deuterium) adsorption onto metals which do not form hydrides (deuterides), like Pt [9] or Fe [10].

(iii) On the surface of transition metal hydrides weakly bound, atomic, positively polarized hydrogen adspecies exist at 78 K under H_2 equilibrium pressure higher than 10^{-3} Torr. Lowering the pressure causes an isothermal desorption of these adspecies. The question arises whether these weakly bound hydrogen (deuterium) adatoms desorb associatively forming admolecules on the surface, or if there is a probability for their direct emission from the surface in the atomic form. The atomic component has indeed been found in hydrogen desorbing from decomposing $PdH_{0.9}$ [11,12]. The mechanism for the atomic hydrogen emission from the decomposing MeH_x is presently not clear.

The aim of this study is to examine deuterium desorption from PdD_y, and to compare this process with hydrogen desorption from PdH_x.

2. *Experimental*

The adsorption method was applied to determine the atomic component in deuterium desorbing from palladium deuteride [11,12]. In this method deuterium desorbing from PdD_y interacts with the surface of an adsorbent which is active for D adsorption, but completely inert to D_2 adsorption. Thus only atomic deuterium is captured from the $D+D_2$ mixtures. Further, atomic deuterium deposits were thermally desorbed and quantitatively determined by thermal desorption mass spectrometry (TDMS).

Sintered thin gold films can be applied as selective adsorbents for H from $H+H_2$ mixtures [13,14]. Therefore, it is reasonable to expect that this adsorbent may also be used for the detection of atomic deuterium. For quantification, calibration experiments were carried out. Atomic deuterium was thermally generated on a hot tungsten filament and adsorbed on thin Au films that were deposited under UHV conditions and sintered. The Au films were maintained at 78 K, as in previous experiments with hydrogen [13]. However, in the experiments described here, the change of the relative resistance of the thin Au films, R_{Au}, caused by the change of temperature of the cell, was also measured. This arrangement is of crucial importance, since the temperature dependent changes of the thin gold film resistance serves as a thermometer during the TD experiments. The dependence of R_{Au} on temperature of thin Au film was previously determined in separate experiments. It has been found that atomic deuterium (hydrogen) adsorption does not influence R_{Au} value within the error of our measurements.

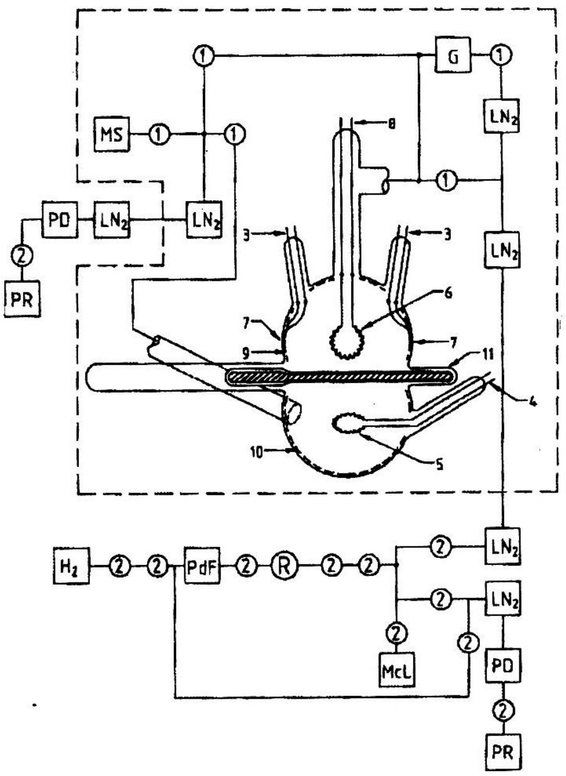


Fig. 1. Schematic diagram of the apparatus. Dotted line indicates the UHV part of the glass system, bakable to 700 K. *The markings denote the following units and compontents: mass spectrometer–(MS), modulated ionization gauge–(G), McLeod mercury manometer–(McL), palladium filter for* H_2 (D_2)*–PdF, callibrated volume for* H_2 (D_2) *dosing–R, hydrogen (deuterium) container–*H_2*, a set of the diffusion mercury pumps (two pumps in series)–PD, rotary pump–PR, liquid nitrogen trap–*LN_2*, greaseless Dekker valve–(1), HV tap–(2), tungsten feedthroughs connected to a thin platinum foil semi–melted onto glass for measurements of thin transition metal film resistance (3) and (7), tungsten feedthroughs and heater for thin* Au *film deposition (4) and (5), tungsten feedthroughs and heater for thin transition metal film deposition (6) and (8), thin transition metal film and thin* Au *film (9) and (10), damper (11).*

In order to determine the atomic component in deuterium desorbing from PdD_y, a special cell was constructed. This cell allowed the following procedures during the course of an experiment:
(i) Deposition of a thin palladium film under UHV conditions (1×10^{-10} Torr).
(ii) "In situ" transformation of the deposited thin palladium film into a deuteride PdD_y under controlled conditions, while simultaneously measuring the thin PdD_y film resistance and the D_2 pressure.
(iii) Thermal decomposition of deuteride PdD_y.
(iv) Collection of atomic deuterium desorbing from decomposing PdD_y on the surface of a sintered thin gold film (previously deposited "in situ" under UHV conditions).
(v) Determination of the amount of atomic deuterium collected on the thin Au film by means of TDMS method recording D_2 spectrum. It has been found that hydrogen (deuterium) desorbs associatively from Au surface.

The cell and a schematic drawing of the associated UHV system is shown in Fig. 1. The cell is made of Pyrex glass and consists of two bulbs separated by a damper which is operated magnetically from outside. The upper bulb is equipped with a heater for thin palladium film deposition (wound fine Pd wire on a tungsten filament) and two platinum foil electrodes, semi–melted onto the glass. This arrangement allows for resistance measurements of thin Pd film during deposition and, later, during the course of the deuteride formation. The lower bulb is equipped with a tungsten heater for thin Au film deposition. Each bulb can be pumped out by a separate set of diffusion pumps. The damper allows separation of the bulbs during thin film deposition and subsequently their joining for studies of PdD_y decomposition.

Thin Au film was deposited at 78 K and sintered at 370 K for 30 minutes. A thin palladium film was then obtained while the entire cell was immersed in a liquid nitrogen bath.

Spectroscopically pure D_2 (purified further by diffusion through a palladium thimble) was introduced in successive, calibrated doses into the cell which was separated from pumps by means of greaseless Dekker valves. The deuterium pressure was measured after every D_2 dose introduction by means of a McLeod manometer. In this way any contact of D_2 with the hot filament of the ionization gauge (leading to deuterium dissociation) can be avoided. Knowing the volume of the cell, the amount of consumed deuterium can be determined. This allows calculation of the atomic ratio D/Pd, since the weight of the thin Pd film is known. Continuous measurements of the thin Pd film resistance during PdD_y formation gives additional information concerning the deuterium concentration, since the dependence of $\Delta R/R$ versus D/Pd has previously been determined [15].

The topographic images of thin Pd and Au films obtained by means of scanning tunneling microscopy (STM) are shown in Fig. 2. The average thickness of the films was around 200 nm. The roughness factors of the thin palladium and gold films were 16 and 1.7, respectively.

When a thin PdD_y film was obtained, the cell was connected to the pumps, evacuated, and the damper pulled, thereby joining the two bulbs. The Dewar flask liquid nitrogen bath was lowered, unveiling the upper bulb with the deuteride, while the lower bulb with the thin Au film was maintained in liquid nitrogen. The thermal decomposition of PdD_y was initiated by heating the upper bulb to 370 K. Desorbing deuterium species impinged upon the surface of the thin gold film. D atoms can be adsorbed, while D_2 molecules are reflected and pumped out. The amount of deuterium adsorbed was then determined by means of TDMS [13,14]. The increase of temperature of the lower bulb was measured by means of a fine thermocouple that was tightly touching its outer wall. The temperature gradient throught the wall caused some differences in the shape of the registered TD peak of D_2 in comparison with the calibration spectrum.

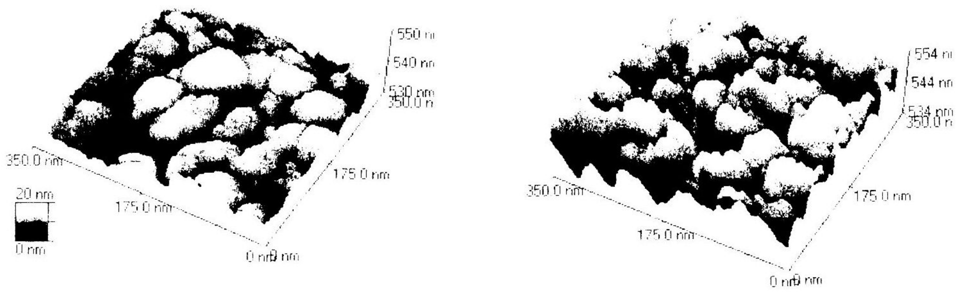


Fig. 2 STM images of a thin Au *film (left) and a thin* Pd *film (right).*

3. *Results and discussion*

TDMS spectra for thermally generated D atoms adsorbed at 78 K on sintered thin gold film are shown in Fig. 3. At low population, a single TD peak with a maximum at $T_{max} \approx 159$ K is observed. An increase of population leads to a shift of T_{max} towards lower temperatures, as expected for the associative desorption. Examination of the desorption rate (according to the Polany's equation) reveals that this process follows second order kinetics, and the calculated activation energy for desorption is 50.7 kJ/mole [13, 14].

A significant increase in the coverage obtained as a result of high exposure resulted in a modification of the low temperature branch of the spectrum, shifting it towards lower temperatures. In our opinion, this modification is caused by formation of deuterium addimers D_{ad}–D_{ad} on the surface of gold, as suggested earlier for H–Au adsorption system [13,14]. The addimers are more weakly bound on the gold surface than D atoms and, as a consequence, they desorb at lower temperature. A large variety of addimers situated at different intermolecular distances should be expected with increasing coverage. The addimers approaching the intermolecular distance characteristic of a D_2 molecule could desorb at 78 K, immediately after admolecule formation (D_2 does not adsorb on gold at 78 K). Therefore, the TD spectrum profile for deuterium deposited on gold is strongly coverage dependent.

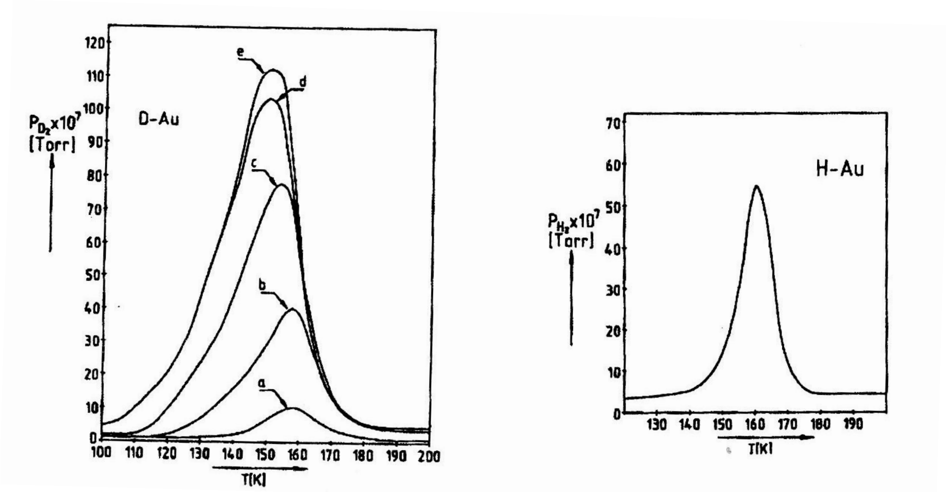
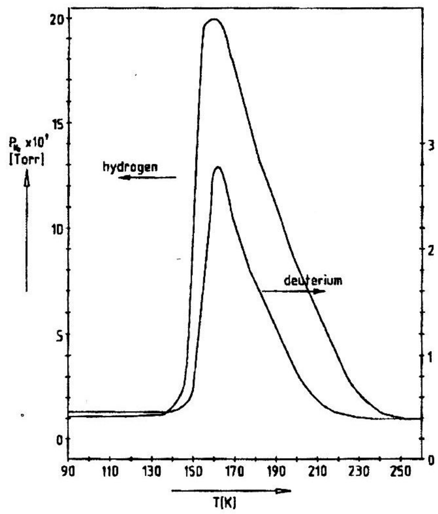


Fig. 3. TDMS spectra for various exposures of thin Au *film (maintained at 78* K*) to atomic deuterium (hydrogen) generated at 1200* K *on tungsten filament at* D_2 *(*H_2*) pressure of* 6×10^{-3} Torr. *The spectra labelled* a,b,c *and* d *were obtained as the result of exposure for 1,2,3 and 5 minutes, respectively, at a tungsten filament temperature* $T_W \approx 1100$ K. *Spectrum* e *was obtained for 7 minutes at* $T_W \approx 1350$ K. *For comparison, a TD spectrum for hydrogen deposit on thin gold film is also shown (3 min. exposure for atomic hydrogen generated at 1100* K *on* W *filament).*

The mass spectrometric signal recorded as the result of thermal desorption of deuterium deposited on gold in the course of $PdD_{0.80}$ decomposition is shown in Fig. 4. For comparison the TD spectrum for atomic hydrogen deposited on gold due to $PdH_{0.88}$ decomposition is also shown. It can be clearly seen that the atomic component is present in deuterium (hydrogen) desorbing from decomposing PdD_y (PdH_x). In our experiments the determined ratio of the atomic to the molecular component (D/D_2) for deuterium desorbing from PdD_y approaches 10^{-4}, while for hydrogen this ratio reaches 10^{-3}. This ratio may be significantly higher, since the unavoidable recombination of some of D (H) atoms occurs as the result of the gas phase collision with the PdD_y (PdH_x) covered wall of the upper bulb in our cell.

We observed previously [12] that the H/H_2 ratio for hydrogen desorption from decomposing PdH_x depends on the film roughness factor as well as on the film thickness. The high roughness factor of thin PdD_y films corresponds to a large surface area, while a high thickness is attributable to a large amount of deuterium (hydrogen) in the deuteride (hydride). It has been suggested [4] that at low temperatures hydrogen (deuterium) adatoms penetrate quickly below Pd surfaces due to a tunnelling effect. If the reverse process were possible during PdH_x (PdD_y) decomposition then the dependence of H/H_2 ratios on the mass and area of the Pd film should be expected. The physical reason for low temperature atomic deuterium emission from the surface of decomposing PdD_y is not yet clear. However, it should be mentioned that an increase of temperature from 78 K to 250 K causes a rapid decomposition of PdH_x and PdD_y, causing a surface and subsurface "explosion". During this process that is far from equilibrium, several mechanisms of desorption can be considered and among them a direct desorption of deuterium atoms.



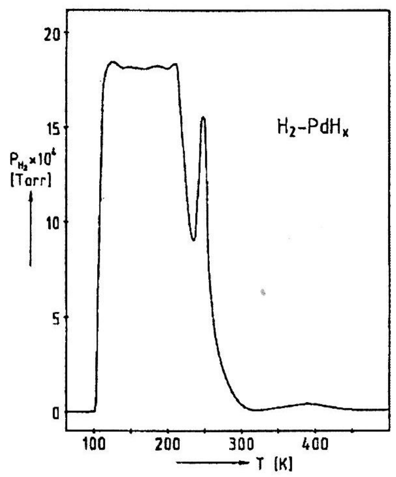


Fig. 4. TDMS spectra obtained from thin Au *film as the result of its interaction at 78* K *with deuterium (hydrogen) emitted from decomposing thin* PdD_y (PdH_x) *films.*

Fig. 5. TDMS spectrum from decomposing thin PdH_x *film (right).*

TD spectrum for thin PdH_x film decomposition, as examined in a separate UHV apparatus, is shown in Fig. 5. Decomposition of PdH_x on the surface and in the bulk occurs immediately at low temperatures. When PdH_x decomposition is complete a minor hydrogen deposit adsorbed on the Pd surface is stable up to 380 K. This state of the adsorbate is well known for hydrogen adsorption on transition metals. TDMS spectra for deuterides are similar.

The interpretation of the results presented here is partly speculative, and it is understood that the reasons for the presence of the atomic component in hydrogen (deuterium) desorbing during PdH_x (PdD_y) decomposition are related to the specific fundamental physical properties of these compounds [16].

4. Conclusions

Deuterium (hydrogen) desorbing from the surface of the decomposing PdD_y (PdH_x) contains an atomic component.

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ISPUŠTANJE ATOMSKOG DEUTERIJA IZ POVRŠINE PALADIJEVOG DEUTERIDA

Proučavana je desorpcija deuterija s površine raspadajućeg PdD_y mjerenjem atomske sastavnice desorbiranog plina. U tu je svrhu upotrebljen tanak listić zlata aktiviran za D adsorpciju, a inertan za D_2 adsorpciju. Deuterij sakupljen na zlatu analiziran je termičkom desorpcijskom masenom spektrometrijom. Eksperimentalni rezultati za PdD_y se uspoređuju s rezultatima za desorpciju iz PdH_x.