The influence of the external electric field on the hydrogen-palladium system

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Abstract. In the course of low-temperature field desorption of hydrogen from palladium surface the occurrence of a wide variety of palladium hydrides species as well as hydrogen ions has been detected by using high-resolution pulsed-laser time-of-flight atom-probe (PLTFAP) field ion microscope. In this paper both experimental and DFT approach has been undertaken in order to study the interaction of hydrogen with palladium surface leading to the formation of palladium hydrides in the interstitial positions within two metal layers. The influence of a homogeneous external electric field of the order of several tens V/nm on the hydrogen/palladium surface binding energy has been examined. On the basis of the obtained results it can be stated that in the presence of an external field the palladium-hydrogen bonds become stronger with the maximum binding energy value at the electric field strength of 25 V/nm. On the other hand in the existence of an external field decreasing of activation energy required for hydrogen diffusion into the subsurface is observed.

Keywords: palladium; hydrogen; field desorption; metal hydride ions; DFT calculations

1. Introduction
In view of high solubility of hydrogen in palladium this system has been investigated by series of methods for a long time [1,2]. It is well known that palladium stable hydrides are produced in the process of direct interaction of hydrogen under a pressure of several MPa over a surface of palladium, usually at a temperature above 200 K [3]. The stoichiometry of palladium hydrides as well as of other metal hydrides depends on the equilibrium pressure the value of which is characteristic for defined temperature conditions. On the other hand, in the process of field desorption, which proceeds at low temperature, PdHx⁺ (x=1,2,3,4) ions are observed [4,5]. It seems that the existence of an external electric field of the order of several tens volts per nanometer causes the changes of the palladium surface reactivity. As a result the occurrence of palladium hydrides of enlarged stoichiometry has been noticed. For some very important applications, such as hydrogen storage as well as hydrogenation reactions catalysis the determination of the electric field influence on the quality and efficiency of surface reaction taking place in palladium/hydrogen system seems to be a problem of a great significance.
In the present paper the palladium-hydrogen complexes formation is discussed in the light of both experimental and quantum chemical computations results. In particular, our attention is paid to the influence of an external electric field on hydrogen-palladium surface nature.

2. Experimental and calculations

The instrument [6] used in this investigation was a high-resolution pulsed-laser time-of-flight atom-probe field ion microscope (PLTFAP). The ultrahigh vacuum experimental conditions and the measurement procedure were those described in [5]. The field emitter tip was obtained from a palladium wire of 99.99% purity by means of electropolishing. The applied electric field strength was 26.7 V/nm and the palladium tip was kept at the temperature of 20 K. The partial pressure of hydrogen was 10^{-6} Pa. Before each experiment, the emitter surface was processed to obtain an atomically smooth end-form by low-temperature field evaporation in the presence of neon. The emission region was from (111) Pd steps.

In order to complete the experimental results some quantum chemical calculations of hydrogen atom interacting with palladium atom cluster have been performed. For numerical computations, the Gaussian 98 program package [7] was employed. The density functional (DFT) approach was used to calculate the energy of the hydrogen-palladium complex by using a hybrid functional. The hybrid functional includes a mixture of Hartree-Fock (HF) exchange and exchange-correlation density functional theory and has the following form [8]:

\[
A * E_x^{Slater} + (1 - A) * E_x^{HF} + B * \Delta E_x^{Becke} + E_c^{VWN} + C * \Delta E_c^{non-local} ;
\]

where the non-local correlation is provided by the correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms (LYP) [9], and VWN is the Vosko, Wilk and Nusair correlation functional, often referred to as Local Spin Density (LSD) correlation [10] (functional III in the paper). The constants A, B and C are those determined by Becke by fitting to the 56 atomization energies and other parameters. The using of the functional has been proved to give the best reliability of description of hydrogen interaction with small palladium clusters [11]. The basis set taken for palladium atom was CEP-4G [12], which enables to take into account some relativistic effects important in heavy atoms.

In the theoretical studies an octahedral void shaped by six palladium atoms cluster with a palladium-palladium distance equals to 0.275 nm is used. The geometry of the void was determined by using crystallographic dates of metals structures [13]. Each of its eight faces can be considered as a model of Pd(111) plane with an fcc site accessible for a hydrogen chemisorbed atom. The diffusion of hydrogen from the surface into the center of the void leads the creation of the interstitial hydride structure.

3. Results and discussion

During the process of field desorption from palladium field emitter tip carried out in a hydrogen atmosphere the ions of hydrogen were detected as well as those of palladium and the palladium-hydrogen ions. The original mass spectrum obtained from a palladium specimen in an atmosphere of hydrogen is shown in Fig.1.
As the natural palladium is a mixture of six isotopes (102, 104, 105, 106, 108 and 110), we could directly find in the spectrum only of these ions which correspond to the hydrides PdH⁺, PdH₃⁺ and PdH₄⁺. The remaining peaks on the spectrum taken correspond to a mixture of various Pd isotopes as well as their hydrides of different stoichiometry. Since the natural isotope composition of palladium is known, we could calculate numerically the fractions of respective Pd hydrides [5].

As Tsong has shown [14] for the low-temperature, laser beam stimulated process of field desorption, in an individual event the surface is left by those atoms or molecules only that are localized on the surface in kink-site positions which were in our experiment the kink-sites of the Pd(111) terrace edges. Based on the consideration of thermodynamic energy cycle for creating n⁺ ion from a kink-site atom, we arrive with the expression for the appearance energy [15]

$$A_n = \sum_{i=1}^{n} I_i + \Lambda' + Q \tag{2}$$

where \(I_i\) is the i-th ionization energy of an atom, \(\Lambda'\) is the binding energy of the atom (or the adsorption energy) in the high electric field and \(Q\) is the activation energy for field evaporation of the atom (relatively small in our case). The binding energy of an adatom/ admolecule on the surface in the high electric field can be written as

$$\Lambda' = \Lambda + (1/2) \alpha' F^2 \tag{3}$$

where \(\Lambda\) is the binding energy of the atom in zero-field and \(\alpha'\) is the effective polarizability of surface atom. For metals, within the limits of the ± 0.2 eV accuracy [14], the binding energy of kink-site atoms is equal to the cohesive energy, or heat of sublimation of the solid. In the present investigation the field ion appearance energy was measured by using the time-of-flight method [16].

Based on the analysis of the spectrum recorded (fig.1) the formation energy of PdH₃⁺ ions can unequivocally be determined only for the PdH₃ and PdH₄ hydrides of the ¹¹⁰Pd isotope. This amounts to 12.32 eV and 11.44 eV, respectively. If the ionization potentials of relevant molecules are known, then their binding energy with respect to the surface kink-position can be determined from Eq.(2). The respective ionization potential have been calculated by the method of density functional for the optimalized geometry of the molecules PdH₃ and PdH₄ [17] to be 8.74 eV and 9.35 eV, which gives the binding energies 3.58 and 2.09 eV. Quite an essential result of the calculations in question was the
conclusion that the molecules of interest as well as their ions are stable in the external electric field up to the strengths 30 V/nm and 35 V/nm, hence they should be stable in the electric fields in our experiment.

Palladium hydrides appear to be much weaker bound to the surface in the high electric field than are palladium atoms themselves whose cohesion energy is equal to 3.89 eV/atom [13]. In view of that the field-evaporation process field strength of palladium in an atmosphere of hydrogen (26.7 V/nm [5]) is lower than in vacuum (32 V/nm), the values obtained seem feasible.

As far as it concerns the palladium hydrides formation in the kink-site positions it has to be noticed that from simple geometry it can be hardly expected that four hydrogen atoms could simultaneously approach Pd atom in this position on the surface to form a bond. It is well known that hydrogen easy dissolves in palladium to produce hydride phases. At first, when hydrogen contents in metal volume is small the formation of hydrogen solid solution in palladium is observed. It is so called α-phase composition of which increases with the sample temperature. Then, when the critical value of hydrogen contents is reached the process of the formation of bulk metal hydrides (β-phase) takes place. For instance, in a thin palladium layer at 78 K, under low hydrogen pressure the β-phase of the composition PdH$_{0.9}$ is produced [18]. The fcc palladium exhibits the structure in which one octahedral void and two tetrahedral voids fall per atom. Theoretically, a complete filling of the voids should correspond to a hydride phase of the stoichiometry PdH$_2$. Analysis of the theoretically derived geometry of the palladium hydride molecule [17] leads to the conclusion that for formation of a surface molecule of PdH$_4$ from a kink-site atom of palladium it is sufficient that one of the closest octahedral voids be filled with a hydrogen atom. In other words, one atom of hydrogen has to migrate in the applied electric field into the void to produce the hydride surface structure.

To verify such a possibility the changes of the binding energy of hydrogen atom with a palladium cluster described above as a function of hydrogen-cluster surface separation distance in the case of no external field was examined (Fig. 2).

![Fig. 2 Hydrogen atom inside the octahedral void](image)

The values of the binding energy were estimated with respect to the minimum energy which corresponds to the chemisorption of hydrogen at fcc site. The minimum energy is set to 0. The chemisorbed hydrogen atom has been located 0.088 nm above the surface and hydrogen-palladium bonding has been equal to 0.181 nm. The last value is consistent with both experimental value of 0.178 nm [19] and periodic band structure calculations results (0.182 nm) [20]. The local minimum of the binding energy curve corresponds to the location of hydrogen inside a cluster close to its geometrical
The equilibrium position of hydrogen inside a cluster is shifted by 0.03 nm towards the surface. Similar effects have been noticed in paper [20] and explained by creating of stronger covalent palladium-hydrogen bonds in view of the existing of unsaturated of the surface layer. The incorporation of hydrogen into the cluster requires the activation energy of 0.92 eV.

As a next step the palladium cluster interacting with a hydrogen atom was put in a homogeneous external electric field the strength direction of which corresponds to that in field ion microscopy experiment. Since we were interested in how the presence of a high electric field influences the nature of hydrogen-palladium surface interaction the dependences of the binding energy of hydrogen at fcc site and inside of octahedral void as well as the activation energy required for hydrogen diffusion into the cluster on electric field strength were determined. The variation of these quantities as a function of external electric field is shown in Figs 3, 4 and 5.

Fig. 3 The binding energy of hydrogen atom with palladium surface

Fig. 4 The binding energy of hydrogen inside the octahedral void
Although the applied model used is quite simplified, the results indicate that, for an electric field strength of 25 V/nm, hydrogen is bound strongest both in the chemisorption position and inside the void, i.e. for the field strength typically required to observe field desorption in experiment. The agreement between the values obtained is striking. All the more interesting is that just for this field strength the activation energy for displacement of hydrogen from chemisorption to hydride position has its minimum (Fig.5). This means that, at this field strength, the field-chemisorbed hydrogen can most easily penetrate into a subsurface void adjacent to a terrace edge of the Pd (111) to be bound with an energy of about 1.55 eV, which value is a local maximum (Fig.4). A similar local maximum occurs for hydrogen chemisorbed in a 3-fold site, where the binding energy amounts to about 0.98 eV. Moreover, the form of the obtained curves in the neighbourhood of these values seems to confirm that the bonding in the electric field is in most part due to the polarization term as written in Eq.(3).

Taking into account the obtained results we can conclude that in the electric field of about 25 V/nm on the field emitter surface of (111)-oriented palladium a surface layer of palladium hydride might have been produced. The presence of numerous bright spots and many structural faults on the FIM pattern taken after field desorption made in atmosphere of hydrogen, speaks in favour of this hypothesis [21]. Those spots likely are originated from the surface palladium hydrides FIM-imaged by the krypton image gas. After heating the field emitter at a temperature of 1000 K quite a clean and regular image of the palladium surface was typically obtained. No change, however, in orientation of the imaged surface was noted in contrast to the case of the field electron emission microscopy observations [22].

4. Conclusions:
In the presence of an external electric field of the order of 25 V/nm hydrogen is bound strongest in the chemisorption position as well as inside the void. At the same field strength, the chemisorbed hydrogen atom can most easily penetrate into a subsurface void adjacent to the terrace edge of the Pd (111).

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