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Electronic properties of Pt(100) single crystal surface: experimental study and theoretical calculations

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Abstract

The density of vacant states (DVS) of Pt(100)-(1 × 1) single crystal surface is investigated by means of disappearance potential spectroscopy (DAPS). Probing hydrogen adsorption is used in order to suppress the strong diffraction background and to display the desirable features in difference spectra. Local density of states is calculated for the several top layers of semi-infinite Pt(100)-(1 × 1) plane. The spectra features are in a good agreement with the peculiarities of electronic structure that resulted from calculations. The comparison of experimental and theoretical data shows that hydrogen atoms adsorbed on the Pt(100)-(1 × 1) surface at 300 K primarily interact with platinum atoms of the second layer. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Disappearance potential spectroscopy (DAPS) is known to originate from excitation of a given core electron of the target by the primary electron beam of variable energy [1]. The threshold excitation process proceeds in such a way that the both electrons (incident and excited) occupy the acceptable vacant state above the Fermi level (E_F) of the sample. The peak in DAP spectrum is obviously located by the respective core binding energy, and the peak features are mainly determined by the self-convolution of one-electron density of vacant states (DVS) [1–4].

The chemical bond formation between solid surface and adsorbate is accompanied by the substantial change of electronic properties of this surface, and therefore by the respective change of the local density of states (LDOS) including the DVS structure. Thus, DVS indirectly participates in the processes of adsorption and surface reactions in adsorbed layer. In particular, one could expect that the peculiarities of DVS structure of solid surface would correlate with its adsorption and catalytic properties. DAPS seems to be a very attractive instrument for investigation of this point, since the DAP spectrum is directly controlled by the DVS features of the surface as it was mentioned above. We should note also the extreme surface sensitivity of DAPS originated from the technique principle [1]. The usual testing depth does not

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exceed two to three monolayers, which are of the top interest from the viewpoint of adsorption and catalysis.

The present paper deals with DAPS study of Pt(100)-(1 × 1) surface. The diffraction features used to hinder the DAP spectra that is especially pronounced for well-ordered surfaces like single crystals. We used exactly unreconstructed surface in order to avoid additional difficulties relating to change of surface structure in the course of adsorption. Local density of states (LDOS) is calculated for the same platinum plane at LMTO-TB (linear muffin-tin orbitals-tight-binding) approximation [5]. Calculations were performed in order to validate the experimental data and to identify the DAP spectra features.

2. Experimental

Experiments were performed in an UHV chamber equipped with the low-energy electron diffraction (LEED), Auger-electron spectroscopy (AES), dipole mass-spectrometer and Ar^+ ion gun. The DAPS technique was realized on the basis of LEED optics. The central LEED electron gun with tungsten filament was used as a source of primary electrons of variable energy (with beam size ca. 1 mm and beam current ca. 1 μA). The DAP spectra were registered as the first derivative of the quasi-elastic yield (of the total collector current I_c) by applying the modulation of about $0.6 V_{pp}$ voltage and ca. 2 kHz frequency to the sample potential. The actual resolution of DAP spectra was about 1.4 eV, whereas the peak position could be measured within 0.1 eV accuracy. All DAP spectra were recorded at 300 K. The surface cleanliness was checked by means of AES.

The Pt(100) single crystal of 99.999% purity (ca. 1 cm width and 1 mm thickness) was oriented within 1° accuracy. The surface cleaning procedure included the several cycles of sequential heating in oxygen at $T = 900$ K and

$P_{O_2} \sim 1 \cdot 10^{-7}$ Torr followed by sputtering with 600 eV Ar^+ ions and annealing in vacuum at 1100 K. The finally observed LEED pattern was typical for the Pt(100)-hex surface [6,7]. The clean unreconstructed Pt(100)-(1 × 1) surface was obtained after the ''NO-receipt'' of Refs. [8,9].

3. Theory

The calculation of Pt(100)-(1 × 1) electronic structure was performed applying the LMTO-TB approximation [5] and the modified tight-binding equation method [10,11]. The surface was considered as an interface between semi-infinite empty and platinum crystals. The empty space was subdivided into muffin-tin spheres of the same radius as for Pt. The basis set of s-, p- and d-function was employed for Pt and s- and p-functions for the empty space. The self-consistent potential parameters for the bulk were taken from Ref. [12]. For calculation of orbital populations at the surface, during self-consistency loop, the Green function technique [11] was employed. The integration over energy was performed by shifting the integration path from real energy axis to the imaginary plane [13]. For integration over perpendicular to the surface wave vector component, the residue theorem was used [14,15]; special points were employed to integrate over the surface Brillouin zone [16].

4. Results and discussion

The threshold excitation phenomenon implies the presence of vacant electronic states at the sample surface available for allocation of both primary and excited electrons and directly relates to LDOS. Fig. 1 shows that the most prominent features of LDOS are attributed by d-electrons but nearly all of the latter are settled below the Fermi level. LDOS at the Fermi level is relatively low, and it decreases above the
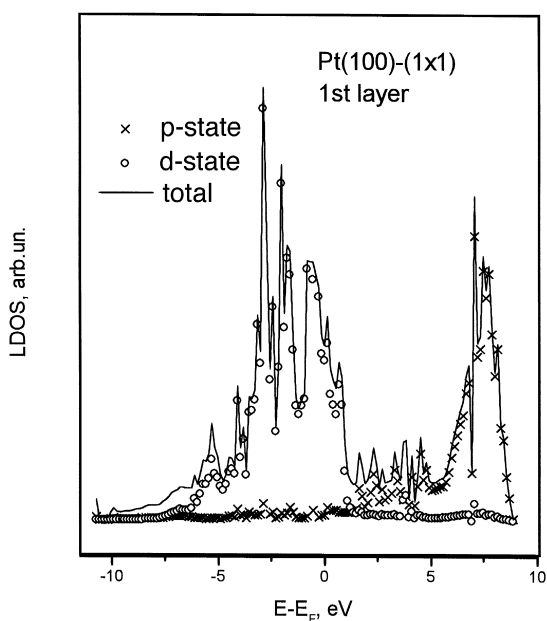
Fig. 1. Local density of states calculated for the 1st layer of platinum atoms of semi-infinite Pt(100)-(1×1) plane. Crosses stand for p-states; open circles stand for d-states; solid line stands for the total LDOS including s-, p-, and d-states.

All the DAP spectra obtained for clean or adsorbate covered Pt(100) surface are very complicated by the strong diffraction features called forth by the single crystal nature of the sample. A survey DAP spectrum shown in Fig. 3a exhibits the continuous sequence of these peaks. The mean peak width at its base is about 15–20 eV, which is a typical characteristic of the diffraction features [19]. The intensity of the diffraction peaks is up to 10^3 times as large as that of DAPS peaks, so that the latest are entirely hidden. In order to extract the desirable information from DAP spectra, we have ''disturbed'' DVS structure of the clean (1×1) surface by introduction of various adsorbates. Then we followed about the difference between the DAP spectrum of the clean surface S_{cl} and DAP spectrum obtained after adsorption S_{ads}.
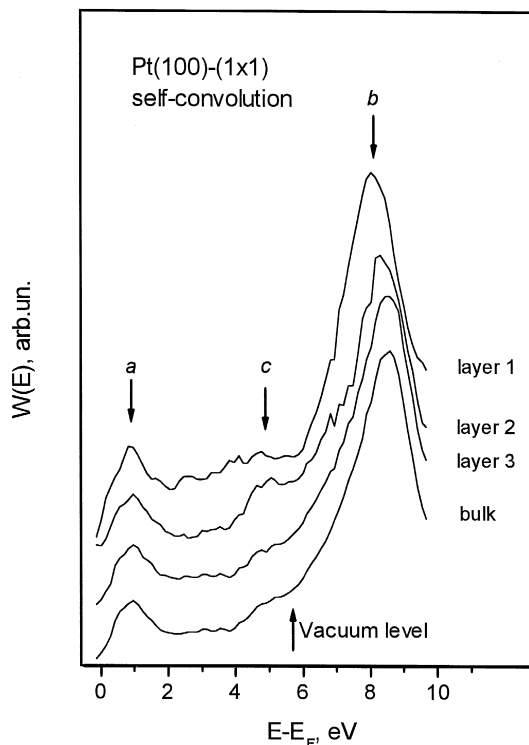
Fermi level. At these circumstances, p-states play a noticeable role as it is seen in Fig. 1. Note that our LMTO-TB calculations give rather narrow width of p-bands that increases the density of p-states, however we believe in qualitative validity of the conclusion.

Fig. 2 shows the self-convolution $W(E)$ of the total DVS distribution for the several top layers of Pt(100)-(1×1) surface. These dependencies are responsible for the most part of the threshold excitation process [1,2,4]. The $W(E)$ distribution reveals two main features designated as a and b, which are contributed by d- and p-states in the main, respectively. Besides, there is another well-distinguishable peak c, which is formed by the comparable contribution of s-, p-, and d-states. The peculiarity of the 1st atomic layer is the lower value of b-state maximum in comparison with that of other layers. The particularly pronounced c-state is the salient feature of the 2nd layer of platinum atoms.

Fig. 2. Self-convolution of the total LDOS vs. energy above E_F calculated for the shown layers of platinum atoms of the semi-infinite Pt(100)-(1×1) plane and for bulk atoms. Vacuum level at 5.63 eV is set according to Ref. [18]. The particularly pronounced states are labeled as a, b, c.

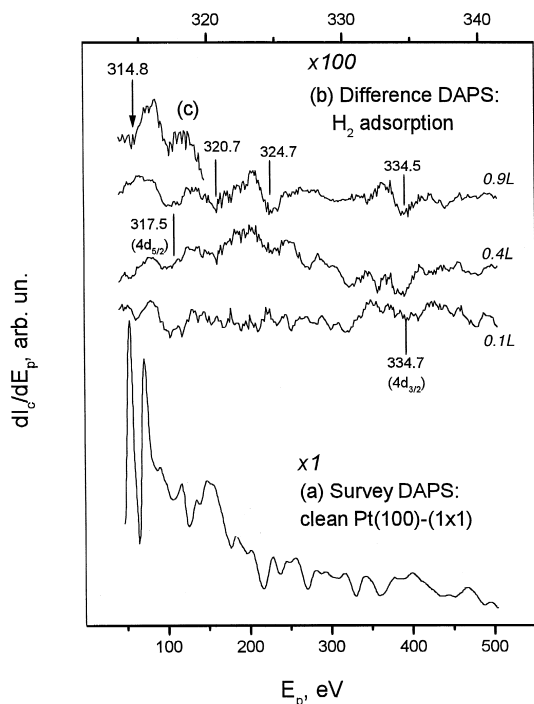Fig. 3. (a) Lower *x*-coordinate: Survey DAP spectrum of the clean Pt(100)-(1×1) surface; (b) Upper *x*-coordinate: Difference DAP spectra corresponding to the shown exposures in Langmuir (L) of the clean Pt(100)-(1×1) surface to hydrogen at 300 K; (c) Part of difference DAP spectrum obtained for the adsorbed system of (H+O)/Pt(100)-(1×1) presented for the more precise determination of the apparent Pt$4d_{5/2}$ core level energy (E_F position) as an intersection of the background and the leading edge of the spectrum peak [22], which was found to be 314.8±0.5 eV; it is very close to the known value of 314.6 eV [17].

The difference spectrum S_{dif} was then constructed by the following subtraction:

$$S_{dif} = \alpha(\theta) S_{ads} - S_{cl} \qquad (1)$$

where $\alpha(\theta)$ accounts for the screening effect of the adsorbed layer at coverage θ corresponding to the given exposure.

Hydrogen, in contrast to CO, NO or O_2, does not form a well-ordered structure in adsorbed layer on Pt(100)-(1×1) surface [20]. Therefore, the diffraction features of the initial and final DAP spectra attributed to surface structure should suppress each other in the difference spectrum under subtraction, whereas new diffraction peaks should not appear. Thus, such a spectrum could reveal those DAPS features of

clean Pt(100)-(1×1) surface which have to do with the H−Pt bond formation.

Indeed, hydrogen exposure of 0.1 L (Langmuir) at 300 K reproducibly reveals two distinguishable features in the difference DAP spectrum shown in Fig. 3b. The peaks with energy extremum at 317.5 and 334.7 eV correspond to the threshold transition of $4d_{5/2}$ and $4d_{3/2}$ core electrons to the vacant state just above E_F, respectively. The energy difference between these peaks of 17.2 eV is close to the spin-orbital splitting of Pt4d level of 17 eV [21]. Further hydrogen exposure of 0.4 and 0.9 L reveal new features at 320.7 and 324.7 eV in the respective difference DAP spectra in Fig. 3b. The peak at 334.7 eV rises and slightly shifts to lower energy as hydrogen exposure increases. The peak
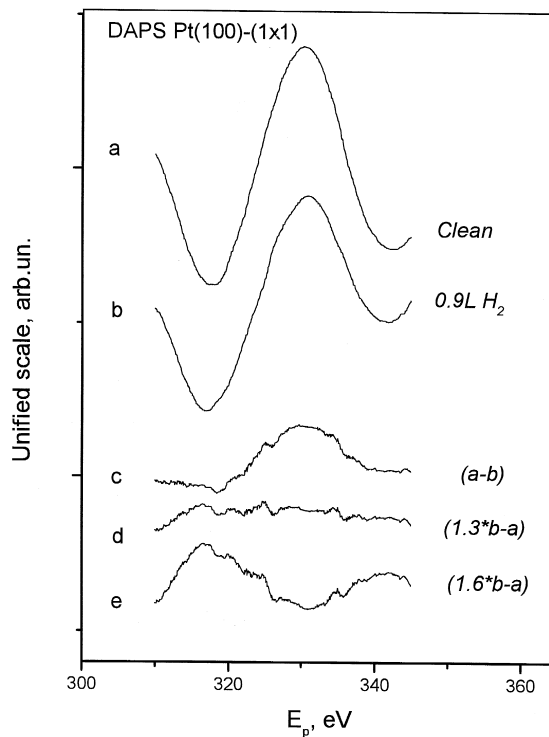

Fig. 4. Difference DAP spectra constructed at various values of screening coefficient $\alpha(\theta)$ in correlation (1). (a) Original DAP spectrum S_{cl} of clean Pt(100)-(1×1) surface; (b) Original DAP spectrum S_{ads} obtained after 0.9 L H_2 adsorption at 300 K on clean Pt(100)-(1×1) surface; (c–e) Difference spectra obtained by subtraction $S_{cl} - \alpha S_{ads}$ at the following values of α: 1 (curve *c*), 1.3 (curve *d*), 1.6 (curve *e*).
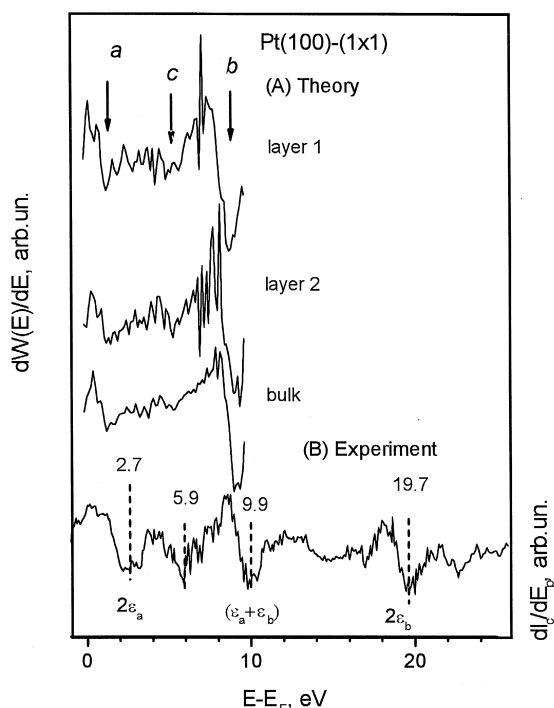
Fig. 5. (A) Three upper curves: Derivatives of LDOS self-convolutions as functions of energy above E_F calculated for the shown platinum layers of Pt(100)-(1×1) plane. (B) Lowest curve: Difference DAP spectrum corresponding to H_2 adsorption on clean Pt(100)-(1×1) surface at 300 K and 0.9 L exposure (replotted from Fig. 3b).

width does not exceed 3 eV for all observed features. The screening coefficient α in correlation (1) is about 1 for hydrogen exposure of 0.1 L, and α of about 1.3 is accepted for the exposures of 0.4 and 0.9 L. The value of $\alpha(\theta)$ was determined so as to minimize the strong background of the attendant diffraction peaks, i.e. to straighten out the given difference spectrum as demonstrated in Fig. 4. We did not

succeed to straighten properly the spectrum corresponding to the medium H_2 exposure of 0.4 L. It is probably due to some ordering in the adsorbed layer at the hydrogen coverage corresponding to this exposure so that new diffraction features show up.

Fig. 5 shows the difference DAP spectrum and the set of dependencies $dW(E)/dE$ vs. energy above E_F for the various platinum layers. We have considered the derivative of self-convolutions reconstructed from data of Fig. 2, because the threshold excitation probability is actually proportional to this characteristic [1–4]. The assignment of the DAPS features is performed using the same designations as in Fig. 2. The respective electron transitions are summarized in Table 1.

The first peak at 2.7 eV of the experimental spectrum in Fig. 5B corresponds obviously to filling the a-state just above E_F. The peak is shifted to a higher energy with respect to the a-state, because of the energy excess $E - E_F$ (i.e. difference between the primary electron energy and $4d_{5/2}$ core binding energy) should be about two times as large as the energy of the a-state in order to localize both electrons (incident and excited) at a-state. Thus, the electron transition can be written as follows:

$$4d_0^{10} + a^0 + b^0 + e^- \rightarrow 4d_{5/2}^9 + a^2 + b^0 + 2\varepsilon_a \quad (2)$$
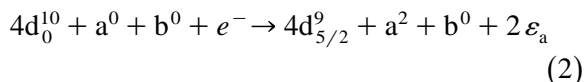
The peak at 9.9 eV corresponds probably to the case, where one of the acting electron pair (incident and excited) is localized at the a-state and another one at the b-state. The peak position above E_F is then determined by adding the

Table 1
The assignment of the difference DAP spectrum features of Pt(100)-(1 × 1) surface according to data of Fig. 5
where a, b are vacant electron states according to designations in Fig. 5, ε_a, ε_b are the respective energies above E_F of a- and b-states, ΔE_{4d} is the spin-orbital splitting of Pt4d level.

Peak energy (eV)	Excited core level	Initial DVS states	Final DVS states	Energy excess
2.7	$4d_0^{10}$	$a^0 + b^0$	$a^2 + b^0$	$2\varepsilon_a$
9.9			$a^1 + b^1$	$\varepsilon_a + \varepsilon_b$
19.7			$a^0 + b^2$, $a^2 + b^0$	$2\varepsilon_b$, $\Delta E_{4d} + 2\varepsilon_a$

energy of the a-state and energy of the b-state according to the electron transition below:

$$4d_0^{10} + a^0 + b^0 + e^-$$
$$\rightarrow 4d_{5/2}^9 + a^1 + b^1 + \varepsilon_a + \varepsilon_b \qquad (3)$$
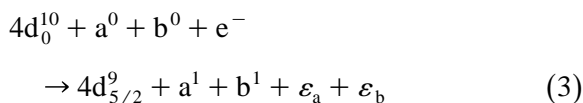
The peak at 19.7 eV may result from the following pathways.

(i) The electron excitation of $4d_{3/2}$ core electron similar to that of Eq. (2):

$$4d_0^{10} + a^0 + b^0 + e^-$$
$$\rightarrow 4d_{3/2}^9 + a^2 + b^0 + \Delta E_{4d} + 2\varepsilon_a \qquad (4)$$
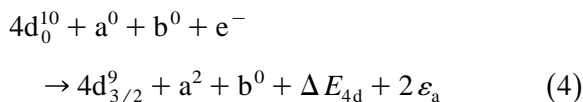
The peak is shifted to higher energy with respect to the similar peak at 2.7 eV of $4d_{5/2}$ core electron excitation by 17.0 eV that exactly coincides with the spin-orbital splitting of Pt4d core level $\Delta E_{4d} = 17$ eV [21].

(ii) The threshold transition of $4d_{5/2}$ core electron to the b-state, and the incident electron is also located at the b-state:

$$4d_0^{10} + a^0 + b^0 + e^- \rightarrow 4d_{5/2}^9 + a^0 + b^2 + 2\varepsilon_b \qquad (5)$$
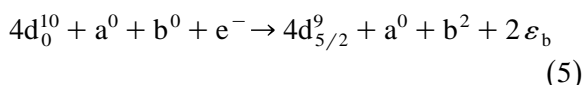
The peak energy is thus determined by the double value of the b-state energy ε_b. Pathway (i) is evidently realized at the H_2 exposure of 0.1 L (the lowest curve in Fig. 3b), where the peak at 334.7 eV is responsible for electron transition (4). Note that it is of similar shape and of lower intensity in comparison with the peak at 317.5 eV, which is responsible for process (2). This behaviour is in line with origin of the core level being excited [1]. The peak at 317.5 eV stays nearly unchanged under an increase of H_2 exposure up to 0.9 L, whereas the peak at 334.7 eV substantially changes its shape and intensity, and slightly changes its location from 334.7 to 334.5 eV. Therefore, the only way (i) cannot be responsible for the spectrum feature at 19.7 eV in Fig. 5B, and the both pathways (i) and (ii) probably take place. Thus, the present experimental data testify to the comparable participation of the vacant states located

Table 2
Comparison of the peak intensity ratios P_a / P_c determined from difference DAP spectrum (Fig. 5B) and from $dW(E)/dE$ dependencies calculated for various platinum layers of Pt(100)-(1×1) plane (Fig. 5A)

Examination object	DAP spectrum	LDOS calculations			
		Layer 1	Layer 2	Layer 3	Bulk
P_a / P_c	1.4	3.0	1.3	3.3	4.6

above vacuum level and at Fermi level in the threshold excitation of platinum core electrons.

The spectrum feature at 5.9 eV corresponds probably to the theoretically predicted c-state. The peculiarity of this peak concerns the ratio of P_a/P_c, where P_a and P_c stand for the peak intensity of the a-state and the c-state, respectively. It is clearly seen from Fig. 5 and Table 2 that experimentally observed P_a/P_c value is close to the characteristics of the 2nd layer of platinum atoms and significantly differs from that of other layers. According to the difference origin of DAP spectrum in Fig. 5B, the latter reveals exactly those DVS of the clean platinum surface, which are involved into the H—Pt bond formation. It means that the adsorbed hydrogen atoms mainly affect the vacant states of the platinum atoms arranging the 2nd surface layer. This statement does not contradict to the known models of hydrogen adsorption [9,23,24]. In particular, the hydrogen adsorption state that we presently deal with is assumed to occupy the four-fold hollow sites of Pt(100)-(1 × 1) surface. Moreover, H_{ads} atom is settled deeply into the surface layer that is accompanied by a work function increase [23,24].

The detailed quantitative analysis and other adsorption systems will be the subjects of further investigation.

5. Conclusions

(i) We succeeded to characterize the DVS structure of the clean Pt(100)-(1 × 1) single crystal surface by means of DAPS. Probing

hydrogen adsorption is used in order to suppress the strong diffraction background and to reveal the desirable features in difference spectra.

(ii) Local densities of states are calculated for the several top layers of semi-infinite Pt(100)-(1 × 1) plane. The experimentally observed features are in a good agreement with the peculiarities of the DVS structure that resulted from the LDOS calculations.

(iii) The comparison of the present experimental and theoretical data shows that the hydrogen atoms adsorbed on the Pt(100)-(1 × 1) surface at 300 K and about 1 L exposure interact primarily with the platinum atoms of the second layer.

Acknowledgements

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