Theoretical And Experimental DAPS Study Of Clean, Oxygen, And Hydrogen Covered Pt(100) Single Crystal Surface

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ABSTRACT

Local density of states and atomic locations are calculated for the three-layer Pt(100) slab covered separately with H and O atoms. Oxygen atoms reveal a stronger influence on LDOS of clean surface and induce larger Pt atoms displacement in comparison with hydrogen atoms. At 1 ML coverage O atom is localized by 1.1218Å below the top Pt layer. Calculated, and experimental disappearance potential spectra related to various H and O coverage of the Pt(100)-(1x1) single crystal surface are in a perfect agreement in spite of pronounced complexity of spectral structures. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Disappearance potential spectroscopy(DAPS) is based on the dependence of intensity of quasi-elastically reflected electron beam on primary electron energy[1,2]. The drastic drop in spectrum is observed whenever the primary electron energy exceeds threshold energy of a possible way of inelastic electron scattering. This process proceeds via transference of incident and excited electrons to available vacant states above the target Fermi level(E_F). DAPS is very surface sensitive technique. The usual testing depth does not exceed 1-3 monolayers(ML) which are of the top interest from the viewpoint of adsorption and catalysis. However, DAPS can find know a very few application for scientific or analytical purposes in spite of its simplicity and availability. This is due first, to the threshold excitation mechanism which provides this technique with an extreme sensitivity to the valence state of top sample layers making interpretation of DAPS results rather difficult; in this way DAPS loses as analytical tool in comparison with

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commonly used methods of AES, ESCA, FTIR, HREELS, etc. Second, the importance of information on the vacant states structure which is the main product of DAPS is not very clear since occupied states, but not empty ones are involved into chemical processes of adsorption, surface reactions and so on. Besides, pronounced DAPS spectra are observed for those samples which have high enough density of vacant states above the fermi level. Unfortunately many catalytically important objects such as Pt with nearly completed d-shell do not have this property. The most part of published papers presents DAPS investigations of samples which are beyond of interest from the viewpoint of heterogeneous catalysis. We have shown previously that detailed analysis of the extended DAPS spectra can reveal novel information on the chemical nature and bonding mechanism of the adsorbed species providing information on a given vacant state structure[3-6]. In particular, the comparison of experimental and theoretical data evidenced that H_{ads} species preferentially interact with platinum atoms of the second layer at hydrogen coverage $\Theta < 0.2$ ML[3,4] that is in accordance with known model of hydrogen adsorption on Pt(100) surface at low coverage[7-9]. The present paper deals with the further theoretical and experimental study of basic electronic peculiarities of hydrogen and oxygen adsorption on the Pt(100) single crystal surface.

THEORY

The electronic structure calculations were performed in the framework of density functional theory(DFT) and local density approximation(LDA). Plane waves were used as a basis set with kinetic energy cutoff for wave functions 20 Ryd and for charge density 80 Ryd. Core electrons were replaced with atomic ultrasoft Vanderbilt pseudopotentials. We model Pt(100) surface with 3-layer slabs. The parameters of 2-dimensional unit cell were taken equal to the corresponding bulk values while interlayer distances were permitted to relax. The calculations were carried out for mono-layer, half mono-layer and quarter mono-layer coverage of the surface with adsorbates. For mono-layer coverage one adatom was added to the unit cell, so the resulting unit cell con-

tains 4 atoms. The position of the adatom was determined by structural optimization. For half and quarter mono-layers coverage one adatom was added to the 2-fold increased unit cells in one and two direction, correspondently, so the total number of atoms in the unit cells was 9 and 13. The positions of the all atoms in the unit cells were structural optimized. Geometry optimization was stopped when the force acting at an atom becomes less than 0.02 eV/Å. All the calculations were performed with program package ESPRESSO[10].

EXPERIMENTAL

Disappearance potential spectrometer was arranged on the basis of 3-grid LEED optics. According to operation techniques DAPS spectra certainly accumulate attendant diffraction features which are to 10^3 times stronger in comparison with true DAPS peaks. This is particularly distinct for the well ordered substrate such as a single crystal surface. In order to suppress the strong diffraction background the difference DAPS spectra were taken into consideration. The difference spectra were constructed by the following sequential steps:

1. Registration of original DAP spectrum corresponding to the clean Pt(100)-(1×1) surface S_{cl}, and to the same surface covered by given adsorbate S_{ads};
2. Digitizing of the scanned spectrum at step 0.1 eV within the desired energy region;
3. Computer construction of difference spectrum S_{dif} according to equation:

$$S_{dif} = a(q) \times S_{ads} - S_{cl} \tag{1}$$

where α (θ) accounts for screening effect of the adsorbed layer at coverage θ corresponding to the given exposure.

The optimal α value in the range of 1-1.2 it was determined so as to minimize the background of attendant diffraction peaks, i.e. to straighten out the given difference spectrum. There is certainly no diffraction effect in theoretical spectra that corresponds to screening effect of $\alpha=1$. Experimental difference spectrum is still usually hampered by the strong broad peak of diffraction nature originated from the ordered adsorbed layer formation. To get rid of that hindrance the Gaussian fit was subtracted from a

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given spectrum.

Unreconstructed Pt(100)-(1×1) single crystal surface was studied in the present work in order to keep substrate structure invariable during experiment since the stable Pt(100)-hex surface reconstructs readily by the influence of various adsorbates[11,12]. All DAPS spectra were obtained after various exposure of O_2 or H_2 at 300K on that surface. Respective coverage was estimated according to sticking coefficient of s=0.2 for H_2[13] and of s=0.1 for O_2[14] and respective saturation coverage at room temperature[9,15].

The threshold excitation of platinum 4f core electron should be more effective in comparison with that of 4d electron due to higher quantity and higher ionization cross-section of the former[16]. However we have investigated the energy range of 300-350 eV around the Pt4d core level excitation because of the much lower diffraction influence in that region.

A Pt(100) single crystal of 99.999% purity(~1cm width and 1 mm thickness) was oriented within 1°. The surface cleaning procedure included several sequential cycles of heating in oxygen at T=900 K and P_{O2}~1·10⁻⁷ Torr followed by sputtering with Ar⁺ ions of 600 eV and further annealing in vacuum at 1100K. The surface cleanliness was checked by Auger electron spectroscopy. The finally observed LEED pattern was typical for the Pt(100)-hex surface[17]. The clean unreconstructed Pt(100)-(1×1) surface was obtained by 'NO-receipt' of[7,18]. The surface finally showed a good(1×1) LEED pattern. Experimental details and DAPS spectra processing can be found elsewhere[5,6].

RESULTS AND DISCUSSION

Electronic structure calculations

Structural optimization shows that energetically preferred adsorption site for hydrogen and oxygen atoms, as expected, is middle of square between four surface Pt atoms[7]. TABLE 1 presents atomic z-coordinates, which are perpendicular to the slab surface. TABLE 1 evidences that O atoms adsorption results in larger Pt atoms displacement compared to H atoms adsorption. It is especially pronounced for 1 ML coverage. In the last case O atom penetrates by 1.1218Å below the top Pt layer that is significantly

TABLE 1: Atomic Z-coordinates calculated with respect to plane over the middle layer Pt atom centers of the clean 3-layer Pt slab; values are given in units of the nearest atomic distance of bulk platinum a=2.774 angstroms

Coverage, ML	0.00	0.25	0.50	1.00
O	-	0.5719	1.0359	0.4453
Pt-top layer	0.6670	0.3870	0.6766	0.8497
Pt-2nd layer	0.0000	0.0647 0.0278 0.0278 0.0170	0.0353 -0.0730	-0.2694
Pt-3rd layer	-0.6670	-0.3144	-0.6756	-0.9257
H	-	0.5056	0.9496	0.9172
Pt-top layer	0.6670	0.3902	0.6828	0.7154
Pt-2nd layer	0.0000	0.0521 0.0408 0.0408 0.0254	0.0350 -0.0303	0.0000
Pt-3rd layer	-0.6670	-0.3064	-0.6600	-0.6612

larger than value 0.25Å estimated by the Rutherford backscattering in[14,15]. This theoretical result is consistent with formation of the subsurface oxygen state which was observed experimentally at elevated exposure and/or temperature on the Pt(100) and other platinum single crystal surfaces[19]. Calculations also revealed that O atoms adsorption induces larger Pt atoms displacement along X and Y in comparison with H atoms adsorption.

Figure 1 shows local density of states(LDOS) calculated for the clean and adsorbate covered platinum surface at Θ=1ML. LDOS for the lower coverage does not differ significantly from that of the 1ML one. DOS of clean Pt in the region below the fermi level (E_F) and up to ~0.5 eV above E_F is nearly completely formed by d-states. At higher energies DOS consists of an s- and p-state mixture. The main difference between the clean Pt DOS and DOS for Pt covered with adsorbates is significant increasing of DOS in lower part of presented energy region. The most prominent peak in the region is marked with dotted line in figure 1. The peak is much more pronounced in the case of oxygen coverage in comparison with hydrogen one. The contributions to DOS of adsorbates and substrate states in this energy region are approximately the same that is a witness of the covalent bonding realized by these states. DOS around the
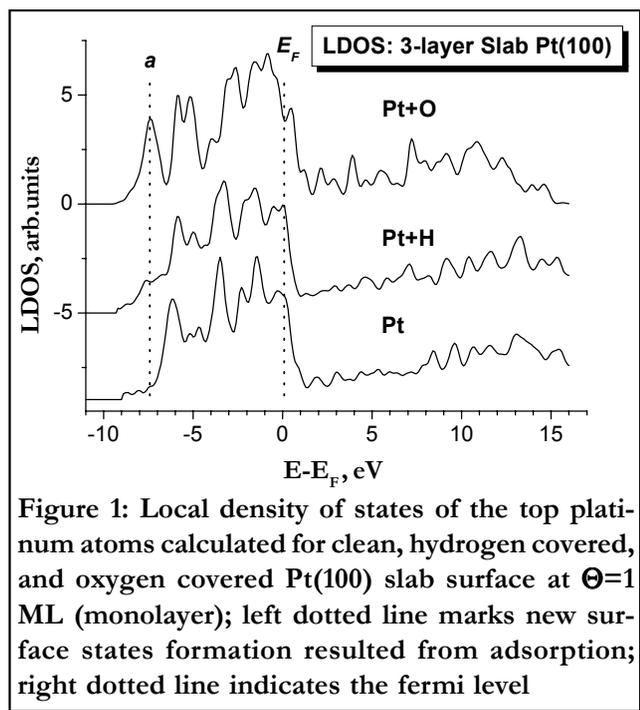
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Figure 1: Local density of states of the top platinum atoms calculated for clean, hydrogen covered, and oxygen covered Pt(100) slab surface at Θ=1 ML (monolayer); left dotted line marks new surface states formation resulted from adsorption; right dotted line indicates the fermi level

fermi level is also changed. The changes can be described as a DOS shift below E_F under the hydrogen adsorption, and above E_F for oxygen adsorption.

Disappearance potential spectra

The dependence of threshold excitation probability on energy W(E) is determined by self-convolution of the vacant DOS with weight function f(E, ε) of the primary and core level electron transitions to states ε and E-ε above E_F, respectively according to one-particle theory[20]:

$$W(E) = \frac{1}{E} \int_0^E f(E, \varepsilon)\sigma(E-\varepsilon)\sigma(\varepsilon)d\varepsilon \qquad (2)$$

Where σ is density of vacant states; f(E, ε) is assumed to be independent on E in a given energy interval.

Equation(2) is rather approximate since it does not account for the many-particle phenomena such as shake-up and shake-off effects, plasmon excitation which are not described by (1) and which can result in additional spectral satellites observation[5,6]. Not intensity of the quasi-elastically reflected electron current but its energy derivative is measured experimentally, and therefore we calculated:
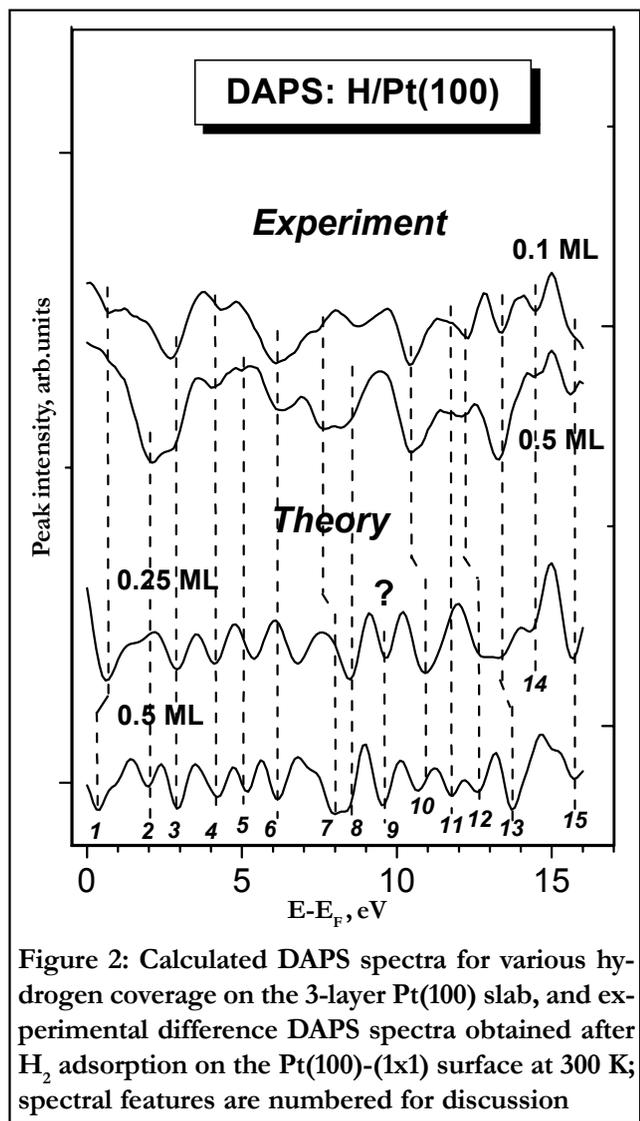
$$I(E) \sim -\frac{dW(E)}{dE} \qquad (3)$$

Where sign "−" takes onto account a reduction of the intensity of elastically reflected electron with an appearance of a new channel of non-elastic reflection. Expression(3) was calculated for clean I_c and adsorbate covered I_a Pt surface and then was constructed the difference spectra:
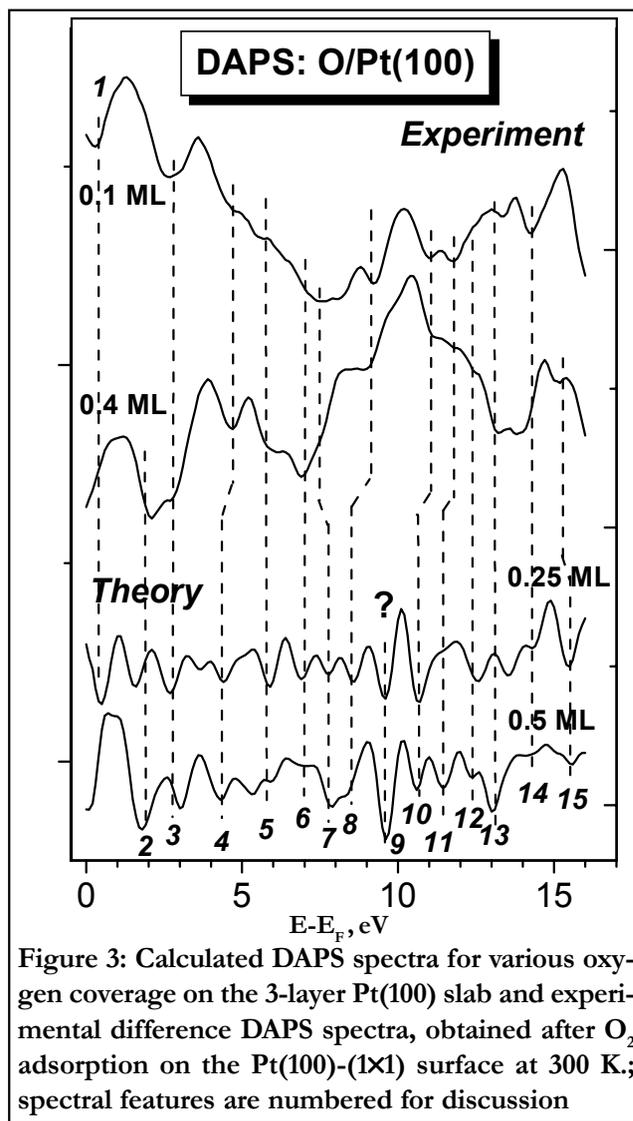
$$I_d = I_a - I_c \qquad (4)$$

Comparing the experimental and calculated spectra one should take into account the following point. The calculated spectra correspond to α=1 in eqn.(1), and so we deal with true difference spectra while in experimental spectra due to some uncertainty of α one can expect the tracks related to clean Pt which are removed completely from true theoretical difference spectra. Obviously, this can introduce additional reason for difference between experiments and calculations.

Figure 2 demonstrates a satisfactory agreement between calculated and experimental DAPS spectra related to hydrogen covered Pt(100) surface. Indeed, the downward intensity of peak Nos. 1, 10, 12, 14, 15 decreases, and intensity of peaks Nos. 2, 7, 11, 13 increases on H coverage rise in both theoretical and experimental spectra. Other peak intensities do not depend significantly on hydrogen coverage. Finally, only one peak of fifteen at 9.6 eV in theoretical spectrum cannot find an adequate feature in experimental one. Figure 3 shows similar calculated and experimental DAPS spectra related to different oxygen coverage of the Pt(100) surface. The majority of theoretical spectral features can also find a respective response in experimental spectra, but agreement is not as complete as in the case of H coverage. In particular, peak intensity Nos. 2, 7, 8, 13 increases, and that of Nos. 1 and 6 decreases as O coverage rises, but other features in experimental and calculated spectra reveal an opposite behavior. Besides, a larger number of peak locations are shifted with respect to each other in the latter case. This may be due to reasons mentioned above. Namely O atoms make stronger change to surface LDOS as demonstrates figure 1, and induces larger Pt atoms displacement as shown in TABLE 1 being compared to H atoms. These reasons can make a sequential change in the reflected electron beam which is responsible for the respective DAPS spectrum formation.

Figure 2: Calculated DAPS spectra for various hydrogen coverage on the 3-layer Pt(100) slab, and experimental difference DAPS spectra obtained after H$_2$ adsorption on the Pt(100)-(1x1) surface at 300 K; spectral features are numbered for discussion

Figure 3: Calculated DAPS spectra for various oxygen coverage on the 3-layer Pt(100) slab and experimental difference DAPS spectra, obtained after O$_2$ adsorption on the Pt(100)-(1×1) surface at 300 K.; spectral features are numbered for discussion

The only supplementary theoretical feature at 9.6 eV in figure 2 and figure 3 may originate first, from the finite quality of the slab accepted as a model for calculations. Second, this feature can result from the spectra subtraction procedure. Both reasons seems possible because in the case of O adsorption figure 3 shows an intensive calculated feature at 9.6eV, and a small peak shoulder only in experimental DAPS spectrum at high coverage.

A good agreement between theoretical and experimental data enhances reliability of each other and confirms the real density of vacant state structure. It evidences also for the following points: (i) the multipeak spectral structure is called forth by not calculation imperfections or experimental noise, but by the LDOS nature of a given adsorption system;

(ii) threshold excitation cross-section is similar for any state above the substrate Fermi level because f(E) dependence in equation(2) is neglected in calculated spectra, and experimental DAPS spectra are resulted actually from the subsequent scanning of vacant states by an excited platinum core electron.

CONCLUSIONS

Local density of states and atomic locations are calculated for the three-layer Pt(100) slab surface covered separately with H and O atoms. Oxygen atoms reveal a stronger influence on LDOS change and induce larger Pt atoms displacement in comparison with hydrogen atoms. At 1 ML coverage O atom is localized by 1.1218Å below the top Pt layer.

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Calculated and experimental disappearance potential spectra related to various H and O coverage of the Pt(100)-(1×1) single crystal surface are in a good agreement in spite of pronounced complexity of spectral structures. Remarkable similarity between theoretical and experimental results enhances reliability of each other, and subsequently evidences for correctness of used theoretical approach, for the substantial scope of DAPS technique, and for proper data processing.

ACKNOWLEDGMENT

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