H- and O-induced compressive surface stress on Pt(111): Experiments and density functional theory calculations

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Surface-stress changes induced by the adsorption of oxygen and hydrogen on clean Pt(111) are measured at 320 K under UHV conditions with an optical crystal curvature method and are calculated using density-functional theory. A compressive surface-stress change is measured upon exposure of Pt(111) to either H_2 or O_2. The magnitude of the adsorbate-induced surface-stress change is in quantitative agreement with our calculations. Our results indicate that both electropositive (H) and electronegative (O) adsorbates may induce a compressive surface-stress change. The significance of these results for the understanding of adsorbate-induced surface stress is discussed.

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The lack of bonding partners above a surface of a solid induces a significant redistribution of electronic charge near the surface region. As a result, bonds within the surface layer and to adjacent layers underneath are modified as compared to their bulk counterparts. One consequence is that *forces* act between atoms of the surface layer and a surface-stress results. Surface stress for metals is calculated to be positive, i.e., tensile.[1] Thus, surface atoms experience a force which favors shorter bonding distances to the neighboring surface atoms.

The interest in a detailed understanding of surface stress is manifold. Surface stress is expected to influence the dynamic properties of surfaces, and the peculiar phonon dispersion of the Rayleigh wave has been ascribed to it.[2] A large magnitude of surface stress has been correlated with surface reconstruction.[3] Also, surface-stress *changes* have been discussed as a possible driving force for adsorbate-induced surface reconstructions.[4–6]

The measurement of the absolute surface stress of a single crystal remains an unresolved experimental challenge. In this respect, the combined efforts of theory and experiment are highly beneficial, and are presented here, as without additional support from theory, the absolute magnitude of surface stress remains unknown.[6–8] This is however an important quantity to appreciate the role of surface stress for dynamic and structural properties of surfaces.[4,5,9]

A comprehensive theoretical surface-stress study has been performed before for Pt(111) and the adsorption of H and O on Pt(111).[10] This previous work also presents a very lucid description of various models which have been employed to qualitatively understand the physics behind adsorbate-induced surface-stress changes in an attempt to derive the systematics of surface stress.

In this Brief Report, we present experimental data on the H- and O-induced surface-stress change on Pt(111) to allow for a comparison between experiment and the previous theoretical description.[10] Surprisingly, the experimental results indicate a significantly *smaller* adsorbate-induced surface-stress change as compared to the previous calculations and experiments on O/Pt(111). The discrepancy between our experiment and theory is largest for H-induced surface stress.

This triggered our new calculations, which reveal important subtleties of the *calculation* of H-induced surface stress, which have not been identified before. We also offer an explanation for the discrepancy between our new and the previous experimental results for O/Pt(111) by discussing the experimental progress of recent years, which is ascribed to our application of an optical two-beam curvature measurement. Our results support the previous conclusion,[10] that charge polarization upon adsorption does not determine the sign of adsorbate-induced surface stress.

The experiments are performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of 3×10^{-11} mbar. The stress change is obtained with an optical two-beam curvature measurement.[11] We use a Pt(111) single crystal as the cantilever sample (thickness=0.1 mm; free length=12 mm; width=3 mm). A clean Pt(111) surface is prepared by Ar^+ bombardment (1.5 keV, 3 μA) at 320 and 800 K, respectively. Surface contaminations are further removed by annealing in oxygen ($P_{O_2}=5 \times 10^{-7}$ mbar) at 800 K. After subsequent annealing at 1100 K, a clean Pt(111) is finally obtained, as checked by Auger-electron spectroscopy and a clear (1×1) low-energy electron diffraction (LEED) pattern is observed.

The *ab initio* results are obtained using the VASP code[12] in the framework of the local-density approximation. The exchange-correlation functional implemented in the calculations is that of Ceperley and Alder[13] as parameterized by Perdew and Zunger.[14] The sampling of k space is performed with the method of Monkhorst and Pack.[15] Projector-augmented wave (PAW) potentials[16] of Pt $(5s^1, 4d^9)$, O $(2s^2, 2p^4)$, and H $(1s^{0.5})$ from the standard VASP database[17] are exploited in our calculations. The Fermi-level smearing approach of Methfessel and Paxton[18] with a Gaussian width of 0.2 eV is employed for electronic states near the Fermi level. The optimized atomic geometries are achieved when the forces are smaller than 0.005 eV/Å. The cutoff energy of 500 eV is used. The bulk lattice constant of Pt is found to be 3.906 Å. Our calculations are performed for symmetric slabs of 13 Pt layers with four nonequivalent atoms within the layer. A vacuum region of 18 Å separates the slabs. Our results are obtained using a $9 \times 9 \times 1$ mesh in the Brillouin zone.

TABLE I. Calculated deviation of the out-of-plane spacing between first and second d_{12}, and second and third layers d_{23}, of clean and adsorbate-covered Pt(111), as compared to the calculated Pt(111) bulk value $d_b=2.255$ Å. The calculated binding energy E_b, absolute surface stress and its adsorbate-induced change with respect to clean Pt(111) are given. Theoretical results from a previous work (Ref. 10) are quoted for comparison.

	Pt(111)	0.25 ML O/Pt(111)	1 ML H/Pt(111)
$(d_{12}-d_b)/d_b$	+0.7%	+1.3%	+2.2%
Ref. 10	+0.44%	+0.64%	+2.3%
$(d_{23}-d_b)/d_b$	−0.4%	+0.3%	+0.3%
Ref. 10	−0.31%		+0.075%
τ (N/m)	+5.9	+3.1	+4.8
Ref. 10	+6.3	+3.1	+1.7
$\Delta\tau$ (N/m)	0.0	−2.8	−1.1
Ref. 10	0.0	−3.2	−4.6
E_b (eV)		5.53	2.50
Ref. 10		5.51	2.62

In Table I, we present the results of the *ab initio* calculations of layer relaxation for different structures and the respective surface stress. Our results on layer relaxation, absolute surface stress of Pt(111), binding energies of O and H, and surface-stress change in O/Pt(111) are close to those obtained previously.[10] This favorable comparison between previous and present calculations supports our view that the employed theoretical setup is suitable for the calculation of stress changes. A large discrepancy in surface-stress change is observed for H/Pt(111). This discrepancy is ascribed to a decisive detail of the calculations, as discussed below.

The surface-stress change measured during H adsorption on Pt(111) at 320 K is presented in Fig. 1. The hydrogen partial pressure P_{H_2} is monitored by a quadrupole mass spectrometer. We introduced a pressure change by quickly opening the H_2 leak valve and keeping it open for 150 s. Figure 1(a) shows that P_{H_2} increases to 5×10^{-7} mbar and stays constant until the hydrogen valve is closed. P_{H_2} gradually decreases to 3×10^{-9} mbar after 400 s, due to the pumping

FIG. 2. Surface-stress change $\Delta\tau$ as a function of H coverage θ_H. Open squares are experimental data obtained at 320 K. Filled triangles represent the result of our *ab initio* calculations.

of the UHV system by a turbomolecular pump. The surface-stress change $\Delta\tau$ is measured simultaneously, as shown in Fig. 1(b). $\Delta\tau$ drops by -0.65 N/m after the hydrogen valve is opened. $\Delta\tau$ reaches a constant value after 50 s, until the hydrogen valve is closed. With decreasing P_{H_2}, $\Delta\tau$ reverts toward the initial value.

To elucidate the time dependence of the H-induced surface stress, we calculate the H coverage θ from the integration of its rate equation,[19]

$$d\theta/dt = [(2\pi MRT)^{1/2}P_{H_2}s_0 f(\theta) - \delta g(\theta)]/n_{Pt},$$

where the desorption rate δ is given by

$$\delta = \nu_d n_{s,max}^2 e^{-E_d/RT}, f(\theta) = (1-\theta)^2, g(\theta) = \theta^2.$$

$\theta=1$ indicates one H atom per Pt surface atom ($n_{Pt}=1.5\times10^{15}$ cm^{-2} surface density of Pt atoms, M—molecular weight, P_{H_2}—hydrogen pressure, T—temperature, $s_0=0.1$—initial sticking coefficient, $n_{s,max}$—maximum density of adsorbates, $\nu_d=3\times10^{-9}$ cm^2/s—frequency factor, R—ideal-gas constant, and $E_d=11$ kcal/mol—activation energy for desorption). Note that the value of E_d ranges from 9.5 to 17.5 kcal/mol according to previous studies.[19] We take $E_d=11$ kcal/mol, as this value leads to the same time depen-
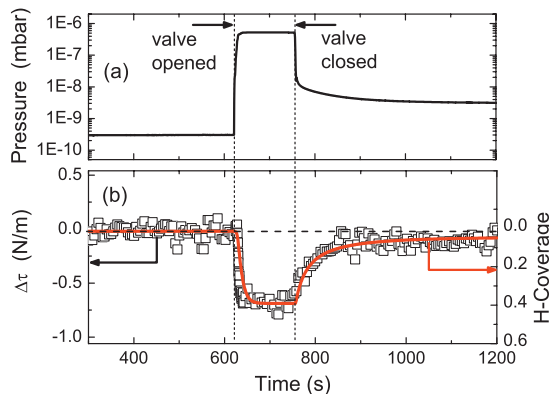

FIG. 1. (Color) Measured (a) pressure P_{H_2} and (b) surface-stress change $\Delta\tau$ during hydrogen exposure of Pt(111) at 320 K. The calculated H coverage is shown by the red curve in (b).
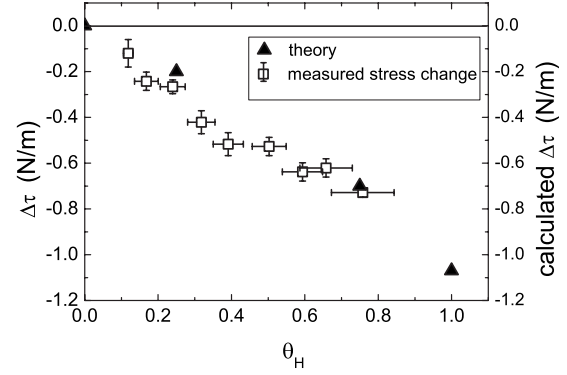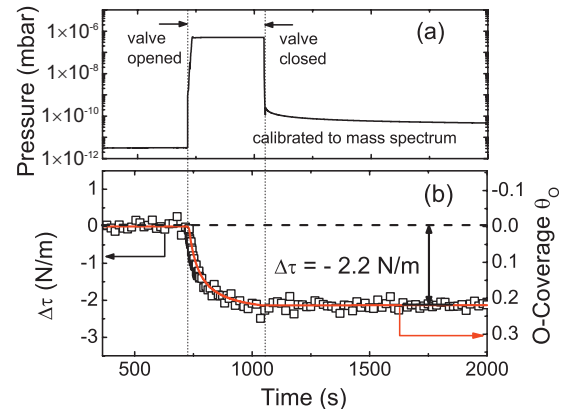

FIG. 3. (Color) Measured (a) pressure P_{O_2} and (b) surface-stress change $\Delta\tau$ during O exposure of Pt(111) at 320 K. The red curve shows the calculated θ_O.

dence of the H coverage as compared to the H-induced surface-stress change, as shown by the red curve in Fig. 1(b). θ changes from 0.02 at $P_{H_2} = 3 \times 10^{-10}$ mbar to 0.4 as P_{H_2} increases to 5×10^{-7} mbar at $T = 320$ K. $\Delta\tau$ changes in proportion to θ_H within this analysis of the data of Fig. 1.

We performed a series of measurements during steplike pressure changes in different magnitude. The resulting surface-stress change as a function of calculated θ_H is plotted in Fig. 2. We find a compressive $\Delta\tau$, which shows a monotonic change with θ_H. Note the favorable agreement between experiment and theory at $\theta_H \approx 0.25$ and 0.75. The latter marks the largest experimental H coverage. To achieve an higher H coverage, an exceedingly large H partial pressure in excess of 10^{-4} mbar would be required. We avoid such high pressures to ensure clean surface conditions.

Figure 3 shows the measured surface-stress change during O exposure of clean Pt(111) at 320 K. A compressive stress change in $\Delta\tau = -2.2$ N/m is measured. In contrast to the stress behavior shown in Fig. 1, here the stress remains constant after the oxygen valve has been closed. The LEED pattern changes from (1×1) of clean Pt(111) into $p(2 \times 2)$ patterns after O_2 exposure, and this reveals the formation of a $p(2 \times 2)$ O structure.[20]

To appreciate the time dependence of the O-induced surface-stress change, we calculate the O coverage from the same expression as above, where the desorption rate δ is given by

$$\delta = \nu_d n_{s,max}^2 e^{-(E_d - \alpha\theta)/RT}, f(\theta) = (1-\theta)^2, g(\theta) = \theta^2$$

and appropriate parameters are used[21] ($\nu_d = 0.024$ cm^2/s; $E_d = 50.9$ kcal/mol; $\alpha = 10.0$ kcal/mol; $s_0 = 0.066$ for $T = 320$ K). The result is shown as the red curve in Fig. 3(b). The time dependence of both the integrated θ_O and measured $\Delta\tau$ are identical. From Fig. 3, we conclude that the surface-stress change in -2.2 N/m is ascribed to an O coverage of 0.22. The comparison with our calculated stress values of Table I shows a surface-stress change in -2.8 N/m for an O coverage of 0.25. Thus, we find a close agreement between our experimental and calculated O-induced surface-stress change.

Our measurements of the time-resolved adsorbate-induced surface-stress change in Figs. 1 and 3 reveal for both adsorbates a kinetic behavior which is well described by surface adsorption and desorption. This experimental finding supports the assumption that under these experimental conditions, adsorption on the surface of the Pt(111) crystal needs to be considered, and penetration of the adsorbates into the bulk of the crystal is ruled out. We refrain from an in-depth analysis of the surface stress-coverage dependence for H adsorption, as our present H-coverage data are calculated from the adsorption-desorption kinetics. Possible dependencies of the relevant parameter on the H coverage cannot be excluded, and they offered a mechanism for a substantial error bar for the calculated H coverage.

The comparison between the measured H-induced surface-stress change at $\theta_H = 0.76$ of -0.73 N/m agrees favorably with our calculated value of -0.7 N/m for $\theta_H = 0.75$ while it is roughly a factor 4–5 smaller as compared to the previous calculations.[10] The reason of this discrepancy is

not entirely clear to us. However, it is worth to note the following point. For the surface-stress computation, we have employed the PAW potential of H with a half of valence electron $(1s^{0.5})$. Our test calculations demonstrate that the results on surface stress on H-covered Pt(111) are close to those from Ref. 10, if the PAW potential of H with one valence electron $(1s^1)$ is involved.[22] On the other hand, this potential overestimates the bonding between H and Pt atoms. As a result, the basic characteristics of a H-covered Pt(111) obtained using this potential differ from those computed in Ref. 10. For instance, (i) the binding energy per H adatom in the H(1×1)/Pt(111) configuration is about 3.3 eV vs 2.5 eV for H$(1s^{0.5})$ and (ii) the calculated outer-layer relaxations in the same structure are $(d_{12} - d_b)/d_b \approx +3.5\%$ and $(d_{23} - d_b)/d_b \approx +0.7\%$ instead of +2.2% and +0.3%, respectively (see Table I). Therefore, employing the PAW potential of H with one valence electron seems to be inappropriate for the system studied.

For the O-induced surface-stress change, we face a strong deviation between our experimental value of -2.2 N/m and the much larger previously published experimental value of -4.0 N/m (Ref. 2). This strong deviation is clearly beyond the experimental error bar, which amounts atmost to ± 10–20 %. This estimation reflects the largest possible uncertainties in the measurement of the most crucial experimental parameters such as sample thickness, length, and dimensions of the composite sample holder of the previous measurements by a capacitive deflection detection,[2,23] and of the separations of the two laser beams of the two-beam optical curvature measurement used here.[11] We stress that the above-mentioned discrepancy of the experimental values persists even after the issue of one-dimensional bending of the crystal used in the previous measurements is accounted or, and the quoted previous experimental value of -4.0 N/m is already corrected accordingly.[2,24]

A detailed analysis of the impact of crystal clamping on the stress-induced crystal curvature reveals the largest impact for a deflection measurement, which was used previously.[2,24] The smallest detrimental impact is found for a curvature measurement, which is employed here.[11] An important quantity in this respect is the length-to-width ratio of the sample, which is 4 for our crystal. We conclude that the clamping-induced deviation from a true two-dimensional stress-induced curvature is not significant here.[24]

We speculate that the composite sample holder used in previous stress measurements[2,5] might be a source of experimental error, which has not been addressed before. In these previous experiments, a round Pt(111) crystal (diameter 11 mm and thickness 0.3 mm) was mounted in between sheets of Mo for clamping at its upper end, and for extending the crystal curvature via a deflection of a Mo sheet at the lower end. This lower extension serves as a capacitor plate of the capacitive deflection measurement.[25] We tentatively suggest that possibly the crystal cleaning by sputtering and annealing in UHV also changed the surface state of the Mo sheets in proximity of the crystal. Thus a subsequent exposure to gas adsorbates could also influence the surface stress of these sheets, leading to an additional curvature. The resulting signal change would be larger than expected, if only the Pt crystal contributed to the measured deflection. This potential

complication is avoided in our present measurements, where the curvature of the Pt(111) crystal is analyzed directly. We regard this as an important experimental progress for a quantitative surface stress analysis.

In conclusion, our combined experimental and theoretical study of the H- and O-induced surface-stress change on Pt(111) reveals a compressive stress change for both adsorbates in favorable quantitative agreement. Its magnitude is stronger for O, where −2.2 N/m are measured at a coverage of 0.22 ML whereas a coverage of 0.22 ML hydrogen induces a ten times smaller stress change.

Our work reveals a smaller magnitude of the measured adsorbate-induced surface stress as compared to previous experimental studies of the same system. It remains to be seen in future work whether this indicates a general finding, which might have important consequences for the appreciation of the role of surface stress for structural and dynamical properties. Our results provide experimental and theoretical support for the previously expressed notion[10] that both electropositive (H) and electronegative (O) adsorbates will induce a compressive surface stress change on Pt(111). This implies that charge polarization at a surface is not a valid indicator for the sign of adsorbate-induced surface stress.

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