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Oxygen adsorption on stepped Pd(100) surfaces

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ABSTRACT

We use scanning tunneling microscopy (STM) and high-resolution core-level spectroscopy (XPS) measurements to study the initial oxidation of vicinal Pd(100) surfaces exhibiting close-packed (111) steps. The XPS data analysis is supported by detailed surface-core level shift calculations based on density-functional theory. Both STM images and the XPS spectra are found to be perfectly consistent with a characteristic zigzag O decoration of the Pd steps predicted by a preceding cluster-expansion based theoretical study [Y. Zhang and K. Reuter, Chem. Phys. Lett. 465, 303 (2008)]. Continued oxygen uptake leads to the additional stabilization of a $p(2\times2)$-O overlayer on the Pd(100) terraces, and ultimately to step bunching with the resulting large Pd(100) terraces covered by the PdO(101) surface oxide.

1. Introduction

The interaction of oxygen with transition metal surfaces has long gained significant attention in both fundamental and applied research, due to its importance in heterogeneous catalysis and corrosion. For well-defined low-index single crystal surfaces this has established a rather profound understanding, which ranges from the early stages of on-surface oxygen adsorption to the formation of surface- and bulk-oxide phases [1]. Recently and as a step toward higher material's complexity, the interaction of oxygen with vicinal metal surfaces, consisting of periodic arrays of atomic steps, has become an intriguing subject of investigation. Generally anticipated is a significant impact of the modified electronic structure in the vicinity of the lower coordinated step atoms on the surface oxidative and catalytic properties. Seminal studies have indeed already demonstrated that the steps of vicinal transition metal (Pt, Pd, Rh) surfaces exhibit an enhanced reactivity toward oxidation, leading to the formation of novel one-dimensional (1-D) oxidic configurations [2–5].

Understanding their structure at the atomic level is a challenging task, even in the combination of state-of-the-art experimental and theoretical methods. For stand-alone predictive-quality theory the situation is even more daunting, with a most formidable limitation imposed by the vast number of possible geometric configurations. In an attempt to overcome the prevalent approach of simply restricting the calculations to a handful of (chemically motivated) candidate structures, some of us have recently proposed a cluster-expansion based approach for a more systematic exploration of configurational space [6]. In the application to the oxygen adsorption at stepped Pd (100) this identified a large range of oxygen chemical potentials where oxygen atoms decorate alternating sites at close-packed (111) steps in a characteristic Pd–O zigzag structure, with the (100) terraces either empty or covered by a chemisorbed $p(22)$-O layer. At higher chemical potentials more dense oxygen structures form both at the steps and the terraces, signaling the onset of surface oxide formation [6].

While clearly a step forward, the cluster-expansion based structure determination still has its limitations, most notably in that it was restricted to the lattice spanned by on-surface adsorption sites. Its capabilities can therefore not extend to the situation where the formation of oxides is accompanied by substantial substrate rearrangement. The motivation of the present work is therefore to assess the validity of the theoretical predictions with a dual experimental approach that has already proven to be a most powerful tool for unraveling complex surface structures: Atomically resolved imaging of the step structure by scanning tunneling microscopy (STM) combined with core-level photoelectron spectroscopy (XPS) with its intrinsic sensitivity to the local chemical and geometrical environment.

Investigating the adsorption of oxygen on stepped Pd(119) and Pd (1 1 17) surfaces at oxygen pressures below 1×10^{-8} mbar, our STM images fully confirm the predicted zigzag step decoration. Analyzing the complex surface core-level shift (SCLS) data with density-functional theory (DFT) calculations allows even to disentangle

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small geometric differences in this zigzag-decoration, depending on whether oxygen is also present at the terraces or not. At higher oxygen pressures the regular step periodicity is not preserved anymore and significant step bunching occurs. While this is outside the realm of the preceding cluster-expansion work, the observed formation of the PdO(101) surface oxide [7,8] on the resulting large Pd(100) terraces concurs again fully with the expectations from previous *ab initio* atomistic thermodynamics studies on this low-index surface [6,9–11].

2. Experimental and computational setup

Two stepped Pd(100) surfaces have been employed in our experimental investigation: Pd(119) and Pd(1 1 17). As illustrated in Fig. 1 both surfaces consist of (100) terraces that are 5 and 9 atom rows wide, respectively, and separated by {111} faceted steps, 12.5 Å and 23.4 Å apart. STM and low-energy electron diffraction (LEED) measurements have been performed in Graz in a custom-designed ultra-high vacuum (UHV) system with a base pressure of 1×10^{-10} mbar, equipped with a variable-temperature AFM-STM (Omicron), four-grid LEED optics and sample heating and cleaning facilities [12]. The STM was operated at room temperature and in a constant current mode. The STM tunneling conditions were set to achieve the best atomic resolution. Depending on the tip termination, bias voltages between a few mV and 1 V have been used. High-resolution XPS experiments have been performed at beamline I311 at MAX-lab, Lund, Sweden [13]. The photoemission spectra have been collected at normal emission angle and photon energies of 120, 400 and 620 eV for the valence band, Pd 3*d* and O 1 *s* core level regions, respectively. The total energy resolution in the present experiments was ~100–200 meV. The vicinal Pd surfaces have been cleaned by 1.5 keV Ar^+–ion sputtering followed by annealing to 1000 K for several minutes, and by heating cycles in O_2 atmosphere at 570 K followed by a final short flash to 1000 K. Oxygen has been introduced into the UHV systems via leak valves at pressures varying between 5×10^{-9} and 5×10^{-7} mbar; the oxygen exposures are given in Langmuir ($1\ L=1\times10^{-6}$ torr s).

The DFT calculations were performed within the full-potential augmented plane wave (LAPW/APW + lo) framework [14], treating electronic exchange and correlation at the level of the generalized gradient approximation due to Perdew, Burke and Ernzerhof [15]. The Pd(119) surface was described in a supercell setup with symmetric 33 layer slabs, a vacuum separation of 10 Å, (2 × 1) surface unit-cells, and oxygen adsorption at both sides. All structures were fully relaxed, keeping only the atomic positions in the central two Pd(119) slab layers at their fixed bulk positions. The LAPW/APW + lo basis set parameters are identical to those used in our preceding work on oxygen at vicinal Pd(100) [6,16,17], where also the numerical convergence with respect to the key structural and electronic quantities has already been described in detail. The procedure to obtain initial- and final-state contributions to the SCLSs is exactly the same as detailed in ref. [18], in which the initial-state shifts are simply given by Kohn–Sham eigenvalue differences and the final-state screening is computed within the Slater–Janak transition state approach by an impurity calculation with half an electron removed from the core state considered.

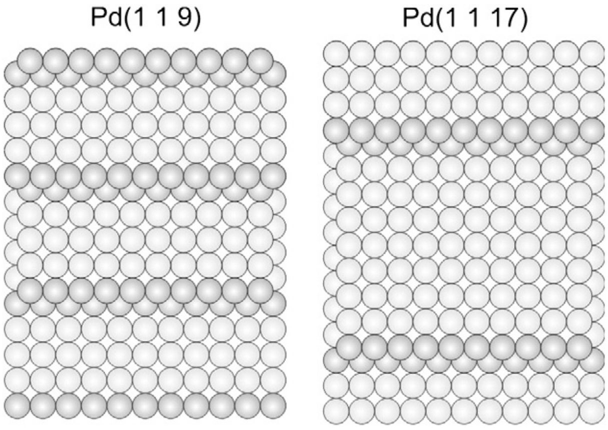

Fig. 1. Schematic top views of the Pd(119) (left) and Pd(1 1 17) (right) surfaces. Step atoms are darkened for clarity.

3. Results and discussion

3.1. Morphology and structure overview

Fig. 2a shows an STM image of the Pd(119) surface exposed to 6 L of oxygen at 5×10^{-9} mbar, with the sample kept at 520 K. To avoid a possible reaction of the chemisorbed oxygen layer with residual gas molecules (such as e.g. CO or H_2) from the UHV background, the sample has been kept at the same oxygen pressure and room temperature during the STM measurements. The STM image reveals a regular array of steps with an average periodicity of 12.5 Å ± 0.2 Å, which is identical with the theoretical step separation of 12.5 Å of the clean Pd(119) surface. The corresponding LEED pattern (inset of

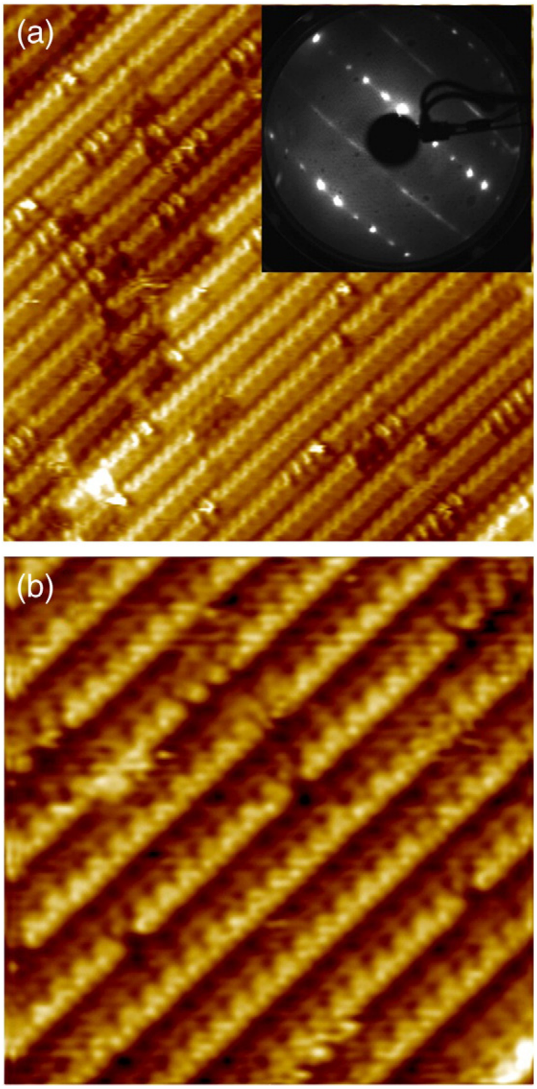

Fig. 2. STM images of the Pd (119) surface after 6 L oxygen dose at 5×10^{-9} mbar and substrate temperature of 520 K: (a) (200Å × 200Å, + 1.0 V, 0.1 nA); (b) (100Å × 100Å, + 0.4 V, 0.1 nA). The inset in panel a shows the LEED pattern of this surface ($E=65$ eV).