Structure and Electronic Properties of CoO Nanostructures on a Vicinal Pd(100) Surface

Li-Ying Ma, ‡ Andrea Picone, †§ Margareta Wagner, † Svetlozar Surnev, † G. Barcaro, ‡ A. Fortunelli, ‡ and Falko P. Netzer*†‡

†Surface and Interface Physics, Institute of Physics, Karl-Franzens University, A-8010 Graz, Austria
‡CNR-IPCF, Istituto per i Processi Chimico-Fisici, I-56124 Pisa, Italy
§CNISM, Dipartimento di Fisica, Politecnico di Milano, I-20133 Milano, Italy

ABSTRACT: Quasi-one-dimensional CoO nanostructures have been fabricated by step decoration growth on a Pd(1 1 23) surface, a vicinal of Pd(100). The step decoration is dominated by Co−Pd atomic exchange processes, which lead to the formation of 2−4 atom-row wide CoO nanostripes attached to and partially embedded into the outer terrace areas; the CoO stripes grow in a pseudomorphically strained hexagonal phase, as evidenced by atom-resolved scanning tunneling microscopy images and density functional theory simulations. A fraction of the Pd atoms ejected from the steps and outer terraces in the Co−Pd exchange assemblies into short monatomic chains, which are periodically attached to the CoO steps. The local electronic structure of the CoO rows at the steps as measured by scanning tunneling spectroscopy is distinctly different from those of embedded CoO rows and of two-dimensional CoO monolayer phases at the terraces, with a significantly higher density of O 2p and Co 3d states around the Fermi energy as confirmed by density functional theory analysis.

1. INTRODUCTION

Low-dimensional model systems are of fundamental importance for the elucidation of emergent phenomena in condensed matter physics and chemistry. The reduced atomic coordination in two-dimensional (2-D) layers or in one-dimensional (1-D) atom chains together with the coupling to a given substrate and the proximity of the respective interfaces have profound consequences for the structural, electronic, magnetic, and chemical response of these structures.1−5 The local electronic configuration of low-coordinated atomic ensembles imprints particular chemical properties on to the nanostructures, which can be exploited in the catalytic performance of such systems.6 The preparation of well-defined ensembles of 1-D and 2-D systems by atomic engineering using self-assembly techniques on suitable substrates has been established and has been applied successfully to metallic systems.1,6 The use of vicinal metal surfaces as a natural template for the epitaxial growth of 1-D structures via step decoration is a suitable preparation strategy for the preparation recipe but has also been achieved recently.8−10

The resulting oxide nanowires of atomic widths, coupled elastically and electronically to the steps of a different metallic host, constitute a quasi-1-D oxide−metal hybrid system, which provides excellent model character for studies of advanced catalysis.11 Indeed, the steps of metallic Cu nanoparticles decorated with a ZnO phase have very recently been identified as the active sites in an industrial catalyst for methanol synthesis.11 This is in line with the observation of enhanced chemical reactivity for the CO oxidation reaction in a model system, consisting of NiO2 nanowires of monatomic width coupled to the steps of vicinal Rh(111) surfaces.12

Here, we report on a study of the growth of CoOx nanostructures on a Pd(1123) surface, a vicinal of Pd(100) consisting of 12 atom-row wide (100)-type terraces (∼31.5 Å) separated by monatomic (111)-type step facets. We have followed the morphology and surface geometry during growth of the CoOx structures as a function of oxide coverage using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) and have probed their local electronic properties by scanning tunneling spectroscopy (STS) in a low-temperature (5 K) STM instrument. The atom-resolved STS data have allowed us to derive the chemical identity of the nanowire structures that develop at the step edges. Moreover, we find a strong variation of the electronic structure at a local scale, which is confirmed by an analysis of the electronic local density of states (LDOS) for a CoOx nanowire structural model obtained via band-structure calculations at the density functional theory (DFT) level.

In the low-coverage regime, an interesting growth phenomenon has been observed, where exchange reactions between Co and Pd atoms at the step edges dominate the step decoration process, leading to the formation of strained hexagonal CoOx nanowire structures, 2−4 atom rows wide, partially embedded into the outer Pd terrace regions. Short chains of ejected Pd...
atoms decorate parts of the CoO₉ step edges in a periodic fashion, creating particular hybrid sites. With increasing coverage, the CoO nucleates on top of the embedded CoO₉ phase at the upper step edges and then grows into the terrace areas displaying locally ordered c(4×2) and c(2×2) structure motifs with only moderate long-range order; these structures are understood as being derived from elements of a CoO(100)-type surface by introducing cation vacancy defects. At monolayer oxide coverage and for a lower chemical potential of oxygen during preparation, a (9×2) monolayer structure of the hexagonal CoO(111)-type is formed, covering the entire surface; the latter is also a stable structure on the flat Pd(100) surface. The STS spectra and the theoretical analysis reveal that the 1-D CoO₉ step edges display a significantly higher electronic density of states around the Fermi energy than the other 2-D oxide regions: we speculate that the former may form sites with a particular catalytic activity.

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

The experiments have been performed in a 3-chamber low-temperature STM system (Createc, Germany) at a base pressure of <5 × 10⁻¹¹ mbar, operating at a measurement temperature of ~5 K in the liquid He STM cryostat stage. Sample surface cleaning and preparation in situ STM tip treatments have been performed in the preparation chamber, which is equipped with a LEED optics, a heatable/coolable
The Journal of Physical Chemistry C

(∼15 K) sample manipulator and the usual provisions for surface cleaning, controlled thin film deposition and gas inlet. Electrochemically etched W tips have been treated in situ by electron bombardment heating and by field emission via voltage pulses. Spectroscopy of the differential conductance (dI/dV versus V) was measured by a lock-in technique with 1.1 kHz modulation frequency and 30–100 mV modulation amplitude at a constant height with the feedback loop switched off. Scanning tunneling spectra in the regime of field emission resonances17 (sample bias voltages: +2–10 V) were obtained with the feedback loop connected and the variation of the tip–sample distance z was recorded at constant current as a function of the sample voltage. The differentiated (dz/dV) versus V curves are equivalent to the spectra of the differential conductance in this voltage range. The STS spectra presented are the averages of many spectra taken at equivalent surface locations.

The Pd(1123) surface has been cleaned by repeated cycles of Ar ion sputtering (1 keV) and annealing in vacuum at 920–970 K. Heating cycles in O2 at 670 K were necessary to remove residual surface carbon contamination, and they were repeated periodically. However, O2 pressures had to be kept <1 × 10−7 mbar during annealing since significant oxygen-induced Pd step bunching occurs at higher O2 pressures.18 For the growth of CoOx nanostructures, the Pd(1123) surface has been precovered by chemisorbed oxygen. The starting surface for growth has been prepared by exposing the clean Pd surface to 1–2 L (1 Langmuir (L) = 1 × 10−6 Torr·sec) O2 at 570 K followed by cooling down to 300 K in oxygen. According to previous work,19 the resulting Pd surface (see Figure 1a) is decorated by a zigzag arrangement of O atoms at the step edges, sitting in upper and lower edge sites, and covered by a p(2 × 2)-O chemisorption layer at the terraces (see insert, Figure 1a). The oxygen covered Pd(1123) surface is morphologically stable but sensitive to reduction via clean-off reactions of oxygen adatoms with residual gas molecules (mainly H2 and CO);16 it has therefore been kept in a 7 × 10−9 mbar O2 background pressure during measurements at room temperature. In the low temperature STM stage, however, the reduction reactions are suppressed and the p(2 × 2)-O surface is stable for several days. Co adatoms were deposited reactively from a commercial electron beam evaporator in an O2 pressure of 1 × 10−8 mbar with the substrate slightly above room temperature (340–350 K), and the evaporation rate was monitored by a quartz microbalance. After deposition, annealing of the sample at 470–670 K in the 7 × 10−9 O2 background was applied to improve the ordering of the CoOx deposits. Deposition of cobalt onto the clean Pd surface followed by postoxidation led to a less complete step decoration and to a disordered surface morphology. The CoO coverages are expressed in terms of Co monolayers deposited (one ML is referenced to the atom density of the Pd(100) surface, i.e., 1.32 × 1015 atoms/cm2).

DFT+U calculations19 were performed using the QuantumEspresso package20 employing a basis set of plane waves, ultrasoft pseudopotentials,17 and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-)functional.22 The addition of a Hubbard U term into the DFT Hamiltonian is necessary to better describe the electronic states of CoOx nanostructures.15 Values of 40 and 400 Ry were chosen as the energy cutoffs for the selection of the plane waves for the description of the wave function and the electronic density, respectively. All the calculations were performed spin-polarized.

The unit cell of the Pd p(2 × 2)-O phase was modeled by taking a (2 × 2) portion of the Pd(100) surface and symmetrically adsorbing two oxygen atoms on both sides of the metallic slab in two hollow sites; the metallic slab was modeled by 7 Pd layers, where the inner three layers were frozen in their bulk lattice positions, and the external four (2 on each side) were relaxed together with the positions of the oxygen atoms until the forces resulted smaller than 0.01 eV/Å. The first-neighbor distance in the metal support was set to 2.80 Å, corresponding to the equilibrium lattice parameter of bulk Pd according to our DFT approach, to be compared with an experimental value of 2.75 Å. The first Brillouin zone was k-sampled by employing a (4,4,1) grid, and the electronic levels were broadened with a Gaussian smearing of about 0.03 eV.

The unit cell of the CoOx (9 × 2) phase was modeled by taking a (2 × 9) portion of the Pd(100) surface extending 5.6 Å along the x axis and 25.2 Å along the y axis. In this case, the metal support was modeled by 4 Pd layers in (100) stacking, where the bottom 2 layers were kept frozen in their bulk lattice positions. The oxide monolayer was described by organizing 16 Co and 16 O atoms in four alternating rows running along the longer axis of the unit cell (see Figure 4 of ref 15) and relaxing the structure. The first Brillouin zone was k-sampled by employing a (4,1,1) grid, and the electronic levels were broadened with a Gaussian smearing of about 0.03 eV.

The unit cell of the CoOx c(4 × 2) phase was modeled by taking a (2 × 4) portion of the Pd(100) surface. The metal support was modeled by 4 Pd layers in (100) stacking, where the bottom 2 layers were kept frozen in their bulk lattice positions. The oxide monolayer was described by organizing 6 Co and 8 O according to the pattern reported in ref 15 and relaxing the structure. The first Brillouin zone was k-sampled by employing a (4,2,1) grid and the electronic levels were broadened with a Gaussian smearing of about 0.03 eV.

The unit cell of the double-row CoO phase was modeled by taking a (2 × 8) portion of the Pd(100) surface extending 5.6 Å along the x axis and 22.4 Å along the y axis. The metallic slab was modeled by 2 atomic layers in (100) stacking kept frozen in their bulk positions and adding a portion of a third layer extending only 5.6 Å in length in order to simulate the monatomic step. The CoO pseudomorphic phase was created by adsorbing a CoO double-layer next to the step, decorating the remaining Pd with a p(2 × 2) pattern of oxygen adsorbates (see Figure 5a), and relaxing the structure. The first Brillouin zone was k-sampled by employing a (4,1,1) grid, and the electronic levels were broadened with a Gaussian smearing of about 0.03 eV.

In all cases, along the z axis, a minimum empty space of 15 Å was chosen to avoid interactions between replicated cells. A dipole correction13 was applied to cancel spurious Coulombic interactions among replicated images. STM images were simulated applying the Tersoff–Hamann approach24 at a constant height of about 2 Å above the oxide surface.

3. RESULTS AND DISCUSSION

3.1. Growth and Structure of CoOx Nanowires at Pd(1123) Steps. The morphology of the oxygen precovered Pd(1123) surface is illustrated by the topographic constant-current STM image of Figure 1a: straight step edges mark the terrace boundaries with a limited number of kink and vacancy defects. The high-resolution image in the insert displays the square lattice of the p(2 × 2)-O structure at the (100) terrace; at the given tunneling conditions, the oxygen zigzag-
ment at the step edges is not apparent. After reactive deposition of \( \sim 0.08 \) ML of Co, the STM images of Figure 1b–d have been recorded. Note that this coverage corresponds approximately to the density of step sites on the Pd(1123) surface. The STM images demonstrate that the step sites have been decorated by CoO\(_x\) nanostructures, which display a different chemical contrast and consist of 2–4 rows of a higher brightness, while most of the terrace areas are still covered by the p(2 \( \times \) 2)-O chemisorption layer. This step edge decoration is highlighted in Figure 1c,d by the dashed lines, but in the higher-resolution STM image (Figure 1c), the brighter rows with distinct atomic contrast are clearly recognized. These rows

Figure 2. STM images of 0.12 ML CoO\(_x\) on Pd(1123) (a,c). The insert in panel a is a high-resolution image with a quasi-hexagonal unit cell indicated. The lines in panel c mark the directions of the line scans displayed in panel d. (a, (144 \( \times \) 144 Å\(^2\)); \( V_s = -0.144 \text{ V; } I_T = 0.77 \text{ nA; insert, (40}\ \times \ 40 \text{ Å}^2\); \( c, (100 \times 100 \text{ Å}^2); \ V_s = +0.027 \text{ V; } I_T = 0.16 \text{ nA}. (b) LEED pattern of the surface of panel a (electron energy 57 eV). Unit cell directions and reflection indices are indicated; note the splitting of the half order spots in the (0, ±1) directions (ellipses).
are partly embedded into the outer terrace areas. Somewhat less than one-half of the step edges are decorated by the CoO nanostructures at this coverage, which is in line with the step decoration phase consisting of 2–4 atomic rows. In addition to the embedded CoO₆ structures, rod-like features of approximately 1 nm in length are attached periodically to the outer step edges (see arrows and ellipses in Figure 1b,d). Oxidic nanowires of strictly monatomic width, as they have been observed for NiO₆ and MnO₆ decorating the steps of vicinal Rh₇,8 and Pd₉,10 surfaces, respectively, have not been detected for CoO₂; the narrowest decoration features observed here are double rows of CoO₆.

Figure 2 corresponds to a slightly higher CoO₆ coverage of 0.12 ML. In the STM images of Figure 2a,c, most of the step edges are decorated by 2–4 rows of CoO₆. As mentioned before, the CoO₆ rows display a different chemical contrast than the O-covered Pd terrace regions, with brighter and better resolved atomic protrusions forming a quasi-hexagonal lattice. The latter is particularly apparent in the insert of Figure 2a, in which it is also seen that the contrast along the rows running parallel to the step edges is modulated periodically in brightness: this is an important observation for the identification of the hexagonal CoO₆ phase. The lattice parameters of the hexagonal CoO₆ structures can be measured by the line scans in Figure 2d, which have been taken along the lines 1–3 in Figure 2c. Accordingly, the atomic protrusions in the CoO₆ chains in the direction parallel to the step edges (line scan 1) are spaced by 2.72 ± 0.1 Å, which is consistent with the lattice constant of the Pd substrate underneath (aₚd = 2.75 Å), and thus, growth is pseudomorphic in this direction. In contrast, the distance of protrusions is 3.20 ± 0.1 Å along the other two hexagonal directions (line scans 2 and 3), indicating that the CoO₆ lattice is significantly expanded in the direction perpendicular to the step edges. Thus, the CoO₆ phase is compressed in the direction parallel to steps by the partial embedding into the outer terrace regions, but as a result of this uniaxial strain, it is expanded in the direction perpendicular to the steps, leading to a quasi-hexagonal lattice.

The rod-like structures observed decorating the outer step edges (see arrows and ellipses in Figures 1 and 2a) constitute another interesting feature of the growth pattern of the CoO₆ nanostructures on Pd(1 1 2 3). They are about 1 nm in length (statistical evaluation yields 1.1 ± 0.3 nm) and they appear to be periodically arranged along the step edges. Indeed, this periodicity can be spotted in the STM image of Figure 1b and in the LEED pattern of Figure 2b. The reflections of the Pd substrate and of the (2 × 2)-O chemisorbed layer display the well-known splitting in the direction perpendicular to the step edges (±1, 0 directions in Figure 2b) as a result of the terrace periodicity. There is, however, an additional splitting in the orthogonal (0, ± 1) direction - best visible at the (±1/2,0) order spots (indicated by the ellipses in Figure 2b), which is due to the in-phase scattering of the periodic rod-like features arranged along the step edges: evaluation of the spot splitting along the (0, ± 1) direction in Figure 2b gives a rod periodicity of ~4 nm. The rod periodicity can also be obtained from the Fast Fourier Transform (FFT) of the STM image in the insert of Figure 1b. A line scan along the dotted line in the FFT (i.e., in the direction parallel to the step edges) gives weak periodic maxima separated by ~4 nm, in excellent agreement with the LEED analysis.

To assist with the chemical identification of the rod structures, differential conductance STS spectra in the region ±1 V around the Fermi energy (E_F = 0 V) have been recorded from the p(2 × 2)-O region, from a rod-like structure, from the CoO₆ step edge without rod, and from an embedded CoO₆ line, as shown in Figure 3. The STM image of Figure 3a illustrates the locations (circles), from where the STS spectra (b) have been taken. Significantly, the STS signatures of the p(2 × 2)-O surface and of the rod structures are very similar, and both are different from the CoO₆ lines, especially in the region above the Fermi level; further, the outer CoO₆ edge line is electronically different from the CoO₆ embedded lines. The similarity of the former indicates that the rod structures are related to the p(2 × 2)-O surface but that they are electronically and possibly chemically different from the CoO₆ decoration structures. Additional information may be
obtained from STS spectra in the region of field emission resonances (FER),17 that is at bias voltages +2−10 V above $E_F$. The FER peaks are coupled and thus related to the local surface potential (i.e., the work function), but it is not trivial to derive the actual value of the local work function because the Stark effect of the field between tip and sample influences the FER energies in a nonlinear way.25 However, here we use the FERs in a qualitative fingerprinting way, and quantitative knowledge of the work function value is not necessary for the present purpose. Figure 4c compares FER STS spectra of the relevant surface structures, the STM images of Figure 4a,b specify the locations of the STS measurements (circles). The bottom spectrum of Figure 4c is from the clean Pd surface: the series of distinct peaks, in the region from +6 V to +10 V, represents the FER sequence with $n=1−4$ ($n$ refers to the hydrogenic-like level quantum number17). On the p(2 × 2)-O surface, the FERs are shifted to higher energy, and this shift is consistent with an increase of the work function upon oxygen chemisorption.26 The FER signature of the rod structures is very similar to the one of the p(2 × 2)-O surface, but distinctly different from the FER spectrum of the CoO$_x$ edge and embedded lines. The CoO$_x$ edge line spectrum appears to be a superposition of CoO$_x$ embedded and p(2 × 2)-O spectra. Taken together, the STS spectral evidence indicates that the rods are electronically and chemically akin to the p(2 × 2)-O surface. We therefore propose that the rod structures consist of chains of individual Pd atoms, on average $4 \pm 1$ atoms long, which are most likely associated with chemisorbed oxygen atoms. The Pd atoms have been ejected from the Pd step edges and from the outer terrace regions during the early stages of the CoO$_x$ step decoration and embedding process. The CoO$_x$ step decoration is dominated by Pd−Co exchange processes. The propensity of Co adatoms to exchange with Pd atoms at the step edges (and subsequently with Pd atoms in the rows next to the steps) is, however, not entirely surprising. Wei et al.27 have reported recently that monatomic Pd chains are formed on the Pd(110) surface after deposition of Co atoms, which substitute for Pd atoms of the substrate. This intermixing with Pd substrate atoms and the incorporation of deposited Co adatoms into the Pd(110) surface followed by the assembly of the expelled Pd atoms into atomic chains at the surface has been investigated using DFT calculations by Stepanyuk et al.,28 and it was found to be energetically favorable.

The structure of the quasi-hexagonal CoO$_x$ nanostructures that decorate the Pd step edges is interpreted in terms of a CoO(111)-type bilayer, as it has been described for the (9 × 2) monolayer structure on flat Pd(100).15 The latter consists of a hexagonal oxygen surface layer on top of a hexagonal Co layer, which is at the Pd interface, thus forming a bilayer with a CoO(111) stacking sequence. The STM images of the CoO (9 × 2) structure show typical brightness modulations of atomic protrusions along the long (×9) side of the unit cell (see ref 15 and Figure 7), which are due to height modulations in the hexagonal oxygen surface layer as a result of a polarity compensating relaxation mechanism. The CoO$_x$ nanostructures decorating the Pd step edges display a similar contrast.
modulation in the respective STM images (Figure 2), which supports this structure interpretation. The partial embedding of the CoO(111)-type stripes into the Pd terrace areas causes a contraction of the CoO in the long (×9) direction of the (9 × 2) unit cell due to the pseudomorphic epitaxy and an expansion in the (×2) direction (perpendicular to the steps). It is significant that the CoO decoration forms stripes of 2−4 atom rows wide only: no monatomic chains nor wider stripes are observed. The presence of wider stripes may be precluded by the compressive strain in the pseudomorphic embedded growth direction (parallel to the step edges). The absence of single monatomic CoO lines indicates that a double-atom CoO stripe is a more stable situation at the step edges. This may be related in part to the growth mechanism of the hexagonal CoO stripes at the step edges: after formation of the first CoO2 step decoration line, additional Co adatoms prefer the bridge sites for attachment to the Co step atoms to optimize the Co−Co bonding. The structural modulation of the (9 × 2) CoO monolayer phase in the direction perpendicular to the surface is presumably amplified in the decoration phase at the stepped surface as a result of the additional strain due to the partial embedding into the Pd surface. This creates inequivalent bonding sites at the step edges, which provide the basis for the periodic attachment of the Pd atom rods; their observed length and periodicity distance remains, however, unexplained at this point. It is obvious that only a minority of the ejected Pd atoms is observed in the form of rod-like structures at the step edges. Their majority has presumably diffused to other parts of the surface and contributes to larger defected areas on the stepped Pd surface.

To validate and provide support to the previous analysis of experimental data, a structural model of a Pd(100) p(2 × 2)-O step edge decorated by a double-row CoO nanowire has been set up and its structural and electronic properties investigated via DFT+U simulations. The relaxed geometry of such a model is displayed in Figure 5a together with the corresponding simulated STM image. The stoichiometry of the 1-D nanostructure as CoO is derived from the assumption that this phase decorates the step via a Pd−Co exchange process and is pseudomorphic with the underlying Pd(100) surface. From an inspection of Figure 5a, one can see that the simulated STM image is in good agreement with the experimental STM images from Figures 2 and 3 and clearly exhibits an enhanced brightness at the step. This is a consequence of the fact that the
Figure 6. STM images of the Pd(1123) surface covered by progressively increasing CoO coverage: (a,d) 0.31 ML; (b,e) 0.46 ML; (c,f) 0.62 ML. Rhombic c(4×2) and square c(2×2) structure elements are indicated in (d–f). (a–c, (200×200 Å²); $V_S = -0.31$ V; $I_T = 0.4$ nA; d, (100×100 Å²); $V_S = -0.051$ V; $I_T = 0.4$ nA; e, (35×35 Å²); $V_S = -0.003$ V; $I_T = 0.27$ nA; f, (35×35 Å²); $V_S = -0.369$ V; $I_T = 0.77$ nA).

Figure 7. STM images of Pd(1123) covered by one monolayer of the (9×2) CoO structure. (a, (290×290 Å²); $V_S = +0.289$ V; $I_T = 0.27$ nA. b, (100×100 Å²); $V_S = -0.295$ V; $I_T = 0.94$ nA). The insert of panel a displays a LEED pattern of the surface (electron energy, 57 eV); the two bright spots at the left are characteristic of the (9×2) superstructure. A (9×2) unit cell is drawn in panel b.
compression of the CoO phase due to epitaxial requirements shifts upward the oxygen atoms of the internal row, thus greatly increasing the brightness of the corresponding STM spots, whereas the O atoms at the very edge (outer row) move downward to increase their coordination. This might explain the absence of single monatomic CoO lines observed experimentally as due to an energetically unfavorable CoO terminal configuration.

3.2. Growth of CoO at Pd(1123) Terraces. The partial embedding of the CoO step decoration phase into the Pd terrace areas is stopped after a maximum of 4 atomic rows. Additional Co deposition results in the growth of CoO on the upper terraces (w.r.t. the CoO decoration). It appears that the boundaries of the embedded CoO phase with the p(2 × 2)-O covered Pd surface act as nucleation centers for further oxide growth. Figure 6 shows STM images for progressively increasing CoO coverage. The oxide phase, displaying the brighter contrast, extends from the step edges into the upper terrace areas and locally ordered structure elements develop gradually (see, e.g., Figure 6d). In particular, rhombic c(4 × 2) and square c(2 × 2) unit cell ensembles become apparent (as indicated on the lower-panel images (d–f)). These structures can be understood by comparison with the c(4 × 2) Co3O4 monolayer structure, which has been clarified on the flat Pd(100) surface.14 The latter has been rationalized in terms of a CoO(100)-type monolayer, in which 0.25 ML cation vacancies are introduced, which define the c(4 × 2) periodicity and the Co3O4 stoichiometry. As demonstrated by DFT, this vacancy formation is an effective mechanism for interfacial strain release.14 The local c(2 × 2) elements of the structures in Figure 6 are formed by antiphase domain sections of the c(4 × 2) structure ensembles. The surface imaged in Figure 6c is covered by approximately one ML of the c(4 × 2)/c(2 × 2) phase, where a large number of domain boundaries separate small locally ordered regions, while the long-range order remains modest. It is important to notice that no signs of step flow growth are observed for the CoO on Pd(1123). This is clearly evidenced by the persistence of the Pd rod structures, which can still be recognized on the surfaces fully covered by the c(4 × 2) or (9 × 2) CoO structures (Figures 6 and 7).

The surfaces shown in Figure 6 have been prepared under standard reactive evaporation and annealing conditions as specified in the experimental section. By lowering the chemical potential of oxygen (adjusting pO2 and/or T) during Co deposition and annealing, the stepped Pd surface can be covered entirely by a monolayer of the (9 × 2) CoO structure, as illustrated in Figure 7. Note that the (9 × 2) structure, with a CoO stoichiometry,15 corresponds to a lower formal oxidation state than the c(4 × 2) Co3O4 structure. The morphology of the stepped surface is essentially preserved in the presence of the CoO overlayer (Figure 7a), though the step edges appear somewhat more ragged. The (9 × 2) unit cell is oriented with its long (×9) side parallel to the [011] step direction (Figure 7b), and the pronounced contrast modulation, displaying
alternatingly four brighter and four darker protrusions, is in good agreement with previous results on Pd(100). The LEED pattern in the insert of Figure 7a confirms the good surface order of the (9 × 2) overlayer structure. The growth of 2-D CoO layers on the terraces of Pd(1123) thus follows closely the pattern observed on the flat Pd(100) surface.

3.3. Electronic States of 1-D and 2-D CoO Nanostructures. The STS spectra (dI/dV vs V) in the vicinity of the Fermi energy $E_\text{F}$ ($V = 0$) of the 2-D and 1-D CoO nanostructures are compared in Figure 8. The peaks in the differential conductance spectra can be typically associated with the local density of states (LDOS). The spectral signature of the 2-D (9 × 2) and c(4 × 2) structures displays little local variation across the respective surfaces and are both characterized by a low intensity at $E_\text{F}$, by a broad resonance in the region of the filled electronic states from $E_\text{F}$ to −0.75 eV below $E_\text{F}$, and by a broad peak in the empty state region at around +0.65 eV. Two spectral features can be resolved in the (9 × 2) structure in the region below $E_\text{F}$, whereas the c(4 × 2) structure has only one broad intensity maximum. The spectrum of the quasi-1-D embedded CoO lines is similar to the more extended (9 × 2) structure, with a broad spectral intensity peaking also at −0.25 eV, thus underlining the structural similarity of the embedded CoO phase with the (9 × 2) structure; there is, however, a more pronounced empty state feature at +0.35 eV in the case of the embedded CoO lines. The CoO line at the step edge shows a significantly different STS spectrum than the other CoO phases: while the overall broad spectral intensity below $E_\text{F}$, with a clear peak at −0.17 eV in this case, is a common feature of all probed CoO structures, the high intensity at the Fermi level is a distinct characteristic of the 1-D CoO edge row. This suggests that the CoO edge atoms, which are coupled to a row of partly exposed lower terrace Pd atoms, feature an increased LDOS around the Fermi energy.

This is confirmed by theoretical analysis. In Figure Sb–d, the electronic DOS as projected onto O(2p) and Co(3d) atomic orbitals (both spin-majority and spin-minority components) is shown. It is noteworthy to observe that in all cases for both oxygen and cobalt atoms one finds for the CoO edge structure an appreciable increase in the LDOS around the Fermi level (one can note, e.g., the intense peak in the spin-minority component at about 0.8 eV above the Fermi level; Figure 5d), where the electronic states are most polarizable and responsive to environment. Such high LDOS is analogous to that observed for the p(2 × 2)-O phase (see Figure 3), which is known to have specific catalytic activity. Indeed, it has been argued that a high LDOS at $E_\text{F}$ of transition metal step edges decorated with 1-D oxide nanowires provides surface sites beneficial for a high reactivity in the CO oxidation reaction. We thus speculate that the CoO decorated Pd steps investigated in this work also create specific sites, which are active in oxidation reactions of surface catalysts. This conjecture is in line with the recent report from an industrial catalyst for methanol synthesis, where ZnO decorated step edges of Cu nanoparticles have been identified as the catalytically active sites. The here-presented oxide–metal hybrid system, consisting of step edges of a vicinal metal surface decorated with and coupled to 1-D oxide line structures, may thus be an interesting model system for further studies of advanced catalysis.

4. CONCLUSIONS

We have studied the geometry and electronic structure of a periodic array of quasi-one-dimensional CoO nanostructures, prepared by step decoration growth on a vicinal Pd(1123) surface, using STM, LEED, STS, and DFT calculations. The step decoration is dominated by Co–Pd atomic exchange processes, leading to 2–4 atom-wide CoO rows at the step edges, which are partly incorporated and embedded into the outer terrace areas. As indicated by atom-resolved STM images and DFT simulations, the CoO decoration phase is a pseudomorphically strained CoO monolayer phase of the hexagonal (9 × 2) type; the latter has been observed previously on the flat Pd(100) surface. A fraction of the Pd atoms ejected from steps and outer terrace areas during Co–Pd exchange assemble into short monatomic rows that decorate the CoO step edges in a periodic fashion. The electronic structure of the CoO decorated Pd surface has been measured by STS and displays strong local variations. The CoO step edges are distinctly different in their electronic density of states from CoO embedded into the terrace areas and from the extended 2-D (9 × 2) and c(4 × 2) CoO monolayer phases: the CoO step edges show a significantly higher local DOS around the Fermi energy in STS than the other CoO phases, and this is substantiated by the DFT model calculations. It is conjectured that this enhanced local density of O 2p and Co 3d states around the Fermi energy may be associated with a high catalytic activity in oxidation reactions.

AUTHOR INFORMATION

Corresponding Author
*(F.P.N.)* E-mail: falko.netzer@uni-graz.at. Phone: +433163805189.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the ERC Advanced Grant SEPON.

REFERENCES


