Atomic engineering of oxide nanostructure superlattices

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ARTICLE INFO

Article history:
Received 16 March 2010
Accepted 14 May 2010
Available online 24 May 2010

Keywords:
Manganese Oxide
Nanosystems
Superlattices
Steped single crystal surfaces
Scanning tunneling microscopy

Abstract

Low-dimensional nanoscale oxide-metal hybrid structures have been fabricated by decoration of a vicinal noble metal surface, Pd(1,1,17), by 1-D and 2-D Mn-oxide nanowires and nanostripes. STM and LEED demonstrate that highly ordered superlattices of Mn-oxide nanostructures can be obtained. The coupling of the oxide nanophases to the metal steps and terraces leads to a mesoscopic stabilization of the step–terrace morphology thus creating nearly perfect nanopatterned oxide systems.

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Nanoscale oxide structures find widespread use as active and passive elements in many diverse areas of modern nanoscience, such as in oxide nanoelectronics [1], nanocatalysis [2,3], or as model systems in fundamental studies of the emergent properties of novel low-dimensional materials [4]. The fabrication of nanoscale structures is typically achieved by following one of the two routes: the top-down or the bottom-up approach. While the top-down routes retain the lithographic design motifs by making use of tools such as nanolithographic techniques and scanning probe microscopies, the bottom-up methods encompass self-assembly processes and templated synthesis. In the latter case, vicinal metal surfaces, which provide regular arrays of monatomic steps that may act as nucleation centers, have been employed as templates for engineering patterned nanostructures by directed growth in physical vapor deposition procedures [5–7]. Here we report the creation of superlattices of low-dimensional oxide nanosystems, in the form of oxide nanowires and nanostripes, by using a vicinal metal surface as a template for directed self-assembly of an oxide phase of a different metal: the systems of study in this work are manganese oxides patterned by a Pd(1,1,17) surface, which is a vicinal of Pd(100).

Vicinal, i.e. high Miller index, metal surfaces may be visualized in the ideal case as a regular staircase of low-index terrace planes separated by monatomic steps [8], which create a superlattice of step structures acting as patterning centers. In reality, however, vicinal surfaces resemble rarely the ideal picture and, in particular for larger terrace widths, a regular step–terrace pattern is difficult to achieve, resulting in surfaces with a wide distribution of terrace widths and irregular step edges. This is in part due to the relatively weak repulsive

step–step interaction energies, which are responsible for producing the step ordering, and in part to the propensity of vicinal surfaces to facet into more stable low-index configurations [9]. Here we show that the decoration of the metal step edges and terraces by pseudomorphic oxide nanolayers leads to a mesoscopic stabilization of the step morphology and to the creation of highly ordered superlattices of oxide nanostructures. Using this design approach, we are able to prepare ordered arrays of one-dimensional (1-D) Mn-oxide nanowires pseudomorphically coupled to the step edges of the stepped Pd(1,1,17) surface, and of two-dimensional (2-D) Mn-oxide nanostripes incommensurate overlayers covering the terraces of this stepped Pd surface. The formation of a particular oxide phase can be tuned by appropriate choices of the Mn coverage, substrate temperature and oxygen chemical potential.

The Mn-oxide nanostructures reported here have been atomically characterized by STM and LEED in a multi-task custom-designed system as described previously [10]. The Pd(1,1,17) surface, which has been used as template in the directed growth experiments in this work, consists of (100)-oriented terraces ~8.5 atoms (23.4 Å) wide separated by monatomic steps exposing (111)-type microfacets. Fig. 1a shows a schematic model of the ideal stepped surface, which can be compared to the experimental STM image of the clean Pd (1,1,17) surface in Fig. 1b. We notice that the step edges of the clean Pd surface display only short straight sections (<50 Å) separated by kinks in a random sequence, and that the terraces are irregular and have a large width distribution (Fig. 1e, red bar diagram), centered around a terrace width of ~23–24 Å, as expected for a (1,1,17) vicinal Pd surface. Deposition of 0.1 monolayer (ML) — as defined with respect to the atom density of the bare substrate surface) of Mn atoms at 300 K, followed by oxidation in 1 × 10−8 mbar O2 at 470 K results in a regular decoration of the Pd step edges by monatomic rows of MnO2 structures, which are clearly recognized by the brighter chemical
The contrast in the STM images of Fig. 1(c–d). The morphology of the steps has changed significantly as a result of the decoration process with MnO$_x$ rows, displaying now perfectly straight step edges extended over many hundreds of Ångström. The terrace width distribution is not much narrower (see the green bar diagram in Fig. 1e). The high-resolution STM image of Fig. 1d allows us to determine the structural details of the Mn-oxide nanowires: the monatomic MnO$_x$ rows are attached to the Pd step atoms in a pseudomorphic 1-D ($\times 1$) structure, i.e. displaying the same lattice constant as the Pd substrate ($a_{\text{Pd}} = 2.75$ Å) along the step edge direction as indicated in Fig. 1d. On the terraces a p($2 \times 2$) superstructure is recognized, which is due to a chemisorbed oxygen overlayer formed as a result of the oxidation process. The Mn 2p$_{3/2}$ XPS spectrum, recorded with Al K$_\alpha$ radiation in a different system and shown in Fig. 1f, confirms that the Mn atoms are oxidized: the Mn 2p$_{3/2}$ core-level, which due to final state effects displays a complex structure [11], is shifted
by ~0.8 eV to higher binding energy with respect to metallic Mn adatom species, a clear indication of an oxidized Mn nanostructure.

1-D oxidic nanowire superstructures, albeit less well-ordered and less regular, have been reported previously for monatomic NiO lines decorating the steps of a vicinal Rh(111) surface [12]. They have been interpreted on the basis of density functional theory (DFT) calculations in terms of a formal NiO2 stoichiometry, i.e. each Ni step adatom is coordinated to four oxygen atoms, two at the lower and two at the upper step edge as shown schematically in Fig. 1a, right hand side. The Ni 2p3/2 XPS spectrum displayed a chemical shift of 0.7 eV to higher binding energy between the oxidized NiO2 nanowires and metallic Ni adatoms [12], which is very similar to the chemical shift observed here in the Mn 2p3/2 spectrum of Fig. 1f. It is thus most natural to associate the 1-D Mn-oxide structures on stepped Pd surfaces with nanowires of formal MnO2 stoichiometry.

The pseudomorphic coupling of the MnO2 lines to the Pd step edges creates artificial quasi-1-D oxide–metal hybrid structures with Mn–Mn distances close to metallic but strained with respect to oxidic Mn phases (dMn-Mn in Mn metal is 2.73 Å, in oxides typically > 3 Å). The step morphology at the Pd(1,1,17) surface is significantly modified by the MnO2 decoration, in that step edge fluctuations and kink formation become suppressed and straight step edges are stabilized over remarkably long distances. The here fabricated 1-D Mn-oxide — Pd hybrid structures may be interesting model systems for studying low-dimensional electronic and magnetic behavior and for nanocatalytic applications. Preliminary experiments indicate indeed that these oxide–metal hybrid surfaces are highly reactive towards residual gases suggesting a high catalytic activity for e.g. oxidation reactions.

Different oxide nanostructures, in form of oxide nanostripes, can be fabricated by completely covering the terraces of the vicinal Pd(1,1,17) surface by a Mn-oxide wetting layer, as depicted in Fig. 2. The STM images of Fig. 2(a–b), recorded after deposition of 0.75 ML Mn at room temperature (RT) followed by oxidation in 5 × 10⁻⁸ mbar O₂ at 800 K, show a well-ordered step superlattice with terraces covered by a c(4×2) MnO₂ superstructure. The oxide overlayer stabilizes a step morphology with straight edges and regular terrace widths, creating a surface with perfect regularity and high surface order. The latter is highlighted by the sharp LEED pattern in Fig. 2c and the narrow terrace width distribution displayed in Fig. 2d. It is remarkable that the mean terrace width of this c(4×2) MnO₂ covered Pd surface is expanded to ~28–29 Å: this corresponds to adding two atomic Pd rows to each terrace of the (1,1,17) surface, thus faceting the (1,1,17) into a (1,1,21) surface. The faceting of vicinal metal surfaces is not uncommon and has been reported, for example, for the Rh(553) surface under the influence of oxygen [13]. We note that the overall (macroscopic) orientation of the original vicinal surface is maintained after the faceting by the introduction of multi-atomic steps, as also seen experimentally. The here observed faceting is driven by the interaction of the (100)-type terraces with the Mn-oxide overlayer. The c(4×2) MnO₂ overlayer structure has also been observed on the flat Pd(100) surface and has been rationalized, using a combination of several experimental techniques and DFT calculations, as a MnO(100)-type monolayer with a c(4×2) superlattice of Mn vacancies, thereby

Fig. 2. (a) Large scale STM image of the c(4×2)–Mn-oxide/Pd(1,1,21) surface (400×400 Å², sample bias U = 1.5 V, tunneling current I = 100 pA). (b) High-resolution STM image of the c(4×2) surface displayed in the derivative mode (100×100 Å², U = −0.2 V, I = 100 pA). A primitive c(4×2) unit cell is indicated. (c) LEED pattern of the c(4×2) surface taken with primary energy E_p = 120 eV. A primitive c(4×2) unit cell is indicated. (d) Terrace width distribution of the c(4×2) oxide surface.
yielding a formal Mn$_3$O$_4$ stoichiometry [14]. It has been suggested that the formation of this Mn vacancy defect lattice is a mechanism for the relaxation of epitaxial strain, which is caused by the large lattice mismatch between the MnO and the Pd lattices (~14%). The step edges of the vicinal substrate surface provide additional means for the relaxation of overlayer strain, and this is at the root of the formation of this perfectly well-ordered c(4×2)−Mn$_3$O$_4$ covered Pd(1,1,21) surface. We note parenthetically that on the flat Pd(100) surface the c(4×2)−Mn$_3$O$_4$ overlayer forms ordered areas of only limited size, which are separated by disordered regions as a result of residual interface strain [14]. The detailed discussion of the stress relief in the c(4×2)−Mn$_3$O$_4$ nanostripes on the stepped Pd surface is beyond the scope of this paper and will be the subject of a forthcoming publication.

As seen in Fig. 2b, the terraces of the Pd(1,1,21) facet can accommodate three primitive unit cells of the c(4×2)−Mn$_3$O$_4$ structure. Experimentally we observe that the vicinal Pd substrate has to be fully covered by the Mn-oxide overlayer in order to establish the exceptional surface order as apparent in Fig. 2. We conjecture therefore that both the faceting transition and the stabilization of the step–terrace morphology into a superlattice with high perfection are driven by the match of the Mn$_3$O$_4$ overlayer lattice to the substrate terrace width and the concomitant minimization of the electronic (bonding) and elastic (strain) energy contributions. DFT calculations with hybrid functionals predicted a ferromagnetic ground state for the strained c(4×2) Mn$_3$O$_4$ overlayer on Pd(100) [14]. The Mn$_3$O$_4$ nanostripes on the vicinal Pd surface may thus provide an interesting system to investigate the role of lateral confinement and strain relief on the magnetic properties of low-dimensional oxide structures.

The chemical potential of oxygen as a growth variable during the oxidation step of the preparation procedure crucially determines the atomic structure of the particular oxide phase formed. Deposition of 0.75 ML Mn onto Pd(1,1,17) at RT and oxidation in 5×10$^{-8}$ mbar O$_2$ at 500 K (as opposed to 800 K in the case of the c(4×2) structure), i.e. applying a higher chemical potential of oxygen, results in the formation of nanostripes of MnO$_x$ with a p(2×1) structure covering the terraces of the Pd vicinal surface. As apparent from Fig. 3, the superlattice of oxide nanostripes is again established with high quality; the sharp LEED pattern (Fig. 3c) and the narrow terrace width distribution (Fig. 3d) give evidence of a well-established long-range order of the step–terrace morphology. The analysis of the terrace widths yields a mean width of ~28–29 Å, corresponding again to a (1,1,21) orientation of the average Pd substrate surface. The p(2×1) MnO$_x$ phase thus also appears to stabilize the (1,1,21) Pd facet, if a full oxide overlayer coverage is established. The high-resolution STM image of Fig. 3b indicates that three p(2×1) unit cells can be placed across each substrate terrace. The atomic structure of the p(2×1) MnO$_x$ nanostripes is presently still unresolved, but detailed inspection of high-resolution STM images recorded with different tunneling conditions suggests a square symmetry of the basic oxide lattice [15], as e.g. in a buckled MnO(100)-type structure. It is clear, however, that also in the p(2×1) MnO$_x$ case the oxide overlayer provides a highly stabilizing agent for the step superlattice geometry thus creating an array of highly ordered oxide nanostripes.

**Fig. 3.** (a) Large scale STM image of the p(2×1) Mn-oxide/Pd(1,1,21) surface (500 × 500 Å$^2$, sample bias $U=1.0$ V, tunneling current $I=100$ pA). (b) High-resolution STM image of the p(2×1) surface displayed in the derivative mode (90 × 90 Å$^2$, $U=5$ mV, $I=100$ pA). A p(2×1) unit cell is indicated. (c) LEED pattern of the p(2×1) surface taken with primary energy $E_p = 80$ eV. A p(2×1) unit cell is indicated. (d) Terrace width distribution of the p(2×1) surface.
As demonstrated here for Mn-oxides on Pd, the decoration of vicinal metal surfaces by oxide nanostructures provides a successful route to fabricate well-ordered superlattices of low-dimensional oxide systems. The structures created constitute novel hybrid materials with as yet unexplored physical and chemical properties. The physical origin of the mesoscopic stabilization of the regular step–terrace morphology of the vicinal metal surfaces by decoration with oxide nanostructures is presumably due to a twofold effect: the substrate steps become rigid due to the coupling to pseudomorphic oxide line structures, and particular terrace widths become preferred thanks to the interfacial matching with the lattice of 2-D oxide wetting layers. The provision of strain release at the step edges may provide additional stabilization for particular oxide nanophases. The here described route of atomic scale engineering of nanopatterned oxide surfaces may be applied to a variety of metal–oxide hybrid combinations, thus creating new avenues for the study of physical and chemical phenomena at the nanoscale.

Acknowledgement

This experimental work has been supported by the FWF through the NFN network “Nanoscience on Surfaces” and by the ERC Advanced Grant SEPON.

References

[15] This is significant, because a NiO(111) type structural model has been proposed for a g(2×1) structure of Ni-oxide on Ag(100) by M. Caffio et al., J. Phys. Chem. 108 (2004) 5919.