Lattice Strain Defects in a Ceria Nanolayer

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Supporting Information

ABSTRACT: An ultrathin two-dimensional CeO2 (ceria) phase on a Cu(110) surface has been fabricated and fully characterized by high-resolution scanning tunneling microscopy, photoelectron spectroscopy, and density functional theory. The atomic lattice structure of the ceria/Cu(110) system is revealed as a hexagonal CeO2(111)-type monolayer separated from the Cu(110) surface by a partly disordered Cu−O intercalated buffer layer. The epitaxial coupling of the two-dimensional ceria overlayer to the Cu(110)-O surface leads to a nanoscopic stripe pattern, which creates defect regions of quasi-periodic lattice distortions. The symmetry and lattice mismatch at the interface is clarified to be responsible for the topographic stripe geometry and the related anisotropic strain defect regions at the ceria surface. This ceria monolayer is in a fully oxidized and thermodynamically stable state.

Chemistry on oxide surfaces is to a large extent determined by surface defects, which provide the most reactive centers for interacting atoms and molecules.1 In addition to morphological defects such as steps, corners, and kinks, oxygen vacancies are key to oxides’ reactive behavior. Concentration, distribution, and energy of creation of oxygen vacancies essentially determine the catalytic activity of oxide surfaces,2−6 and this is particularly true for cerium oxide (ceria, CeO2), whose diverse applications in physics and chemistry (catalysis,7 solid oxide fuel cells,8 or biomedicine9) are controlled by whose diverse applications in physics and chemistry (catalysis,7 solid oxide fuel cells,8 or biomedicine9) are controlled by

The reduction of dimensionality in an oxide system may also lead to novel structural phenomena. Here, we show that in a two-dimensional (2-D) ceria monolayer, grown epitaxially on a Cu(110) surface, dimensionality reduction leads to the creation of a different kind of surface defect, a so-called “lattice strain defect”. Lattice and symmetry mismatch between the hexagonal 2-D ceria overlayer and the rectangular Cu(110) substrate surface conspire to induce the spontaneous formation of quasi-periodic stripes, which as a result of the frustration of the chemical bonding at the interface lead to a nanoscopic topographical modulation of the oxide lattice. The latter creates a range of anisotropic lattice distortions in the 2-D ceria layer, finally giving rise to a nanoscale strain defect pattern, as identified in ultrahigh resolution scanning tunneling microscopy (STM) images and rationalized by first-principles analysis. As local strain interfaces in the modification of the electronic structure,17,18 a particular chemical behavior is expected at these defect sites.

An atomically ordered ceria monolayer has been grown on a clean Cu(110) single crystal surface by deposition of cerium metal at 300 K followed by oxidation in (1−5) × 10−8 mbar oxygen at 750−800 K and further annealing in oxygen at 800 K. The surface morphology and atomic structure has been probed in a low-temperature (5 K) STM system, the oxide stoichiometry has been established by X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) in its DFT+U form (i.e., adding a Hubbard U term to the energy expression) has been applied to model the ceria/Cu(110) surface structure. The details of the experimental setup and procedures as well as of the theoretical modeling are given in the Methods Section and Supporting Information (SI).

Figure 1A shows a topographic constant current STM image of cerium oxide on Cu(110) (oxide coverage ≈0.85 monolayer, ML), illustrating the morphology of the overlay. The ceria grows as a 2-D wetting layer with a number of vacancy holes, which reach down to the Cu substrate; the Cu surface in the holes is oxidized to the (2 × 1)-O surface reconstruction,19 under the given oxide preparation conditions. The vacancy holes feature shapes with hexagonal geometry elements in accord with the atomic order in the oxide layer (see below). The significant observation in the oxide morphology is that the surface displays a texture in a preferential direction: stripes of
bright and dark contrast run along the [1−10] direction in the STM image, i.e., along the dense-packed rows of the Cu(110) substrate. The stripe pattern is quasi-periodic, but shows distortions as the oxide layer approaches the monolayer coverage. For lower coverage, the oxide grows in the form of islands and the stripes are more regular (see Figure 1B for ~0.6 ML ceria coverage. Note that in the zoomed image frame of Figure 1B the Cu(110) (2 × 1)-O reconstruction is visible in the vacancy holes as lines in the [001] direction, i.e., in the direction orthogonal to the ceria stripes. The distortions in the oxide stripe pattern (Figure 1A) are the result of extra strain produced when the oxide islands percolate at higher coverage.

The ceria overlayer is atomically well ordered: Figures 1(C,D) show high resolution STM images of the ceria surface. In Figure 1(C), the stripe pattern is well resolved and a hexagonal lattice of bright atomic-size protrusions is recognized. All the STM images shown here have been recorded with positive sample bias, i.e., tunneling into the empty states of the sample (see the discussion of simulated STM images below). The oxide lattice is particularly well resolved in the STM image of Figure 1D, from which the lattice parameter of the oxide layer can be extracted. The STM scanner has been calibrated against the c(6 × 2)-O reconstruction of the Cu(110) surface that coexists with ceria islands at submonolayer coverages under certain preparation conditions (see SI and Figures S1, S2) and a value of \( a_{\text{ceria}} = 3.84 \pm 0.03 \, \text{Å} \) has been derived. This is close to the \( a = 3.89 \, \text{Å} \) value of the hexagonal CeO\(_2\)(111) bulk terminating surface. Since the (111) face is the most stable surface termination of bulk CeO\(_2\), it is most natural to propose a (111)-type O−Ce−O trilayer slab as a structural model of the present ceria overlayer, as confirmed below via a

Figure 1. STM images of ceria on Cu(110), recorded at 85K. (A) Oxide coverage ~0.85 ML (115.5 × 115.5 nm\(^2\); sample bias \( V_s = +1.453 \, \text{V}; \) tunneling current \( I_T = 0.11 \, \text{nA} \)). (B) Oxide coverage ~0.6 ML (28.9 × 28.9 nm\(^2\); \( V_s = +1.453 \, \text{V}; I_T = 0.11 \, \text{nA} \)). Inset: (80 × 80 nm\(^2\); \( V_s = 2.0 \, \text{V}; I_T = 0.21 \, \text{nA} \)). (C) (20 × 20 nm\(^2\); \( V_s = +0.325 \, \text{V}; I_T = 0.26 \, \text{nA} \)). Note the Cu−O (2 × 1) reconstruction at the lower right corner. (D) (7.2 × 7.2 nm\(^2\); \( V_s = +1.347 \, \text{V}; I_T = 0.1 \, \text{nA} \)).
first-principles analysis, which will refine this model and provide additional insights.

The stoichiometry of the ceria overlayer has been determined by Ce 3d core level spectral analysis. The Ce 3d XPS spectrum is complicated with many components due to initial state and final state effects, and the determination of the relative amounts of Ce$^{3+}$ and Ce$^{4+}$ species, and thus the stoichiometry, requires a complex spectra decomposition procedure (see SI; Figure S3A). The stoichiometry of the 2-D ceria on Cu(110) grown under present preparation conditions has been evaluated to be CeO $\sim$ 1.95. This is slightly understoichiometric (as compared to CeO$_2$) but well compatible with the range of stoichiometries of ultrathin ceria films reported in the literature. It is also consistent with the proposed (111)-type O−Ce−O trilayer structure model. The O 1s XPS spectra have been recorded and the O 1s intensity of the ceria/Cu(110) has been evaluated quantitatively using the Cu(2 $\times$ 1)-O structure for calibration purposes (see SI, Figure S3B). The measured O 1s intensities are in good agreement with the DFT derived structure model, as detailed below.

The low-energy electron diffraction (LEED) pattern of the ceria/Cu(110) surface in Figure 2(A) features sharp reflections confirming an overall long-range order, but there is some diffuse intensity in the [001] direction, which suggests some uniaxial structural imperfection or disorder; the latter will be addressed further below. If the measured ceria lattice constant of 3.84 Å is allowed to contract only slightly (<1%) to 3.82 Å, the resulting hexagonal overlayer fits exactly onto Cu(110) in a (3 $\times$ 11) coincidence lattice, as shown in the schematic drawing of Figure 2B. A simulation of the LEED pattern of the superimposed (3 $\times$ 11) ceria and Cu (2 $\times$ 1)-O lattices in the left panel of Figure 2(B) contains most of the fractional order spots of the experimental pattern, but it does not account for the diffuse stripes in the [001] direction.

The STM image of Figure 2C together with the line scan in Figure 2D illustrates the details of the ceria stripe pattern. The pattern shows a flexible behavior with variable periodicity, ranging from ~8 nm, in the left part of the line scan, to ~5 nm in the right part. The apparent STM corrugation of the pattern as measured from the line scan is 2−3 Å. An important geometry parameter of a 2-D oxide structure is the thickness of the layer, or equivalently the step height from a substrate surface to the oxide surface. STM measurements across a metal-oxide step edge give typically only an apparent height, since electronic effects in the tunneling process interfere with the topography. However, it has been shown that when measuring step heights as a function of the tunneling bias, the step height obtained with the bias outside the oxide band gap approaches the geometrical height. Figure 2E displays a graph of the measured STM heights of the ceria layer with respect to the Cu(110) (2 $\times$ 1)-O surface as a function of the tunneling bias. The step height increases with increasing positive bias, but converges to ~4.15 Å for V > 1.5 V, which is outside the measured band gap of the ceria layer (see Figure S4 of the SI for further details), thus providing a benchmark value for the comparison with theoretical modeling.

The (3 $\times$ 11) unit cell was approximated in the DFT calculations in a first scan with a (3 $\times$ 2) cell, measuring 7.65 $\times$ 6.88 Å; see Figure S5 of the SI, where the oxide was elongated by about 3.8% along the y direction (from 6.62 to 6.88 Å). Selected simulations were also performed with the much bigger and computationally demanding (3 $\times$ 11) unit cell. Four possible structures with different stoichiometry were sampled for a CeO$_2$ monolayer growing on an unreconstructed Cu(110) surface (see SI, Figure S6, and the energetics reported in Table S1). The lowest-energy one, shown in Figure S6A, has CeO$_2$ stoichiometry and O−Ce−O stacking. This structure is favored by its bulk-like stoichiometry and short-range order and by exposure of O atoms at the interface with Cu(110), which gets partially oxidized. This arrangement is similar to previously investigated CeO$_x$/Cu systems, which, however, exhibit a reduced oxidation state for Ce, in contradiction with the present XPS results. Similarly, the lowest-energy bilayer structure (reported in Figure S7 of the SI) mimics the configuration of bulk ceria. However, the difference in height between the topmost oxygen of the CeO$_2$ bilayer and the Cu(110) surface is close to 7 Å, which is much larger than the experimental value.

In the search for alternative models, starting from the ML configuration of Figure S6A, with a formal stoichiometry of Ce$_x$O$_y$ per unit cell, further Cu and O atoms were added at the interface between the metal support and the oxide overlayer. The model with the lowest energy is shown in Figure 3(A). Its formation reaction:

$$\text{Ce}_x\text{O}_y + 4\text{Cu} + 2\text{O}_2 \rightarrow \text{Cu}_4\text{Ce}_4\text{O}_{12}$$  \hspace{1cm} (1)
has a $\Delta E$ of about $-0.37$ Ry per cell and a $\Delta G$ of about $+0.01$ Ry, obtained by using the Gibbs free energy of O$_2$ molecule in the gas phase under the given (P,T) conditions and estimating the chemical potential of a Cu atom as the Cu bulk energy at the DFT level. Although the $\Delta G$ of the formation reaction is slightly positive, it is so by a minor amount within DFT typical accuracy, while a further stabilization can come from the relaxation taking place in the (3 $\times$ 11) cell (see below).

The "real" (3 $\times$ 11) cell was built taking S.5 times the oxide layer obtained from the model in Figure 3A and DFT-relaxed geometry. The optimized configuration is shown in Figure 3B together with a simulated STM image at a bias of +1.0 V. The formation energy $\Delta E$ of this phase using the analogue of eq 1 for the (3 $\times$ 11) unit cell is now $-2.44$ Ry, i.e., lower by 0.075 Ry per (3 $\times$ 2) cell than the value $-2.03$ Ry, which would be expected by multiplying by 5.5 times the formation energy of the (3 $\times$ 2) configuration in Figure 3A. This implies that the formation of a coincidence lattice appreciably stabilizes the Cu$_4$Ce$_4$O$_{12}$ configuration.

It is to be noted that in the proposed structure of Figure 3A, the O atoms at the interface oxidize the interface Cu atoms, likely reducing the charge transfer to the ceria monolayer. The model in Figure 3A can thus be described alternatively as a ceria overlayer on a Cu(110)-O surface or as a mixed 2-D (Cu, Ce) ternary oxide. Moreover, in this structure, the average height of the topmost oxygen layer with respect to the topmost atoms in the CuO$_6$ surface layer is about 3.6 Å, in reasonable agreement with experiment (~4.15 Å). Also, the quantitative evaluation of the O 1s spectra is in full agreement with the Cu$_4$Ce$_4$O$_{12}$ structure model.

The obtained optimum structure (Figure 3B,E) produces a satisfactory picture and agreement with experiment. The modulation of brightness in the simulated STM images nicely parallels the experimental observation and can be understood by looking at the side views of the model in Figure 3(E,F), where a modulation in height of the oxide overlayer is apparent. The topmost O atoms are thus imaged in the STM according to a topographic pattern. The origin of this modulation or stripe corrugation can be traced back ultimately to the epitaxial mismatch of the ceria overlayer with respect to the underlying metal surface. The consequent interface frustration in the potentially strong but very short-ranged chemical bonding between O atoms of the ceria and Cu atoms of the CuO$_6$ surface oxide is solvable by creating epitaxially matched regions of strong O–Cu covalent bonds alternating with epitaxially mismatched regions of CeO$_2$/CuO weak nonbonding interactions, in close analogy with homologous ultrathin-dielectric/metal systems.

The structural freedom due to the somewhat disordered Cu–O interface layer—see Figure 3(C) — reflects in the flexibility of the stripe periodicity, i.e., the quasi-periodic behavior of the mesoscopically variable stripe pattern apparent in Figure 2, which also causes the diffuse lines in the LEED pattern in the [001] direction.

Finally, the DFT-predicted work functions (WFs) of the various systems are in good agreement with experiment. The WF of Cu(110) is predicted to be 4.4 eV (experiment: 4.4 eV), increasing to 4.6 eV in the Cu(110)-(2 $\times$ 1) phase (experiment: 4.7 eV), and to 4.7 eV in the (3 $\times$ 11) Cu$_4$Ce$_4$O$_{12}$ overlayer (exp. 4.71 eV).

Figure 4. Ultrahigh resolution STM images of the ceria on Cu(110) surface, recorded at 85K. (A) (10 $\times$ 10 nm$^2$; $V_z = +0.350$ V; $I_x = 0.26$ nA). (B) (5 $\times$ 5 nm$^2$; $V_z = 0.583$ V; $I_x = 0.26$ nA). The dotted lines indicate the direction of atom rows on the dark and bright stripes. A region of distortion of the hexagonal ceria lattice defining the lattice strain defect is encircled.

with the stripe regions of bright and dark contrast (the stripe period is ~4.2 nm in this particular case). The protrusions of atomic maxima are clearly apparent, forming a hexagonal arrangement with rows running across the regions of dark and bright stripes (see the dashed lines on the images ). Closer inspection shows that the atomic rows in the region of the dark stripes are not strictly parallel to the ones on top of the bright stripes: there is a change of direction of atomic rows in the transition region from dark to bright stripes and vice versa - the dotted lines on the images highlight this effect. These kinks in the atomic rows are the result of a local distortion of the hexagonal lattice (encircled in Figure 4B), creating a strained region between dark and bright stripes. This periodic lattice distortion is denoted here as "lattice strain defect" (Figure 4B). These defects constitute a periodic modulation of surface strain, generated by the topographic height modulations of the ceria nanostripes caused by the epitaxial lattice and symmetry mismatch at the ceria/Cu(110) interface.

The physical origin of this lattice defect is based on the epitaxial coupling of the bulk-like CeO$_2$ trilayer to the Cu(110) surface via a Cu–O interlayer. The latter contains rows of Cu and O atoms along the [001] direction with partial disorder (see Figure 3C), yet enabling periodic areas of stronger and weaker chemical bonding between overlayer and substrate; this leads to the observed topographic stripe modulation. The lattice strain defecrs are regions with unidirectional distortions of the hexagonal ceria lattice, in the transition region between brighter (higher) and darker (lower) stripes. Their concentration varies across the surface with the periodicity of the stripes, their spatial extent encompasses approximately the area encircled in Figure 4B.

It is anticipated that the surface chemistry at these strained lattice sites is modified as compared to a regular ceria surface, thereby justifying the term “defect” for these surface regions. Moreover, at variance with conventional 2D-ceria interfacial systems, the present fully oxidized CeO$_2$ phase should give rise to a dramatically different chemical behavior, with the additional benefits of a substantial thermodynamic stability and a structural flexibility due to having a conventional ceria/metal phase relatively close in energy.

Two-dimensional oxide materials display novel structural and electronic properties with a tremendous potential for sophisticated applications in advanced technologies.
we demonstrate that the chemical coupling of a 2-D oxide layer to a symmetry mismatched substrate can induce a morphological phenomenon of nanoscopic stripe formation, which creates a modulation of anisotropic lattice distortions, referred to as lattice strain defects. Given the importance of defects for the chemistry of oxide surfaces, the presented ceria/Cu(110) system is a model with a high potential for studies in oxide nanocatalysis, with the lattice strain defects possibly mediating novel surface chemistry. It is also expected that such morphological behavior is a more general phenomenon of 2-D oxides coupled to symmetry-mismatched interacting substrates. The nanostripe lattice strain defects may act as preferred nucleation centers in templates for the hierarchical growth of functional materials, enabling a further level of complexity in hybrid nanostructures.

■ METHODS

Experiment: Apparatus and Procedures. The STM experiments have been carried out in a low-temperature (5 K) STM system (Crea tec Germany), operated for the measurements presented here with liquid N2 in the cryostat stage, yielding a sample temperature of ~85 K. Sample cleaning and preparation and in situ STM tip treatments were performed in the preparation chamber. Electrochemically etched W tips have been treated in situ by electron bombardment heating and by field emission via voltage pulses. The STM images have been recorded in constant current mode, with the bias applied to the sample. Differential conductance (dI/dV versus V) STS spectra have been recorded with a lock-in technique with a 1.175 kHz modulation frequency and 100 mV modulation amplitude. The photoelectron spectroscopy measurements were carried out in a custom-designed system for X-ray (XPS) and UV photoelectron spectroscopy (UPS) (SPECS Germany); Mg Kα radiation was used for core level XPS and He I radiation for valence band UPS. The sample work function was measured from the low-energy electron cutoff in UPS spectra. Both experimental systems are equipped with LEED, which was used to cross-check the identity and quality of the respective ceria surfaces. The Cu(110) surface has been cleaned by Ar+ bombardment, 700 eV, followed by annealing at 850 K. Cerium metal was evaporated from a Ta crucible in an electron beam evaporator, and the evaporating flux was measured with a quartz microbalance. Various oxide thin film preparation procedures have been tested, such as reactive evaporation of Ce in oxygen atmosphere or postoxidation of Ce metal deposited at the clean and oxygen precovered Cu surface; all procedures resulted in the epitaxial growth of 2-D cerium oxide films. However, the layers with the best structural order have been obtained by the postoxidation method: Ce metal was evaporated onto the clean Cu(110) surface at 300–350 K and postoxidized in (1–5) × 10−8 mbar O2 at 750–800 K, followed by a few min annealing in O2 at 800–850 K. Under these preparation conditions, the ceria stoichiometry is close to CeO2, but slightly underestimated (CeO1.92−1.96) as evidenced by XPS (see Figure S3, S1). For submonolayer oxide coverages, the coexisting Cu(110) surface patches are oxidized to the (2 × 1)-O reconstruction, if the O2 pressure during postoxidation is kept below 1 × 10−7 mbar. For higher oxygen pressures, PO2 ≥ 10−7 mbar, the Cu(110) surface is oxidized to the c(6 × 2)-O reconstruction, and the ceria overlayer becomes stoichiometric CeO2. Using the postoxidation procedure, no influence of the O2 pressure on the 2-D morphology of the ceria overlayer has been observed within the employed pressure range (1 × 10−8 mbar - 5 × 10−7 mbar), in agreement with reports in the literature. The ceria surface coverage has been estimated from the inspection of large scale STM images (1 monolayer (ML) of (111)-type ceria corresponds to 7.9 × 1014 Ce atoms/cm2).

Theory. DFT calculations were performed using the QuantumEspresso code, employing a basis set of plane waves, ultrasoft pseudopotentials, and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-) functional, complemented by the introduction of a Hubbard U term on the Ce atoms with a value of U = 4.5 eV. In a first scan, the (3 × 11) unit cell was approximated with a (3 × 2) cell, measuring 7.65 × 6.88 Å (see Figure S5, S1), where the oxide was elongated by about 3.8% along the y direction (from 6.62 to 6.88 Å). Selected simulations were also performed with the much bigger and computationally demanding (3 × 11) unit cell. Values of 20 and 200 Ry were chosen as the energy cutoff for the selection of the plane waves for the description of the wave function and the electronic density, respectively. The Brillouin zone was sampled at the Gamma point only, which is accurate for such big unit cells. The electronic levels were broadened with a Gaussian smearing of about 0.002 Ry (1 Ry = 13.606 eV) and all the calculations were performed spin-polarized. STM images were simulated applying the Tersoff–Hamann approach at a constant height of about 2 Å above the oxide surface. Along the z axis, a minimum empty space of 15 Å was chosen to avoid interactions between replicated cells. A dipole correction was applied to cancel spurious Coulombic interactions among replicated images. Our DFT approach predicts an equilibrium value of the Cu metal lattice constant of about 2.58 Å, in good agreement with the experimental value of 2.55 Å. In the calculations here presented, the experimental value of the Cu lattice constant was used, and the Cu surface was modeled as a slab with six layers frozen in their crystal positions, while the positions of the atoms in the CeOx/CuOx systems were optimized until the forces were smaller than 10−3 eV Å−1. Our DFT approach accurately predicts the bulk lattice constant of CeO2 fluorite-like crystal structure (where each Ce atom is coordinated by eight O atoms at the vertices of a cube, whereas each O atom is coordinated by four Ce atoms at the vertices of a tetrahedron): 3.89 Å, to be compared to an experimental value of 3.91 Å. As a further validation, we also calculated the formation energy of an oxygen vacancy at a (111) CeO2 surface obtaining a value of 4.83 eV, in very good agreement with the literature value of 4.95 eV obtained by Fabris. We also verified that the electronic distribution around the vacancy is correctly described, with two electrons left by the missing oxygen localized on the 4f states of two cerium atoms next to the vacancy, hence shifting their oxidation state from +4 to +3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b00253. Determination of the ceria lattice constant—STM scanner calibration with the Cu(110) c(6 × 2)-O reconstruction (Figures S1 and S2); photoelectron spectroscopy of ceria on Cu(110) (Figure S3); determination of the ceria overlayer thickness (Figure S4); structural models (Figures S5, S6, S7, Table S1) (PDF)
The authors declare no competing financial interest.

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