Nickel-Oxide-Modified SrTiO$_3$(110)-(4 × 1) Surfaces and Their Interaction with Water

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ABSTRACT: Nickel oxide (NiO), deposited onto the strontium titanate (SrTiO$_3$) (110)-(4 × 1) surface, was studied using photoemission spectroscopy (PES), X-ray absorption near edge structure (XANES), and low-energy He$^+$ ion scattering (LEIS), as well as scanning tunneling microscopy (STM). The main motivation for studying this system comes from the prominent role it plays in photocatalysis. The (4 × 1) reconstructed SrTiO$_3$(110) surface was previously found to be remarkably inert toward water adsorption under ultrahigh-vacuum conditions. Nickel oxide grows on this surface as patches without any apparent ordered structure. PES and LEIS reveal an upward band bending, a reduction of the band gap, and reactivity toward water adsorption upon deposition of NiO. Spectroscopic results are discussed with respect to the enhanced reactivity toward water of the NiO-loaded surface.

INTRODUCTION

Strontium titanate (SrTiO$_3$, STO), the prototypical perovskite oxide, has long been known to show interesting effects taking place on its surfaces. For example, it is commonly used as a substrate for the growth of complex oxides, and it supports the formation of a two-dimensional electron gas on its surfaces. Furthermore, SrTiO$_3$ was one of the first materials to show a photocatalytic water-splitting efficiency than the classical photocatalyst TiO$_2$.

What makes a material a good photocatalyst are an appropriate band gap allowing harvesting most of the solar spectrum (maximum intensity at around 2.4 eV) and a suitable alignment of the valence band maximum (VBM) and conduction band minimum (CBM) with respect to the redox potentials of water. As was found by Scaife, for most semiconducting transition metal oxides, the (H$_2$O/H$_2$) redox potential of water lies around 3 V above the VBM, i.e., inside the band gap for SrTiO$_3$ ($E_g$ = 3.2 eV). This means that band engineering toward an efficient photocatalyst should decrease the magnitude of the band gap while retaining the position of the CBM.

Such band engineering was already successfully demonstrated by Konta et al. by doping STO with rhodium. The rhodium dopants introduce an impurity level located 2.3 eV below the CBM of STO. Visible light can therefore excite electrons from the dopant levels into the conduction band of STO, and the photocatalytic process is initiated. Recently, we have studied the adsorption of water on the pristine SrTiO$_3$(110)-(4 × 1) surface. This reconstruction is formed to compensate for the polarity of the STO(110) surface. The structure consists of six- and ten-membered rings of TiO$_2$ tetrahedra, sitting on a bulk-truncated STO(110) plane, in which titanium is octahedrally coordinated. We found that this surface is remarkably inert toward the interaction with water, providing a very good starting point for studying the effect of promoters.

The photocatalytic activity of the SrTiO$_3$:NiO system has already been demonstrated successfully by Townsend and co-workers. In their study, Townsend et al. showed that "NiO-STO is more likely a three-component Ni-STO-NiO catalyst, in which STO absorbs the light, Ni reduces protons, and NiO oxidizes water". The present study is intended to provide fundamental information on the SrTiO$_3$:NiO system. We have performed X-ray absorption near-edge structure (XANES), X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS), and scanning tunneling microscopy (STM) to determine the effects of adsorption of NiO onto the STO(110)-(4 × 1) surface. NiO was prepared by either (i) postoxidation of STO or (ii) reactive MBE growth of metallic Ni in a molecular oxygen background.
reveals that the nanometer-sized NiO patches that develop on STO(110)-(4 × 1) distort the local surface structure independently of the preparation method. Consistently, XANES indicates a distortion/transformation of the surface TiO₂ tetrahedra upon NiO growth. Band bending is observed in both XPS and UPS, which increases with the amount of NiO. The onset of the VBM is effectively shifted upward, while minimal changes are observed on the CBM, as seen in the XANES results. Combining XPS, UPS, and low-energy ion scattering spectroscopy (LEIS), a clear signature of dissociative adsorption of water is found.

**MATERIALS AND METHODS**

Nb-doped (0.5 wt %) SrTiO₃ single crystals with polished (110) surface were purchased from MaTeK (Germany) and CrysTec (Germany). The STO(110)-(4 × 1) surface was prepared by cycles of sputtering (Ar⁺, 1 keV, 5 μA, 10 min) and annealing (900 °C, 3 × 10⁻⁶ mbar O₂, 1 h). The samples were heated either by passing alternating current (7.6 V, 1.75 A) through the samples or by bombarding them with electrons from the back (900 V, 15 mA). Sample temperatures were measured with an infrared pyrometer (emissivity of 0.8). The STO(110) surface exhibits a series of well-defined reconstructions, which can be tuned by the Sr/Ti stoichiometry in the near-surface region.12 For the present investigation the surface structure was adjusted to yield the 4 × 1 reconstruction, as checked by low-energy electron diffraction (LEED). Nickel metal (purity of 99.999%) was deposited onto the surface from an electron beam evaporator (Omicron EFM3), with a typical growth rate of 0.1 Å/min, as measured in UHV via a home-built analyzer) were acquired with a takeoff angle for the photoelectrons of approximately 55°.

**RESULTS**

Figure 1a shows photoemission spectra (raw data) of the valence band region of differently treated SrTiO₃(110)-(4 × 1) surfaces. The inset shows a zoom into the gap region with the spectra aligned at the O 2p peak at E₀ ≈ 22 eV (not shown). VBM were determined from the intersection of the horizontal (zero counts) line with a straight segment tangent to the leading edge of the UPS spectra, as represented in the inset of Figure 1a. For the clean surface (black curve), the onset of the valence band is located at approximately 3.2 eV below the Fermi level, in nice agreement with the n-type doping of the STO crystals and a reported band gap of 3.2 eV,14 i.e., a flat-band situation. The gap-region of the pristine surface does not show any detectable density of states, meaning that no in-gap states are introduced by the Nb dopants in the STO single crystal.

Evaporation of Ni (red curve) shifts all spectral features to lower binding energies (by 0.22 ± 0.15 eV) and an in-gap state is formed. The adsorption of single Ni adatoms at the SrTiO₃(110)-(4 × 1) surface has been studied recently,15 showing that isolated Ni adatoms are formed up to a coverage of 0.05 Å [see Figure 2b].

Upon postoxidizing the Ni adatoms, the valence band shifts to even lower binding energies by 0.38 ± 0.15 eV compared to the pristine surface, and the in-gap state is shifted downward, forming a shoulder of the valence band. In the case of 0.1 Å Ni postoxidized, the onset of the valence band is shifted to lower binding energies by around 1.5 eV [inset of Figure 1a]. The upward bending of the energy bands as a result of NiO adsorption is consistent with the higher work function of NiO compared to the pristine STO surface (ΩSTO(110)-(4×1) ≈ 4.9 eV, ΦNiO = 6.2–6.7 eV)16 and the measured increase of the workfunction of the NiO-loaded surface (ΩSTO(110)-NiO ≈ 5.3 eV).

Figure 1b shows the Ni 2p core-level spectra measured on deposited 0.1 Å Ni (red) and after postoxidizing the sample (blue). The as-deposited Ni exhibits the typical metallic Ni 2p
core-level features with a binding energy of the \( j = 3/2 \) component of 853.6 \( \pm \) 0.3 eV and a 17.1 eV spin–orbit-split (SOS) 2p_{3/2} peak (compared to 2p_{3/2} photoemission from pure metallic Ni at \( E_B = 852.7 \) eV with a SOS of 17.3 eV).\(^{17}\) Upon postoxidizing the nickel, the Ni 2p core-level features change to the typical NiO line shape, with a binding energy of the \( j = 3/2 \) component of 855.9 \( \pm \) 0.3 eV and a SOS of 17.6 eV (compared to literature values of \( 853.8 \) eV and a 17.1 eV spin–orbit-split \( E_B = 853.8 \) eV of 2p_{3/2} and SOS = 17.5 eV for bulk NiO).\(^{17}\)

The O 1s core-level [Figure 1c] shows only a very weak change. The presence of Ni adatoms causes the main O 1s spectral feature to be damped and a small shoulder at higher binding energy is formed, as seen in the Ti 2p core-level spectra in Figure 1d. This is mostly evident wherever NiO patches extend up to the STO substrate [orange solid lines in Figure 2f]. One type of defect appears as periodic, bright dots centered within the \( (4 \times 1) \) rows [a few marked by green dots in Figure 2a] and another type is a cross-shaped vacancy of defect appears as periodic, bright dots centered within the \( (4 \times 1) \) structure. Finally, localized depressions [see Figure 2a] are stabilized when submonolayer Ni adatoms coalesce into irregularly shaped patches [highlighted by the dashed blue line in Figure 2c], extending over several adjacent \( (4 \times 1) \) lines, and not showing any apparent preferential adsorption site. No clear ordering of atomic-scale features could be observed on such patches, likely indicating the formation of a locally defective NiO structure. Similar morphological and structural features are observed when growth is carried out by reactively depositing Ni in \( O_2 \) atmosphere [Figure 2d,e], and no significant improvement of the measurable atomic-scale structure is obtained upon increasing the deposited Ni amount [cf. Figure 2e]. The area of NiO patches progressively extends with increasing the deposited amount, and 0.3 Å NiO (not shown) nearly fully cover the STO surface, with only little \( (4 \times 1) \) structure visible in STM. LEED images acquired on the samples at different NiO coverages (not shown) do not exhibit any additional features in the diffraction pattern, but an overall increase of the inelastic background upon increasing the deposited material.

It is worth pointing out that a local distortion of the \( (4 \times 1) \) rows is visible in STM in close proximity of the NiO patches. This is mostly evident wherever NiO patches extend up to the dark trenches separating adjacent dotted rows, as indicated by the white arrows in Figure 2c,d. In such regions the dark trenches appear wider in the in-plane direction, and a deeper corrugation (by 10–20 pm) is measured in STM.

Figure 2f shows the sample surface with 0.1 Å NiO postoxidized at 600 °C. The NiO patches coalesce into rectangular islands, and several defect structures are introduced in the STO substrate [orange solid lines in Figure 2f]. One type of defect appears as periodic, bright dots centered within the \( (4 \times 1) \) structure. Another type of defect is a cross-shaped vacancy centered on one of the two rows of periodic dots, which build up the \( (4 \times 1) \) structure. Finally, localized depressions occasionally appear next to NiO patches and possibly correspond to missing units of the surface structure. It should be mentioned that despite the relatively high temperature of 600 °C, only a small decrease (\(<6\%\)) of the Ni 2p XPS intensity.
L2,3 absorption edge for different symmetry in an octahedral (Oh) or tetrahedral (Td) crystal. Following by two overlapping peaks at 459 eV (Ti 2p3/2 → Ti 3d Oh-eg) and 460 eV (Ti 2p3/2 → Ti 3d Td-e) and two broad overlapping features at 463 and 465 eV (Ti 2p1/2 → Ti 3d Oh-t2g and Ti 2p1/2 → Ti 3d Oh-t2g). Note the small shifts of the Ti L2,3 peak at 458 eV for different treatments of the surface. These cannot be ascribed to band bending, which is caused by a local change in electrostatic potential and should therefore affect all core levels and conduction band states equally. The shifts are therefore related to changes in the conduction band, i.e., in the Ti 3d levels. Overall, however, these shifts are below 0.2 eV. This indicates that the CBM is only minimally altered upon adsorption of NiO, compared to the change in the VBM [see inset of Figure 1a].

A strong decrease of the tetrahedral signature after adsorption of Ni and NiO is visible in Figure 3a. This indicates that either the tetrahedral information is damped by the adsorbrates or that the latter distort the TiO4 tetrahedra. The latter possibility is consistent with the distortion, and disruption of the surface structure, which was visible in STM after preparing a NiO-loaded surface at 300 °C [white arrows in Figure 2c,d] and 600 °C [Figure 2f], respectively. In general, Ti L2,3 XANES spectra acquired in SEY mode (not shown) show the same absorption peaks as AEY with the relative peak ratios dominated by the octahedral coordination of Ti in bulk STO. Figure 3b shows the XANES spectrum of the O K edge. The spectrum appears similar for all surface treatments and acquisition modes (AEY and SEY), showing only minimal variations in the relative intensities of the main features. Because of the low signal, related to the small amounts of Ni deposited, the Ni L2,3 XANES spectrum [Figure 3c] was acquired in secondary electron yield mode (see Materials and Methods section). Nevertheless, Ni atoms reside exclusively in the topmost surface layers. Therefore, the use of SEY mode is not limiting the surface sensitivity of the measurement. The photon energy at which adsorption at the L3 edge occurs (approximately 853 eV) is consistent with previous reports for both metallic Ni and NiO samples.20 In the case of postoxidized samples the main features of the characteristic line shape of NiO are observed. Namely, the intensity of the L2,3 white lines with respect to the background is increased due to the oxidation of metallic Ni, resulting in an increased number of d holes for oxidized Ni species.20

**H2O Interaction with NiO-Modified STO(110)-(4 × 1).** Here we studied the interaction of H2O with the NiO-loaded SrTiO3(110)-(4 × 1) surface by means of UPS/XPS and LEIS. The valence states of the adsorbed molecule allow distinguishing whether water is adsorbed molecularly or dissociatively. Molecularly adsorbed H2O is characterized by its 1b1, 3a1, and 1b2 valence orbitals, with typical binding energies of 7, 10, and 14 eV, respectively.21 On the other hand, OH species are characterized by their 1σ (∼6 eV) and 3σ (∼11 eV) valence orbitals.22
Figure 4 shows valence band and O 1s core level photoemission spectra before (blue) and after (green) dosing 50 langmuirs of H2O. An increased density of states is found in regions commonly assigned to adsorbed OH, i.e., the OH 3σ state at 11 eV binding energy [see inset of Figure 4a, in which the spectra are aligned to the O 2s peak at E_B ≈ 22 eV to highlight differences], and the high binding-energy shoulder of the O 1s core-level [inset of Figure 4b, again with aligned O 1s peak energies]. After dosing 50 langmuirs of H2O, the band bending decreased by 0.12 ± 0.15 eV.

A different approach for detecting adsorbed water is low-energy He⁺ ion scattering (LEIS). LEIS is considered one of the most surface sensitive spectroscopic techniques with the ability of resolving small mass differences by choosing a suitable primary ion mass. Figure 5 shows ion scattering spectra of differently treated SrTiO3(110)-(4 × 1) surfaces. The spectrum of the pristine (4 × 1) surface (black curve) shows peaks related to He⁺ ions scattered at 16O (∼400 eV), Ti (∼710 eV), and Sr (∼795 eV) atoms. It should be mentioned that upon impingement of 1000 eV He⁺ ions a progressive degradation of the surface is observed, most likely due to intermixing of the first few surface layers. In particular, an inversion of the apparent Ti to Sr ratio is visible already after 15 scans (each scan takes about 1 min; the ion currents ranged from 15 to 23 nA, which translates into a total ion fluence of (1.1−1.7) × 10¹⁴ ions/cm² for each spectrum). In order to limit beam damage as much as possible while still retaining good statistics, we used only the sum of the first four scans for each LEIS spectrum in Figure 5. To investigate the adsorption of water on the NiO-loaded SrTiO3(110)-(4 × 1) surface, we performed LEIS after dosing up to 100 langmuirs of H2¹⁸O. Dosing up to 100 langmuirs of H2¹⁸O onto the pristine surface does not introduce any further features in the LEIS spectrum, consistent with the inert nature of this surface. We successively deposited increasing amounts of NiO onto the surface and subsequently dosed up to 100 langmuirs of H2¹⁸O, and each spectrum in Figure 5 corresponds to a freshly prepared sample. Nickel introduces a peak in LEIS spectra at a kinetic energy of approximately 770 eV. In addition, a peak at a kinetic energy of 450 eV is evolving. This peak is assigned to He⁺ ions scattered at 18O belonging to adsorbed water. The spectra acquired on samples with different amounts of NiO clearly show that water binds to the NiO-loaded surface, in agreement with the photoemission data in Figure 4. The existence of a larger ¹⁸O peak in the case of 0.2 Å NiO compared to the case of 0.3 Å NiO (close to full coverage) possibly indicates that either H2O adsorption or dissociation takes place at the NiO/SrTiO3 boundary.
DISCUSSION

The combination of various spectroscopic techniques and direct-space imaging provides new insights into the NiO/STO system. UPS and XANES results indicate that the deposition of NiO onto the STO(110)-(4 × 1) surface effectively reduces the band gap of the system from 3.2 to approximately 1.7 eV. This change is visible in the altered onset of the valence band when NiO is present at the surface as well as in the relatively stable positions (within 0.2 eV) of Ti L_{2,3} XANES peaks (probing the CBM) with and without NiO. Assuming that this VBM shoulder is hybridized with the O 2p valence band, these results suggest a considerable reduction of the band gap of the system NiO/STO, allowing harvesting of visible light (1.7 eV corresponding to 729 nm, i.e., near-infrared). Although the present data do not provide information on hybridization of these states, it is known from experiments with N-doped TiO_2 that such VBM shoulders can considerably enhance the visible-light response in photocatalysis experiments. In addition, a pronounced (up to 0.8 eV) upward band bending is observed for the NiO-loaded surface. Photogenerated excitons can effectively dissociate in the electrostatic potential gradient related to the band bending, which drives electrons toward the NiO-covered surfaces. UPS and LEIS experiments confirm that the NiO activates the surface toward dissociative adsorption of H_2O, possibly involving sites at the interface between NiO patches and the substrate.

CONCLUSIONS

We have studied the morphology and electronic structure of the NiO-modified SrTiO_3(110)-(4 × 1) surface. An in-gap state, formed by the deposition of metallic Ni onto this surface, is transformed into a valence band shoulder upon oxidation of the Ni into NiO. This effectively increases the VBM with the CBM being unchanged, as seen in XANES, and therefore decreases the band gap of the system. Band bending is observed, which increases with the amount of NiO deposited. Furthermore, XANES results indicate that surface TiO_4 tetrahedra get considerably distorted or disrupted upon bonding with NiO, as is also evident from STM images of NiO-covered surfaces. UPS and LEIS experiments confirm that the NiO activates the surface toward dissociative adsorption of H_2O, possibly involving sites at the interface between NiO patches and the substrate.

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Notes

The authors declare no competing financial interest.

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