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# Reaction of sulfur dioxide with Ni(100) and Ni(100)- $p(2 \times 2)$ -O

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#### Abstract

XPS, TPD, LEED and STM have been used to probe the interaction between sulfur dioxide and the Ni(100) and Ni(100)-p(2×2)-O surfaces. On Ni(100) at 300 K SO<sub>2</sub> disproportionates according to  $2SO_2 \rightarrow S(a) + SO_3(a) + O(a)$ . Sulfur and sulfite occupy sites in a p(2×2) arrangement, while oxygen adsorbs into c(2×2) domains amid Ni chains of  $(n\sqrt{2} \times 2\sqrt{2})R45^{\circ}/(2\sqrt{2} \times n\sqrt{2})R45^{\circ}$  (n = 7–12) periodicity that are presumed to be due to segregation of oxygen to the subsurface. On Ni(100)-p(2×2)-O at 300 K SO<sub>2</sub>(a) reacts with O(a) to form SO<sub>3</sub>(a). Sulfite adsorbs into p(2×2) islands encompassed by c(2×2)-O. TPD measurements with <sup>18</sup>O are suggestive of a monodentate sulfite binding configuration. © 2005 Published by Elsevier B.V.

Keywords: Scanning tunneling microscopy; Thermal desorption spectroscopy; Surface chemical reaction; Nickel; Sulfur; Oxygen; Sulfur dioxide; Single crystal surfaces

#### 1. Introduction

Sulfur dioxide  $(SO_2)$  is an environmental pollutant. It is a byproduct of the process used to generate electricity in coal-fired power plants [1]. SO<sub>2</sub> emissions can lead to adverse health and environmental effects. SO<sub>2</sub> is an irritant and a key component in the formation of sulfate aerosol particles [2], which act as cloud condensation nuclei in the troposphere. Investigations of the interaction between  $SO_2$  and various heterogeneous (metal and non-metal) surfaces will aid in the understanding of atmospheric phenomena, where an assessment of gas–surface interactions is required for accurate climate models.

Over the past twenty years the adsorption and reaction of  $SO_2(g)$  has been investigated on a number of single crystal metal surfaces with an array of surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS) [3,4], near-edge X-ray absorption fine structure spectroscopy (NEXAFS) [5], temperature-programmed desorption (TPD)

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[3,4,6], reflection absorption infrared spectroscopy (RAIRS) [7,8], high-resolution electron energy loss vibrational spectroscopy (HREELS) [9] and scanning tunneling microscopy (STM) [4,6,10,11]. Depending on the surface temperature, SO<sub>2</sub> adsorbs molecularly and dissociatively with the surfaces of Fe, Rh, W, Ni, Pd, Pt, Cu, and Zn to form SO<sub>x</sub> (x = 1, 2, 3, or 4), whereas adsorption on Ag is only molecular [12,13]. Oxygen adsorbed on the Ag(110) surface affects the oxidation of SO<sub>2</sub> to SO<sub>3</sub> (sulfite) and SO<sub>4</sub> (sulfate) [3,6].

Ohta et al. previously probed the reaction between SO<sub>2</sub>(g) and the Ni(100) and Ni(100)c(2×2)-O surfaces using NEXAFS [5]. Their results indicate that below 300 K SO<sub>2</sub> disproportionates on Ni(100) according to  $3SO_2(a) \rightarrow$ S(a) + 2SO<sub>3</sub>(a). At room temperature a fraction of the sulfite decomposes into SO<sub>2</sub>(g) and O(a), leaving the surface partially covered with sulfur, sulfite and atomic oxygen, i.e.  $2SO_2(a) \rightarrow S(a) +$ SO<sub>3</sub>(a) + O(a). On Ni(100)-c(2×2)-O at 300 K, SO<sub>2</sub>(a) reacts with oxygen to give SO<sub>3</sub> and SO<sub>4</sub> in approximately a 3:1 ratio.

In this paper we report XPS, TPD, LEED and STM studies of the reaction between  $SO_2(g)$  with clean and the oxygen-covered Ni(100)-p(2 × 2)-O. STM has been used to elucidate the interaction between  $SO_2$  and the Ni(100) and Ni(100)-p(2 × 2)-O surfaces. Binding configurations and the distribution of structures produced by the reaction products are discussed.

### 2. Experimental

Experiments were performed in an ultrahigh vacuum chamber equipped with STM, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and a quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD) measurements. The chamber was equipped with a sputter ion gun and stainless steel gas dosers. The system exhibited a base pressure of  $4 \times 10^{-10}$  Torr which rose to approximately  $7 \times 10^{-10}$  Torr during experiments.

The homemade "Johnnie Walker" type STM (RHK STM 100) employed in this study utilized a Pt/Ir tip, which was conditioned via induced field

evaporation onto a gold foil ( $\sim 4 \mu A$ , 15 min) prior to imaging. Unless otherwise stated, all scans were taken in constant height mode.

The Ni(100) crystal used was aligned to within 0.5° of the (110) plane using Laue backscattering and was mechanically polished down to 0.3  $\mu$ m alumina paste. The crystal was cleaned in vacuum by three Ar ion sputter (2  $\mu$ A, 500 eV, 15 min at 600 K) and anneal (800 K, 10 min) cycles, with the first anneal done in an oxygen atmosphere (1 × 10<sup>-7</sup> Torr) to cleanse the surface of impurities observed in STM images. Hydrogen treatment at 600 K followed by another sputter/anneal cycle removed residual oxygen. A sharp p(1 × 1) LEED pattern and AES-spectra showed a well-order surface devoid of sulfur, carbon and oxygen impurities.

The crystal could be cooled to 120 K with liquid nitrogen and heated to 1100 K by electron bombardment to the back of the crystal. The temperature was monitored by a Chromel–Alumel thermocouple spot-welded to the back of the crystal. The STM ramp housing the crystal and the STM scan head were allowed to thermally equilibrate for 30 min prior to STM measurements.

Separate XPS measurements were made in a second UHV system consisting of interconnected preparation and analysis chambers. The analysis chamber exhibited a base pressure of  $2 \times 10^{-10}$ Torr and was equipped with LEED optics, a Perkin-Elmer 04-548 dual anode X-ray source, an EA-10-plus hemispherical energy analyzer from SPECS and a UTI 100c QMS used for TPD measurements. The ionizer of the QMS was enclosed in a glass cap with a small hole facing the crystal surface. A computer connected to the OMS was used to record TPD spectra. The preparation chamber reached a base pressure of  $8 \times 10^{-10}$  Torr and was equipped with a sputter ion gun and stainless steel gas dosers. The two chambers were isolated from each other during experiments.

In this system the crystal was supported by two W wires spot-welded to the back. The temperature was monitored by a Chromel–Alumel thermocouple spot welded to the back edge of the crystal. The surface was cleaned by three sputter-anneal cycles, with the first anneal (800 K) done in an  $O_2(g)$ 

atmosphere  $(10^{-7} \text{ Torr})$ . Hydrogen treatment 600 K followed by a final sputter/anneal cycle removed residual oxygen. Surface cleanliness and composition were probed with XPS using nonmonochromatic MgK $\alpha$  X-rays. The photoelectrons were collected normal to the surface by the energy analyzer utilizing a 25 eV pass energy. Binding energies were calibrated with respect to the Au 4f peak (84.00 eV) and referenced to the Ni(2p<sub>3/2</sub>) peak.

The purity of the SO<sub>2</sub>(g) (Praxair, 99.98%), O<sub>2</sub>(g) (<sup>16</sup>O<sub>2</sub>, Praxair, 99.999%), <sup>18</sup>O<sub>2</sub>(g) (MSD Isotopes, 97.7%) and D<sub>2</sub>S(g) (Cambridge Isotope Laboratories, 98%) were monitored with the QMS during dosing. Unless otherwise stated, all gases were dosed from the background. Exposures are reported in units of Langmuir (1 L =  $10^{-6}$  Torr s). Typical SO<sub>2</sub>(g) dosing pressures were on the order 1 × 10<sup>-8</sup> Torr.

#### 3. Results and discussion

#### 3.1. X-ray photoelectron spectroscopy

XPS spectra following adsorption and reaction of SO<sub>2</sub> on Ni(100) and Ni(100)-p(2 × 2)-O are shown in Fig. 1 and summarized in Table 1. All S(2p) features are doublets, consisting of  $2p_{3/2}$ and  $2p_{1/2}$  components (approximately 1 eV apart), with the former at lower binding energy [14]. The chemical state of the surfaces elucidated by XPS is in good agreement with previous NEXAFS results (see Section 1).

Adsorption and reaction of SO<sub>2</sub> on Ni(100)p(2×2)-O produced a sulfite-covered surface (Fig. 1). The clean surface (Fig. 1a) was initially exposed to O<sub>2</sub>(g) to generate the p(2×2)-O overlayer (Fig. 1b, see STM section) and subsequently exposed to SO<sub>2</sub>(g). The XPS spectrum of this surface (Fig. 1c) shows a S(2p<sub>3/2</sub>) peak at 165.8 eV, which is assigned to SO<sub>x</sub>. Deconvolution of the O(1s) features reveals peaks at 529.0 and 530.2 eV, which are attributable to atomic oxygen and SO<sub>x</sub>, respectively [4]. The SO<sub>x</sub> O(1s) and S(2p) peak area ratio, following correction for the S(2p) and O(1s) photoionization cross-sections (1.64) [15], is 2.98:1, suggesting SO<sub>x</sub> is SO<sub>3</sub>. This result



Fig. 1. XP-spectra for SO<sub>2</sub>(g) on Ni(100)-p(2  $\times$  2)-O and  $SO_2(g)$  on Ni(100). All S(2p) curves are doublets consisting of  $S(2p_{3/2})$  and  $S(2p_{1/2})$  components approximately 1 eV apart, with the former at lower binding energy (eV). All spectra were obtained at 300 K. SO<sub>2</sub> on Ni(100)-p(2  $\times$  2)-O: The surface at 300 K following our cleaning procedure (a) was exposed to oxygen to generate the  $p(2 \times 2)$ -O overlayer (b) and subsequently exposed to SO<sub>2</sub>(g)  $(1 \times 10^{-8}, 10 \text{ min})$  to produce a surface covered by sulfite and oxygen (c). Heating the sulfite and oxygen-covered surface to 600 K desorbed SO2, leaving atomic oxygen on the surface (d). SO<sub>2</sub> on Ni(100): The surface at 300 K following our cleaning procedure (e) was exposed to  $SO_2(g)$  (1 × 10<sup>-8</sup> Torr, 10 min) to generate the sulfur, sulfite and oxygen-covered surface (f), which was subsequently annealed to 600 K to desorb SO<sub>2</sub>, leaving atomic sulfur and oxygen on the surface. Deconvolutions of O(1s) features are shown in (c) and (f).

is consistent with the binding energy of  $SO_3$  observed on other surfaces (Table 1). Thus, the reaction between  $SO_2(a)$  and O(a) gives

$$SO_2(a) + O(a) \rightarrow SO_3(a)$$
 (6)

From the O(1s) peak areas and the initial coverage of oxygen in the  $p(2 \times 2)$ -O covered surface (0.25 ML), the O(a) and SO<sub>3</sub>(a) coverages after reaction are 0.15 ML and 0.10 ML, respectively; approximately 40% of the O(a) reacted with SO<sub>2</sub>

Table 1

Summary of XPS S(2p) binding energies observed in this work (last row) and other relevant investigations

	S	$SO_2$	SO <sub>3</sub>	$SO_4$
Cu(110) [4]	161.4	165.3	166.1	_
Cu(110) [23]	161.3			
Cu <sub>2</sub> S [24]	161.3	_	-	_
CuSO <sub>4</sub> [25]	_	_	-	169.5
Ag(110) [3]	-	165.4	166.1	167.9
Ag(111) [26]	161.8	_	-	168.4
Ag <sub>2</sub> S [27]	161.6	_	-	_
Ni [24]	-	165.8	-	-
Ni(100) (this work)	161.5	_	165.8	-

All S(2p) XPS peaks are doublets consisting of  $2p_{3/2}$  and  $2p_{1/2}$  components. The table entries correspond to the  $2p_{3/2}$  component.

to form SO<sub>3</sub>. Heating the sulfite-covered surface to 600 K desorbed SO<sub>2</sub>(g), leaving approximately 0.25 ML O(a) on the surface (Fig. 1d).

Following adsorption and reaction of SO<sub>2</sub> on Ni(100), XPS features attributable to sulfite, atomic sulfur and atomic oxygen were observed. The surface following cleaning was devoid of sulfur and oxygen-containing impurities (Fig. 1e). XP-spectra following exposure of this surface to  $SO_2(g)$  showed S(2p) peaks at 161.3 eV and 165.9 eV (Fig. 1f), which are ascribed to S(a) and  $SO_x(a)$ , respectively. The O(1s) spectrum (after deconvolution) consisted of peaks at 528.9 and 530.6 eV, which are attributed to photoemission from O(a) and  $SO_x(a)$ , respectively. Following correction for the sulfur and oxygen photoionization cross-sections, the  $SO_x O(1s)$  and S(2p) peak area ratio is approximately 2.99:1, which suggests  $SO_x$ is SO<sub>3</sub>. The S(a) and SO<sub>3</sub>(a) peak area ratio is 0.99:1; The S(a) and O(a) peak area ratio, following correction for S(2p) and O(1s) photoionization cross-sections, is 1.16:1, or nearly one-to-one. The reaction between SO<sub>2</sub> and the clean Ni(100) surface can be written generally as

$$aSO_2(a) \rightarrow bS(a) + cSO_3(a) + dSO_4(a) + eO(a)$$
(1)

Sulfur and oxygen mass balances give

$$a = b + c + d \tag{2}$$

$$2a = 3c + 4d + e \tag{3}$$

From the 1:1 sulfur and sulfite peak area ratio, b = c. Since no S(2p) features were observed within the range 168–170 eV, where SO<sub>4</sub>(a) has been observed on other surfaces [3], 'd' is set to zero, reducing Eq. (1) to

$$2bSO_2(a) \rightarrow bS(a) + bSO_3(a) + bO(a) \tag{4}$$

Eq. (4) has infinitely many solutions, with the simplest non-trivial solution being the one for which b = 1, namely

$$2SO_2(a) \rightarrow S(a) + SO_3(a) + O(a)$$
(5)

The stoichiometry of Eq. (5) is in agreement with the NEXAFS investigation. Heating the surface to 600 K desorbed  $SO_2(g)$  and gave a surface covered by S(a) and O(a). Using the  $p(2 \times 2)$ -S structure at 0.23 ML for reference and correcting for the sulfur and oxygen photoionization cross-sections (1.64) [16], the S(a),  $SO_3(a)$  and O(a) coverages are determined to be 0.20 ML, 0.20 ML and 0.18 ML, respectively.

#### 3.2. Temperature-programmed desorption

TPD measurements of the sulfite-covered surface shows  $SO_2(g)$  evolving in separate states at 380 K and 450 K (Fig. 2a).  $SO_2(g)$  was introduced to the clean surface at 300 K through a needle doser directed at the surface with the opening approximately one inch from the crystal. The surface temperature was ramped at approximately 1 K/s and various gases were detected with the QMS directly in front of the crystal surface. With heating, only  $SO_2(g)$  evolved from the surface.

TPD measurements following SO<sub>2</sub> adsorption onto Ni(100)-p(2 × 2)-O at 300 K showed an SO<sub>2</sub>(g) desorption peak at 350 K and a shoulder at 440 K (Fig. 2b). The p(2 × 2)-O surface was initially prepared via O<sub>2</sub>(g) exposure  $(1 \times 10^{-8} \text{ Torr}, 10 \text{ min})$  at 300 K followed by annealing to 500 K. The surface was then cooled to 300 K and SO<sub>2</sub>(g) was dosed  $(1 \times 10^{-8} \text{ Torr}, 10 \text{ min})$  to generate the sulfite-covered surface. TPD measurements showed only SO<sub>2</sub>(g) evolving from the surface.

Experiments with isotopically labeled oxygen  $(^{18}O_2)$  suggest that the sulfite species has monodentate coordination to the surface (Fig. 2c). The sulfite-covered surface was prepared by exposing



Fig. 2. TPD spectra for (a)  $SO_2(g)$  on Ni(100), (b)  $SO_2(g)$  on Ni(100)-p(2×2)-O and (c)  $SO_2(g)$  on Ni(100)-p(2×2)-<sup>18</sup>O. Only the mass-to-charge (m/z) = 64 signal is shown in (a) and (b). The average heating rate was 1 K/s. The vertical axis corresponds to the QMS signal for the species with the indicated mass-to-charge (m/z) ratios.

Ni(100)-p(2 × 2)-<sup>18</sup>O to SO<sub>2</sub>(g) at 300 K. TPD measurements were subsequently conducted to assess the distribution of evolving gases. Of the possible isotopes for sulfur dioxide which could evolve upon heating, only mass-to-charge ratios of 64 (SO<sub>2</sub>) and 66 (SO<sup>18</sup>O) were detected; 68 (S<sup>18</sup>O<sup>18</sup>O) was not detected. Previous investigators have suggested that sulfite coordinates to Ag(110) through either one (monodentate) or two oxygen atoms (bidentate) [9] and to Cu(100) or Cu(111) by three oxygen atoms [17,18]. Assuming the

O-metal bonds to be equivalent and to be intra convertible among the other S-O bonds, the latter two species would yield SOO to SO<sup>18</sup>O peak area ratios of 1:2, respectively. With the same assumptions, the monodentate sulfite formed by the addition of SO<sub>2</sub>(g) to the surface containing preadsorbed <sup>18</sup>O would yield an infinite ratio of SOO to SO<sup>18</sup>O, as it is based solely on the probability of breaking and making in convertible O-Ni bonds. The observed ratio of the peak areas of approximately ten to one is indicative of the dominance of a monodentate sulfite that decomposes primarily by cleavage of the S-O bond formed between SO<sub>2</sub> and preadsorbed oxygen.

# 3.3. Scanning tunneling microscopy

# 3.3.1. $SO_2(g)$ on Ni(100)- $p(2 \times 2)$ -O

The  $p(2 \times 2)$ -O overlayer was prepared by exposing the clean surface at 300 K to  $O_2(g)$   $(1 \times 10^{-8} \text{ Torr}, 10 \text{ min})$  followed by annealing to 500 K. The surface prepared in this manner



Fig. 3. STM micrographs of a  $p(2 \times 2)$ -O covered surface. (a) Large scale scan showing a large terrace and bunched steps; tunneling conditions: -97.5 mV, 0.97 nA. (b) A zoom-in on a portion of the surface in (a), showing the  $p(2 \times 2)$ -O structure (box); tunneling conditions: -94.3 mV, 1.33 nA. (c) Two-dimensional model of the  $p(2 \times 2)$ -O structure. Arrows 1–3 represent features described in the text (see Section 3.3.1).

exhibited a sharp  $p(2 \times 2)$  LEED pattern. STM measurements showed the surface to consist large terraces and bunched steps (Fig. 3a). A zoom-in on a terrace location shows the  $p(2 \times 2)$ -O structure (Fig. 3b). In this structure, depressions (arrow 1) are interpreted as oxygen local density of states (LDOS), following the work of Kopatzki and Behm [19], less intense depressions (arrow 2) are interpreted as hollow sites centered in-between the  $p(2 \times 2)$ -O structure, and areas between oxygen

atoms (arrow 3) are ascribed to hollow sites between oxygen atoms. The two-dimensional model (Fig. 3c) accompanying the STM scan depicts these features.

Exposure of the oxygen-covered surface at 300 K to 6 L SO<sub>2</sub>(g) produced sulfite islands amid  $c(2 \times 2)$ -O (Fig. 4a). The islands are interpreted as domains of SO<sub>3</sub>(a) because (1) they are the dominant structure, (2) XPS showed sulfite on the surface and (3) they are more corrugated than



Fig. 4. STM scans following exposure of the Ni(100)-p( $2 \times 2$ )-O covered surface at 300 K to SO<sub>2</sub>(g). (a) Wide-area scan, showing sulfite islands on top of the oxygen overlayer; tunneling conditions: -99.0 mV, 0.77 nA (constant current). (b) A scan of the surface in (a) at higher magnification; tunneling conditions: -9.58 mV, 1.68 nA. (c) A magnification of an SO<sub>3</sub> island, showing p( $2 \times 2$ )-SO<sub>3</sub> structures, scattered c( $2 \times 2$ )-SO<sub>3</sub> arrangements, domain boundaries (arrow d) and vacancies (v); tunneling conditions: -9.81 mV, 1.63 nA. Sulfite on opposite sides of the domain boundary (arrow d) are offset by one lattice unit in the direction of the [0 1] vector (broken lines 1 and 2). (d) A magnification of the c( $2 \times 2$ )-O adjoining the sulfite island in (c); tunneling conditions: -9.77 mV, 1.40 nA. Scattered oxide nuclei (arrow p) were observed on this surface.

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domains of oxygen. Similar results were observed for sulfite on Cu(110)-p( $2 \times 1$ )-O [4]. A zoom-in on a portion of the surface in Fig. 4a (box) resolves the  $SO_3(a)$  island and the adjoining oxide structure (Fig. 4b). Magnification of the  $SO_3$  (a) island reveals a  $p(2 \times 2)$  structure, scattered  $c(2 \times 2)$ arrangements, vacancies (v) and domain boundaries (d) (Fig. 4c). The sulfite islands are encompassed by areas of the uncovered  $c(2 \times 2)$ -O and scattered protrusions (Fig. 4d arrow p), which are due to oxide nucleation [20,21]. Evidently, sulfite adsorption is accompanied by compression of the p(2  $\times$  2)-O into the c(2  $\times$  2). The c(2  $\times$  2)-O did not react significantly with  $SO_2(g)$  at the exposures employed in this study, which is similar to what was observed for  $SO_2(g)$  exposure to a saturated  $Cu(110)s-p(2 \times 1)-O$  surface [4]. In that study, the saturated  $p(2 \times 1)$ -O overlayer at 0.5 ML coverage was unreactive toward  $SO_2(g)$ exposure.

A two-dimensional model depicting the oxygen and sulfite structures imaged by STM is shown in Fig. 5. The monodentate sulfite binding configuration is consistent with TPD measurements (see above).



Fig. 5. Two-dimensional model depicting the structures observed following exposure of the Ni(100)-p(2  $\times$  2)-O surface at 300 K to SO<sub>2</sub>(g).

3.3.2.  $SO_2(g)$  on Ni(100)

The clean Ni(100) surface at 300 K was exposed to SO<sub>2</sub>(g)  $(1 \times 10^{-8} \text{ Torr}, 10 \text{ min})$ . As noted above, the surface consisted of a mixture of sulfur, sulfite and oxygen. STM measurements were made on terraces several thousand angstroms in width (Fig. 6a) and at step edges (Fig. 6b). An enlargement of a scan taken at a terrace location (Fig. 6a, inset) reveals two electronically distinct species. Taken as protrusions, the two species occupy equivalent sites. The coverage-weighted ratio of the two protrusions was approximately 1:1 (5% error). These observations suggest that the protrusions are due to sulfur and sulfite. We exclude oxygen from the area in Fig. 6a on the basis that O(a)appears as depressions on the surface amid SO<sub>3</sub> protrusions (Fig. 4) and the structures imaged in Fig. 6b are attributable to oxygen (see below). The more corrugated protrusions are interpreted as sulfite, an assignment consistent with a previous study on Cu(110) in which the electronic corrugation of SO<sub>3</sub> was greater than that of adjoining sulfur atoms [4]. In the present investigation, sulfite adsorbed into scattered  $p(2 \times 2)$  and  $c(2 \times 2)$  structures. The surface structure consisted of defects in which  $SO_3(a)$  was one lattice unit away (along [001] and [010]) from adjoining sulfur atoms (arrow d). Extrapolation from the binding site of the sulfur adatoms-which occupy 4-fold hollow sites-the sulfite occupy 4-fold hollow sites, an assignment consistent with binding site of  $SO_3(a)$ on the oxygen-covered surface (Fig. 4).

STM measurements of the surface at 300 K at an area in the vicinity of that imaged in Fig. 6a reveal chains oriented in the direction of the [001] vector (Fig. 6b). The chains, which are of step height (Fig. 6b, inset), were arranged into structures with  $(n\sqrt{2} \times 2\sqrt{2})R45^\circ$  or  $(2\sqrt{2} \times n\sqrt{2})R45^\circ$ (n = 7-12) periodicity. A scan at higher magnification (Fig. 6c) reveals  $c(2 \times 2)$ -O moieties inbetween the chains. The chains consisted of depressions (arrow d) and protrusions (arrow p), which are two lattice units apart in the direction of the [001] vector. The protrusions are of step height (Fig. 6b, inset), which suggests they are comprised of Ni atoms. Similar structures were observed following oxygen adsorption on Cu(100), which produced a Cu-O missing row structure



Fig. 6. STM micrographs of a Ni(100) surface following exposure to SO<sub>2</sub>(g) at 300 K. (a) Scan at a terrace location, showing (inset)  $p(2 \times 2)$ -S, scattered  $p(2 \times 2)$  and  $c(2 \times 2)$  SO<sub>3</sub>(a) domains, and SO<sub>3</sub>(a) situated in-between two sulfur atoms (arrow d); tunneling conditions: -198 mV, 0.97 nA; inset, -198 mV, 1.22 nA. (b) Scan of the surface next to a step edge, showing chains oriented in the direction of the [001] vector with protrusions of step height (line scan); tunneling conditions: 0.69 V, 2.21 nA. (c) An enlargement of the area indicated in (b), showing chains with  $(7\sqrt{2} \times 2\sqrt{2})R45^{\circ}$  periodicity consisting of depressions (arrow d) and protrusions (arrow p); tunneling conditions: 0.69 V, 2.33 nA.

with  $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$  Cu–O periodicity [22]. The formation of this structure was concomitant with the precipitation of Cu into islands of step height. On that surface, protrusions with  $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ periodicity were interpreted as Cu atoms. Effective medium theory calculations suggested that the oxygen atoms were directly situated on top of Cu atoms below. The Cu(100) work suggests that the  $(n\sqrt{2} \times 2\sqrt{2})R45^{\circ}/(n\sqrt{2} \times 7\sqrt{2})R45^{\circ}$  (n = 7-12) chains are due to oxygen, which may be induced by sulfur adsorption. A two-dimensional model depicting the structures observed in the STM micrographs is shown in Fig. 7.

The lack of reactivity of the  $c(2 \times 2)$ -O toward sulfite formation is consistent with the reaction

between SO<sub>2</sub>(g) and the p( $2 \times 2$ )-O surface (see above). Evidently, domains of c( $2 \times 2$ )-O are energetically stable toward SO<sub>2</sub>(g) oxidation.

#### 4. Summary

Reaction of SO<sub>2</sub> with Ni(100) and Ni(100)p(2×2)-O has been investigated with STM, XPS and TPD and LEED. On Ni(100)-p(2×2)-O at 300 K SO<sub>2</sub> reacts according to SO<sub>2</sub>(a) + O(a)  $\rightarrow$ SO<sub>3</sub>(a). Sulfite adsorbs into islands of a p(2×2) structure while the remainder of the unreacted p(2×2)-O is compressed into a c(2×2) structure. The islands persist to 400 K, above which temper-



Fig. 7. Two-dimensional model depicting the structures observed following exposure of the Ni(100) surface at 300 K to  $SO_2(g)$  (Fig. 6). The depressions and protrusions in Fig. 6c (arrows d and p) have been indicated by gray circles.

ature the evolution of SO<sub>2</sub>(g) reverts the surface to its initially oxidized state. TPD measurements with <sup>18</sup>O are suggestive of a monodentate sulfite binding configuration. On Ni(100) at 300 K SO<sub>2</sub> disproportionates according to  $2\text{SO}_2 \rightarrow \text{S}(a) +$ SO<sub>3</sub>(a) + O(a). Sulfur and sulfite adsorb into scattered p(2 × 2) structures and oxygen adsorbs into a c(2 × 2) structure. Oxygen adsorption is concomitant with the formation of structure with  $(n\sqrt{2} \times 2\sqrt{2})R45^{\circ}/(2\sqrt{2} \times n\sqrt{2}) R45^{\circ}$  (n = 7-12) periodicity, which are interpreted as Ni chains induced by oxygen.

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