



XPS and STM studies of the oxidation of hydrogen chloride at Cu(100) surfaces



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ABSTRACT

The dissociative chemisorption of HCl on clean and oxidized Cu(100) surfaces has been investigated using x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). Whereas the dissociation of HCl at the clean surface is limited to the formation of a $(\sqrt{2} \times \sqrt{2})\text{-R}45^\circ \text{Cl(a)}$ monolayer, the presence of surface oxygen removes this barrier, leading to chlorine coverages up to twice that obtained at the clean surface. Additional features in the STM images that appear at these coverages are tentatively assigned to the nucleation of CuCl islands. The rate of reaction of the HCl was slightly higher on the oxidized surface but unaffected by the initial oxygen concentration or the availability of clean copper sites. Of the two distinct domains of adsorbed oxygen identified at room temperature on the Cu(100) surfaces, the $(\sqrt{2} \times \sqrt{2})\text{-R}45^\circ$ structure reacts slightly faster with HCl than the missing row $(\sqrt{2} \times 2\sqrt{2})\text{-R}45^\circ \text{O(a)}$ structure. The results address the first stages in the formation of a copper chloride and present an interesting comparison with the HCl/O(a) reaction at Cu(110) surfaces, where oxygen also increased the extent of HCl reactions. The results emphasize the importance of the exothermic reaction to form water in the HCl/O(a) reaction on copper.

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1. Introduction

Madix has made many seminal contributions to the area of surface science and to our understanding of the role of oxygen in reactions at surfaces in particular [1–6]. The ability of oxygen to act as a base to abstract hydrogen was recognized early on [7–10], and a huge number of reactions have been studied subsequently, ranging from amines and sulfides to alcohols, alkenes, and acids [9,10,5,11]. One factor influencing reaction kinetics and even reaction pathways has been shown to be the local atomic structure of oxygen at surfaces [12–14] and in 1996 Madix and Guo explored this issue with an STM study of ammonia oxidation at Cu(110) surfaces [15]. They showed that ammonia oxidation at the $\langle 100 \rangle$ ends of oxygen islands was at least 100 times faster than oxidation at the $\langle 110 \rangle$ sides, confirming earlier predictions based on Monte Carlo modeling of XPS data [13]. Extending this work, we have since demonstrated the influence of oxygen islands at surfaces on the pathways, kinetics, and products of a number of different reactions [16,17] but also the way in which reactants such as amines can change the local structure of the oxygen islands and thus influence the reaction rate [18–20]. A particular interest has been to explore the effect of intercepting oxygen in a transient state, i.e. before it forms the more

stable chemisorbed islands. We have demonstrated that this leads to a changed surface chemistry in many cases: mercaptan [21] and aniline [16], for example, form closer packed structures on Cu(110) during reaction with a mobile oxygen transient. Methanol is another example; when oxygen is allowed to form islands on copper surfaces, partial oxidation of methanol dominates, but under coadsorption conditions that minimize oxygen island growth, complete oxidation can be achieved [22,14,23].

Unlike the reactants discussed above, a recent study [24] has shown that HCl at Cu(110) surfaces is not sensitive to the nature of the oxygen state present; in the presence of both preadsorbed and coadsorbed oxygen, STM images reveal identical surface structures consisting of $\langle 100 \rangle$ orientated features that develop into “Cl-fingers” [24,25]. In contrast, the reaction of HCl at clean Cu(110) surfaces forms only a planar $c(2 \times 2)$ structure [24]. The “Cl-fingers” observed in the presence of oxygen have subsequently been reproduced by Andryushkin [26] in the absence of oxygen using $\text{Cl}_2(\text{g})$ and identified by comparing the STM images with DFT modeling as chlorine covered [210] facets. They have also been reported by Wandelt and co workers at Cu(110) surfaces in aqueous solutions of HCl [27,28]. This poses the question of how oxygen facilitates the formation of these facets. Is its role to disrupt the surface of the copper and thus accelerate the mass transport of copper to the reconstruction? Or does oxygen provide a pathway for the removal of hydrogen enabling an increased extent of HCl decomposition? A further question is whether the site blocking effect of high coverages of oxygen

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will influence HCl oxidation as it does with other molecules. To examine these questions, we extend our study of the role of local oxygen structure on the oxidation of HCl at copper surfaces with an investigation of the Cu(100)/O(a) system, considering the effects of oxygen coverage and adsorbate structure. Three separate oxygen coverages have been considered: $\theta_{\text{O}} = 0.75, 1, 1.6$. These were chosen because they represent easily reproducible surface states with distinct oxygen structures.

2. Background

XPS and Auger studies of the reaction of $\text{Cl}_2(\text{g})$ with copper films [29] have identified three different states: a “low coverage” chemisorbed state and “high” coverage CuCl and CuCl_2 states. The Cl(2p) binding energy for both the CuCl and CuCl_2 states was ~ 199 eV. The chemisorbed chloride layer is saturated at very low exposures to $\text{Cl}_2(\text{g})$ but Eltsov et al. observed that extensive exposure was necessary to generate a CuCl state [30,31]. They report a relatively low desorption temperature for the CuCl state (420–480 K) compared to that of the chemisorbed chlorine (770–900 K). More recently, Galeotti et al. and Nakakura et al. have also studied Cl_2 adsorption on Cu(100) and report the formation of the $c(2 \times 2)$ structure with some indication of crystallites assigned to islands of CuCl at higher exposures [32,33].

On Cu(110), high exposures to HCl can drive adsorption above the 0.5 monolayers expected from the $c(2 \times 2)$ structure [34], possibly indicating the existence of a higher coverage chemisorbed structure, but the reaction of HCl with Cu(100) surfaces appears to be limited to the formation of a $c(2 \times 2)$ monolayer with a limiting surface concentration of chlorine atoms of $7.6 \times 10^{14} \text{ cm}^{-2}$ [35]. Even immersion of the copper crystal in aqueous HCl did not increase the Cl concentration above this level, a $c(2 \times 2)$ structure being visible in LEED patterns after removal from solution. Interestingly, exposure of the crystal to the vapor above the HCl solution (containing oxygen as a contaminant) gave rise to extensive corrosion and complete loss of the LEED pattern.

The oxidation of Cu(100) surfaces at room temperature proceeds via a progression of surface structures beginning with a “four spots” LEED pattern that may result from a combination of small domains and that rapidly gives way, with further adsorption of oxygen, to a $c(2 \times 2)$ structure. At higher coverages (>0.3 monolayers), a $(\sqrt{2} \times \sqrt{2})\text{-R}45^\circ$ missing row type reconstruction is formed. This structure has a similar oxygen saturation coverage (0.5 monolayers) to the $c(2 \times 2)$ structure but is stabilized by the loss of a row of copper atoms reducing strain in the adsorbate lattice. The $(\sqrt{2} \times \sqrt{2})\text{-R}45^\circ$ and $c(2 \times 2)$ structures co-exist on the (100) surface up to the completion of the monolayer [36–40]. Subsequent reaction is kinetically very slow, hindered by the slow rate of oxygen diffusing through to the subsurface region. Lahtonen et al. [41] report that exposures of $>100,000$ L are needed at 100°C to increase the oxygen coverage above 0.5 ML and they propose that boundary areas between oxide islands are critical in facilitating this diffusion.

3. Experimental

Experiments were conducted using a combined variable temperature STM/XPS instrument (Omicron Vacuum Physik) equipped with an achromatic dual aluminium and magnesium $k\alpha$ photon source. All spectra were recorded with a pass energy of 50 eV. Spectra were obtained by the combination of between 10 and 20 individual scans over an approximately 25 eV wide region, with an acquisition time of approximately 1 minute per scan. All spectra were calibrated to the Cu ($2p_{3/2}$) peak at 932.7 eV. XPS data were acquired using MATRIX software (Omicron Vacuum Physik) and analyzed using CASA XPS commercial software [42]. Spectra are displayed without any spectral processing. Surface concentrations were calculated from XP peak areas using a method described previously and including the necessary adjustment for the Cl(2p) photoionization cross-section identified previously [43, 44]. Peak areas were obtained by integration using the CASA-XPS

software and a Shirley background. The error in the surface concentration of oxygen is estimated to be $\pm 1.5 \times 10^{13} \text{ cm}^{-2}$ for coverages below a monolayer but slightly greater in the case of chlorine, which has a weaker signal. STM images were analyzed using WSxM software [45]. The background pressure in the system between experiments was $\sim 1 \times 10^{-10}$ mbar. The sample diameter was ~ 10 mm with a thickness of approximately 0.5 mm, it was orientated to within 0.5 degrees of the (100) plane and polished mechanically down to 0.25 μm . Cleaning involved cycles of Ar^+ sputtering (0.65 keV, $20 \mu\text{A cm}^{-2}$ for 10 minutes) and annealing for 40 minutes at 700 K. This resulted in STM images showing flat terraces approximately 15 nm wide separated by steps 1.84 \AA in height. Sample cleanliness was checked by XPS. Gases were dosed via a leak valve at pressures of between 1×10^{-9} to 5×10^{-7} mbar. HCl (Argo international, 99.0%) and oxygen (Argo Ltd, 99.998%) were used without further purification but gas purity was monitored with *in situ* mass spectrometry.

4. Results

4.1. HCl(g) and $\text{O}_2(\text{g})$ adsorption at clean Cu(100) surfaces

The clean Cu(100) crystal was exposed to HCl in a series of sequential doses at room temperature. The concentration of chlorine calculated from the Cl(2p) region of the XP spectra after each individual dose is plotted against total exposure in Fig. 1, together with the equivalent experiment for oxygen. In comparison to oxygen, HCl dissociation on

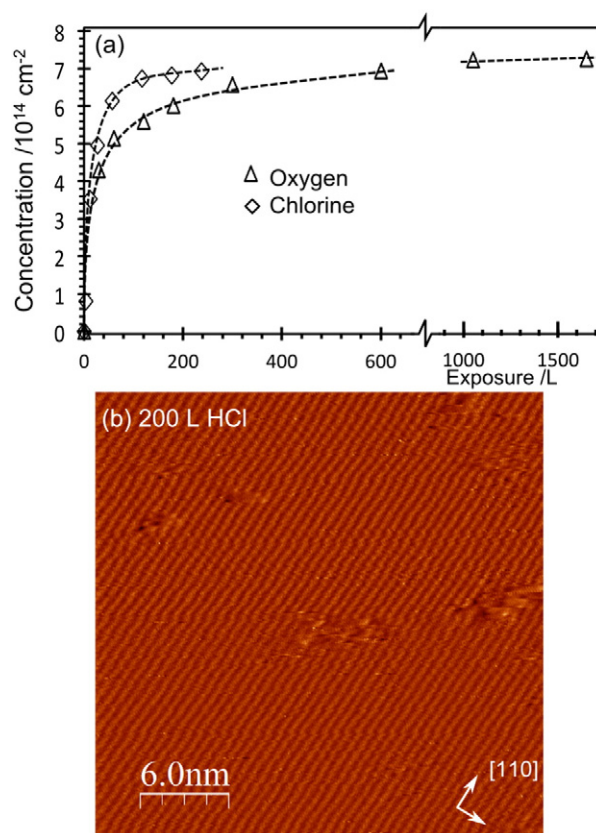


Fig. 1. (a) The chemisorption of chlorine and oxygen at clean Cu(100) surfaces at room temperature after exposure to HCl(g) and $\text{O}_2(\text{g})$, respectively. Surface concentrations are calculated from the XP spectra (see experimental section) and have an accuracy of $\pm 0.15 \times 10^{14} \text{ cm}^{-2}$. Dotted lines are intended to guide the eye. (b) STM image showing the Cu(100) surface covered with a $c(2 \times 2)$ Cl structure. The Cl concentration is 6.7×10^{14} atoms cm^{-2} corresponding to 0.45 ML coverage.

the Cu(100) surface is slightly faster with a saturation coverage of $\sim 7 \times 10^{14}$ atoms cm^{-2} corresponding to ~ 0.45 ML (where 1 ML is defined as the surface atom concentration of Cu(100) i.e. 1.55×10^{15} atoms cm^{-2}) achieved after approximately 120 Langmuir (L). At saturation, STM images show the $c(2 \times 2)$ Cl adlayer covering the entire substrate consistent with a coverage of ~ 0.5 ML.

STM images recorded during the adsorption of oxygen at room temperature are shown in Fig. 2 and are consistent with those published by Fujita et al. [38] and Lahtonen et al. [41]. Initial exposure at room temperature results in a roughening of the surface attributed to the

formation of a $c(2 \times 2)$ O(a) structure. As the coverage increases (>0.3 monolayers), depressions approximately ~ 0.4 Å deep appear in the terraces. These were attributed by Fujita et al. to the development of the $(\sqrt{2} \times \sqrt{2})$ -R45° missing row structure. The $(\sqrt{2} \times \sqrt{2})$ -R45° features increase in frequency until at a coverage of ~ 0.46 M (1200 L) the surface consists of a patchwork of bright and dark stripes. At this stage, small islands of ordered areas are appearing, but they remain roughly the same height as the surrounding surface. By 4000 L, the surface has become a patchwork apparently consisting of irregular islands 0.18 nm above the darker areas—equivalent to a single atomic step.

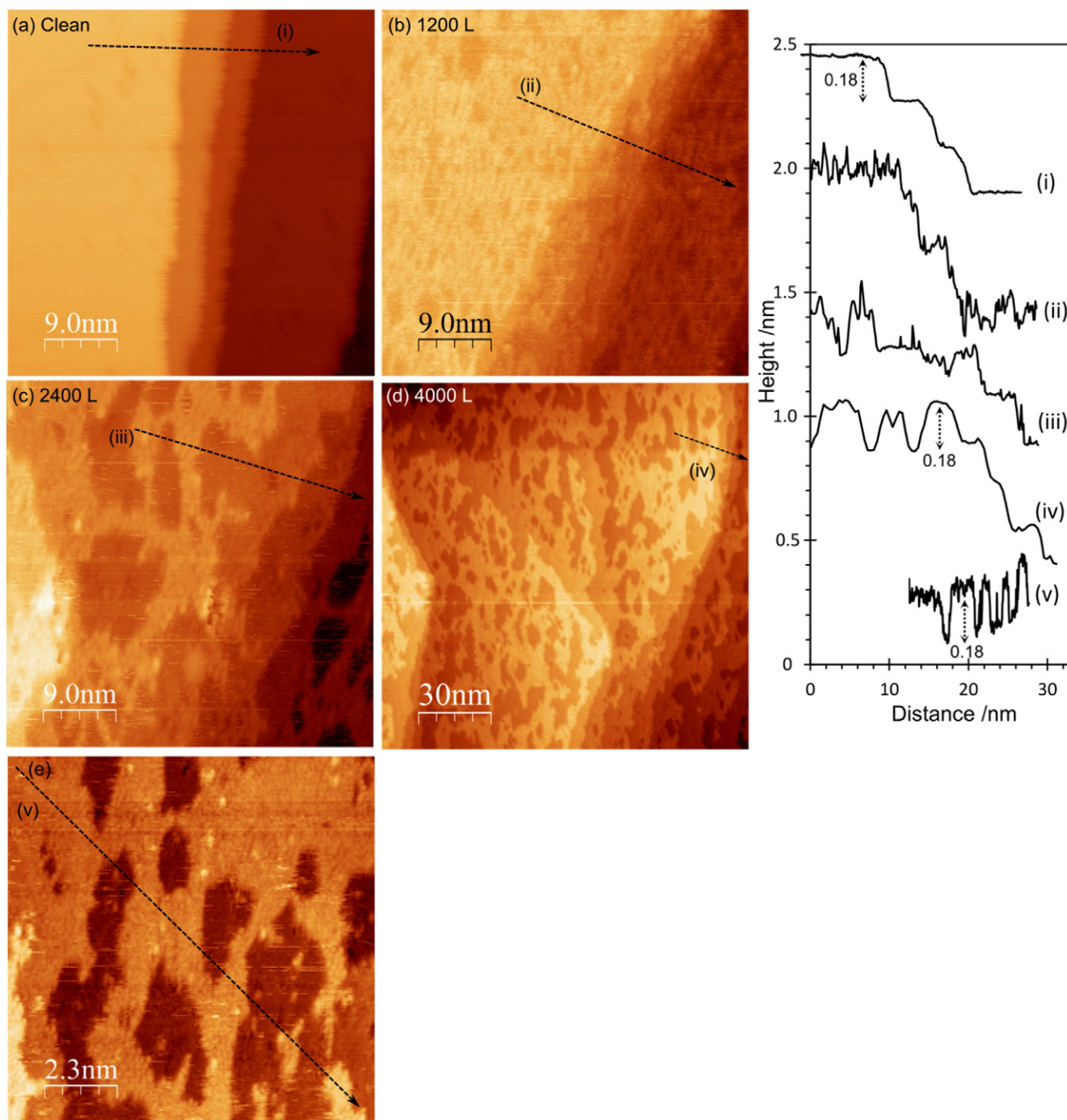


Fig. 2. STM images of oxygen adsorption at a clean Cu(100) surface at room temperature. a–d show images after increasing doses of $\text{O}_2(\text{g})$. (e) Shows a close up an area from (d). Line profiles from each image are given in (f) and show how the step size between levels is maintained as the oxygen concentration increases. Furthermore, the patchwork surface that results from oxygen adsorption also displays the ~ 0.18 nm step heights between light and dark regions suggesting different atomic levels.

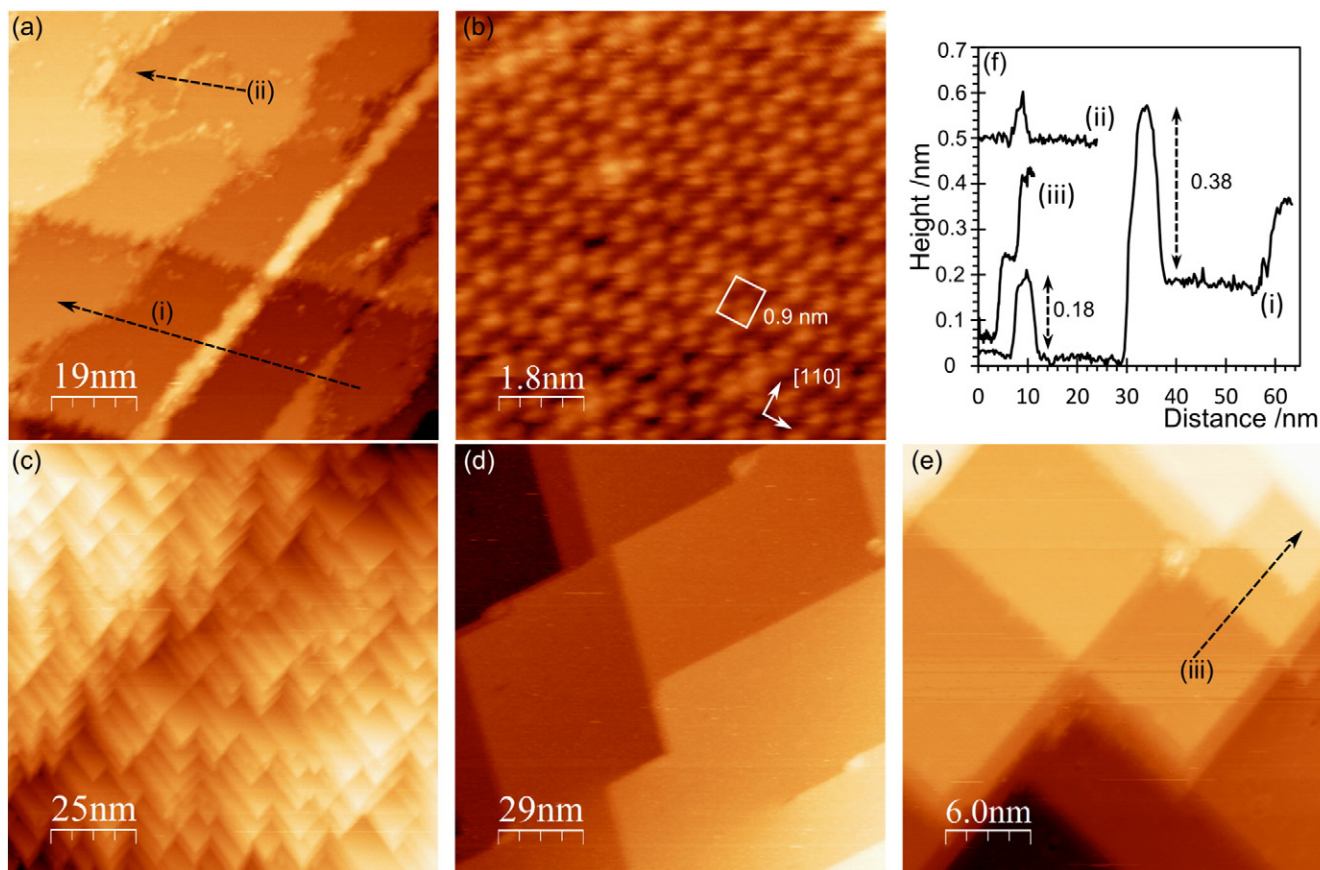


Fig. 3. STM images of oxygen adsorption on clean Cu(100): (a) adsorption at 373 K. Line profiles (i) and (ii) (shown in (f)) show the typical Cu(100) step edge height and the 2 step height ridge generated by copper atoms ejected from the formation of the $(\sqrt{2} \times \sqrt{2})$ -R45° structure. (b) close up of the $(\sqrt{2} \times \sqrt{2})$ -R45° structure showing the typical zigzag pattern; (c–e) STM images of Cu(100) exposed to O₂(g) at 523 K. Line profile (ii) (plotted in (f)) shows that the 0.18 nm step height remains a characteristic of the highly oxidized surface.

Adsorption of oxygen at 373 K produces more regular terraces on the oxidized surface, Fig. 3, and high magnification images show the $(\sqrt{2} \times \sqrt{2})$ -R45° periodicity in the centers of the large domains. The bright structures between domains are less than 0.1 nm high and may be residual areas of $c(2 \times 2)$ structure or simply areas of disorder. The larger features at step edges are ~2 atomic layers high and are due to the accumulation of copper ejected from the reconstruction of the surface. Oxygen adsorption at 523 K is much more extensive than observed at room temperature and after 5760 L a concentration of $1.4 \times 10^{15} \text{ cm}^{-2}$ is calculated from the XP spectra with the STM images showing a surface consisting of highly regular, planar, rectangular structures with step heights of ~0.2 nm. Small features are visible at corners in the terrace steps, which may be the beginnings of the nucleation of copper oxide islands or the accumulation of copper atoms ejected from the reconstructing surface.

4.2. Reaction of HCl with preadsorbed oxygen

4.2.1. $\theta_{\text{O}} \sim 0.35$

An initial concentration of oxygen of $5.5 \times 10^{14} \text{ cm}^{-2}$ was exposed to HCl at 9.5×10^{-9} mbar at room temperature, and the surface concentrations of the oxygen and chlorine calculated from the XP spectra are shown in Fig. 4. Initially, a rapid uptake of chlorine is accompanied by a corresponding decrease in surface oxygen, consistent with a 2:1 reaction stoichiometry to form water (Eq. 1).



However, the process begins to slow after ca. 12 L exposure and the surface chlorine concentration reaches an apparently limiting value of $6.9 \times 10^{14} \text{ cm}^{-2}$. Prolonged exposure to a low background pressure of HCl caused no further increase in surface chlorine concentration but increasing the HCl pressure in the chamber by a factor of 10 resulted in a significant rise in reaction rate and the complete removal of oxygen from the surface. The final concentration of chlorine was $8.7 \times 10^{14} \text{ cm}^{-2}$, which is $\sim 1 \times 10^{14} \text{ cm}^{-2}$ in excess of that expected for a $c(2 \times 2)$ Cl monolayer.

STM images recorded during exposure to HCl show that the bright $c(2 \times 2)$ O domains are most reactive being replaced with the characteristic patterns of the $c(2 \times 2)$ Cl structure, Fig. 4a and b. This is consistent with the higher strain in this structure. The darker $(\sqrt{2} \times \sqrt{2})$ -R45° structure is not replaced until higher exposures are reached and by this stage, imaging of the surface is very difficult reflecting an increased mobility of surface species despite the relatively high overall adsorbate surface concentrations. Chlorine is well known as a facilitator of catalyst sintering and it appears that this surface mobility is true also of the local atomic structure.

4.2.2. $\theta_{\text{O}} \sim 1$

The Cu(100) surface was exposed to 1650 L of oxygen at room temperature resulting in an oxygen surface concentration, calculated from the area of the single peak in the O(1s) region of the XP spectrum at 529.8 eV, of $7.2 \times 10^{14} \text{ cm}^{-2}$. Exposure of this surface to HCl at room temperature was monitored using XPS, Fig. 5. STM imaging was attempted during reaction but obtaining clear images proved very difficult.

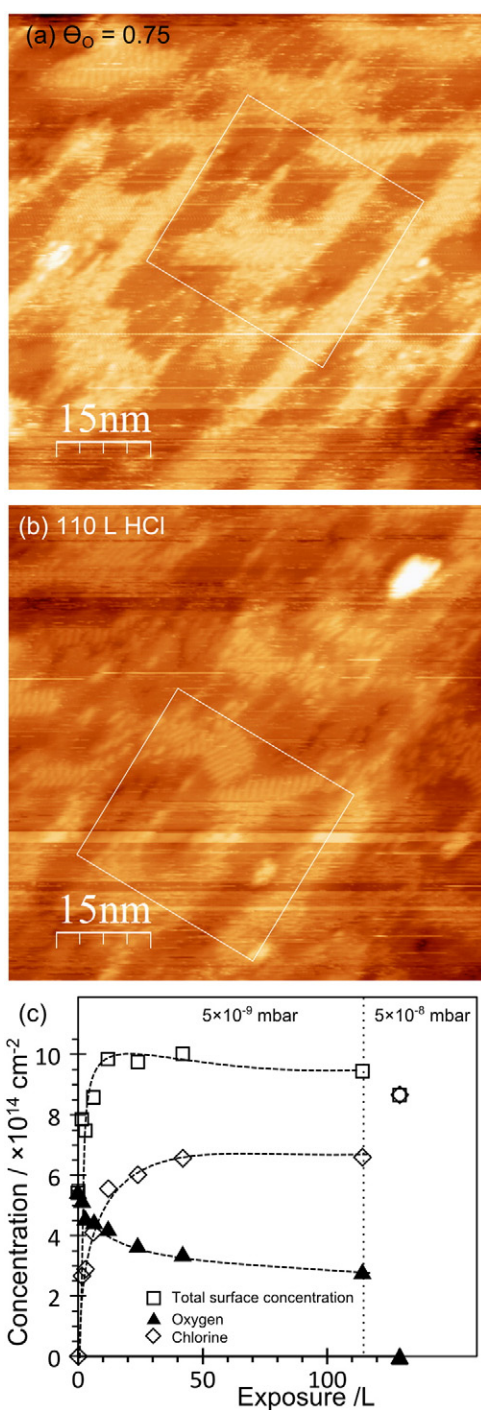


Fig. 4. STM images recorded during exposure of a $\sigma_0 = 5.8 \times 10^{14} \text{ cm}^{-2}$ ML pre-oxidized Cu(100) surface to HCl at room temperature. Bright areas of the image in (a) are etched away on exposure to HCl until the surface becomes difficult to image. (b) Shows an image recorded during HCl exposure after ~ 110 L HCl. White squares in (a) and (b) identify the same area on the surface showing how the sample has drifted during the experiment. (c) Surface concentration data from XP spectra show the decrease of the oxygen and the concomitant growth of the chlorine signal. The reaction reaches a steady state after ~ 45 L HCl but an increase in pressure accelerates reaction leading to the complete replacement of the oxygen by chlorine.

As in the case of the lower oxygen coverage, reaction with the $c(2 \times 2)\text{O}$ domains is preferred and occurs very rapidly with most of the oxygen being replaced by chlorine within 15 L exposure. Beyond this point, the reaction rate slows down and total removal of the oxygen

was not achieved. The total chlorine concentration at the surface at the end of the experiment was close to $1 \times 10^{15} \text{ cm}^{-2}$, well beyond the saturation coverage of the $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ structure, even without the $2.3 \times 10^{14} \text{ cm}^{-2}$ of oxygen which also remains at the surface (according to the XPS and STM observations) and is therefore blocking a proportion of the surface sites.

Although STM images taken during the initial stages of reaction with HCl were very poor, due probably to the significant diffusion of adsorbates during reaction and/or adsorption on the STM tip, the surface could be imaged if left to stabilize over several hours. A patchwork surface was imaged with three distinct areas, Fig. 6. Close up images of the area labeled (iii) show the 0.52 nm periodicity expected of both the $c(2 \times 2)\text{Cl}$ and $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ oxygen structures; we cannot discriminate between the two from the available STM images but the XPS data showing the overwhelming prevalence of chlorine on the surface would indicate that the former is the most likely assignment. The domain labeled (i) is typical of the $(\sqrt{2} \times 2\sqrt{2})\text{R}45^\circ$ oxygen structure [40] and further exposure to HCl during image acquisition hints at the mechanism by which the structure reacts with the typical zigzag pattern being broken down in stages. The rectangular structures (ii) develop over areas of structure (iii) as the oxygen is removed. These are reminiscent of the ordered chloride structures formed on Cu(110)/O on exposure to HCl and are tentatively assigned to a copper chloride phase.

4.2.3. $\theta_0 \sim 1.6$

The large domains of flat $(\sqrt{2} \times 2\sqrt{2})\text{-R}45^\circ\text{O}$ terminating in sharp step edges, created by oxidizing the surface at 523 K, are shown in Fig. 7. This fully oxidized surface was allowed to cool to room temperature and then exposed to a single dose of HCl of 270 L at room temperature. XP spectra recorded before and after exposure, Fig. 8, show the Cl surface concentration increasing to $1.25 \times 10^{15} \text{ atoms cm}^{-2}$ on exposure to HCl with a concomitant decrease in the O surface concentration from $1.25 \times 10^{15} \text{ atoms cm}^{-2}$ to $7.23 \times 10^{14} \text{ atoms cm}^{-2}$; this gives a ratio of Cl adsorption to O loss at ~ 1.7 close to the expected 2:1 ratio. STM images taken during the initial stages of HCl exposure show grooves developing in the oxygen layer attributed to a partial reduction; where the Cl atoms adsorb is not evident from the images but subsequently, larger islands develop on the flat oxide structure that can be attributed to a copper chloride although no fine structure information is available.

5. Discussion

The results presented here for the interaction of oxygen and HCl with the clean Cu(100) surface are in good agreement with previous studies [38,46,41]. Of particular note is the limiting concentration of chlorine at the surface corresponding to the completion of the $(\sqrt{2} \times \sqrt{2})\text{-R}45^\circ\text{Cl(a)}$ monolayer. Neither our experiments, nor those reported by others have shown evidence for chlorine structures formed from HCl with higher densities than $(\sqrt{2} \times \sqrt{2})\text{-R}45^\circ\text{Cl(a)}$. This is in contrast to Cl_2 gas, which is a much more aggressive reagent, as Andryushechkin et al. demonstrated with the Cu(110) surface and Galeotti et al. showed with Cu(100) [33,31]. The high activity in those cases can be attributed to the weaker Cl—Cl bond [26] which we hypothesize is readily broken even in the absence of clean copper sites; the resulting chlorine radicals provide the driving force to reconstruct the surface and disrupt the meta-stable chlorine adlayer initiating the nucleation of copper chloride islands. The H—Cl bond in contrast is too strong to be dissociated without the driving force of a strongly chemisorbed state as a product.

The presence of oxygen changes the kinetics. Fig. 9 compares the measured chlorine adsorption after exposure of a Cu(100) surface with different initial coverages of oxygen to HCl(g) at similar pressures ($\sim 1 \times 10^{-8}$ mbar). Until close to saturation, the rate of adsorption of

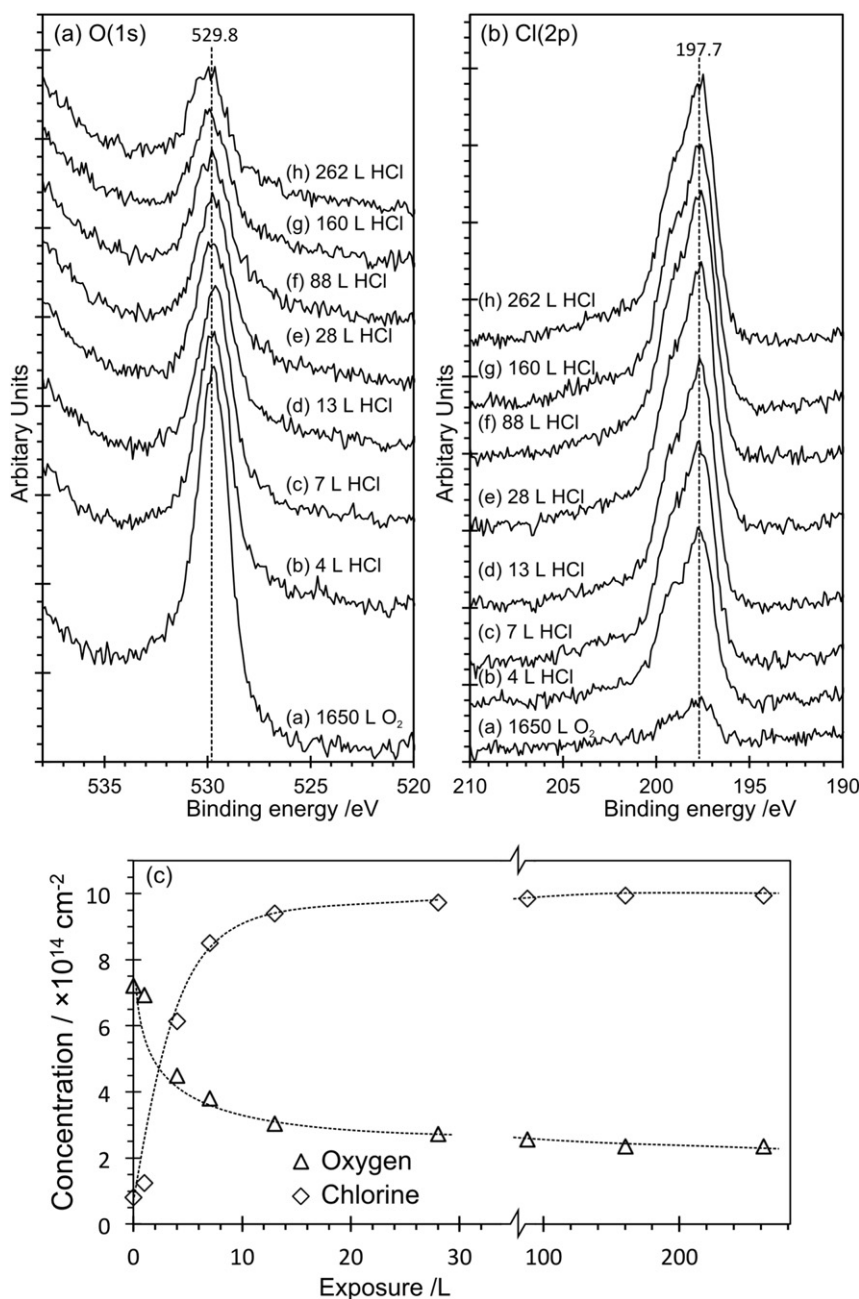


Fig. 5. XP spectra of (a) the O(1s) and (b) the Cl(2p) regions recorded after exposure of a preadsorbed monolayer of chemisorbed oxygen to discrete doses of HCl. (c) Comparison of Cl and O surface concentrations, calculated from the XPS in (a) and (b). Despite extensive exposure to HCl the oxygen adlayer is not completely removed.

Cl(a) for all three experiments behaves as first order with respect to the number of available adsorption sites, expressed as $(\theta_{\max} - \theta_{\text{Cl}})$, where θ_{\max} is taken as the limiting chlorine concentration in each experiment, Fig. 9b. While the rate of HCl adsorption is faster when oxygen is present, it is constant for different initial oxygen concentrations. The implication is that HCl reacts directly with the oxygen adlayer without requirement for clean copper sites as is the case with less reactive species such as alcohols [22,14] or amines [20]. Suleiman et al. recently examined the reaction of HCl with oxygen at a Cu(100) surface using DFT methods [47]. Their calculations included only a single oxygen adsorbate with multiple clean copper adsorption sites available for the HCl. Our experimental results suggest a reaction mechanism that does not rely upon the availability of these

sites and hint that the DFT calculations need to consider the presence of a monolayer of oxygen.

The 2:1 stoichiometry of the reaction dictates that HCl oxidation must rapidly lead to saturation of the surface with adsorbed chlorine, but in the presence of oxygen, the reaction does not seem to be hindered by the limiting value of the $(\sqrt{2} \times \sqrt{2})$ -R45 Cl(a) structure, reaching saturation at almost twice the value ($\sim 1.2 \times 10^{15} \text{ cm}^{-2}$). At these high concentrations, the surface still exhibits the $(\sqrt{2} \times \sqrt{2})$ -R45 Cl(a) and $(\sqrt{2} \times 2\sqrt{2})$ -R45 O(a) phases but new rectangular structures have developed. Since $(\sqrt{2} \times \sqrt{2})$ -R45 Cl(a) is limited to a chlorine surface concentration of $\sim 7.5 \times 10^{14} \text{ cm}^{-2}$, the rectangular structures are probably responsible for the missing chlorine and we hypothesize that they represent the nucleation of copper chlorides. Islands of the latter are much

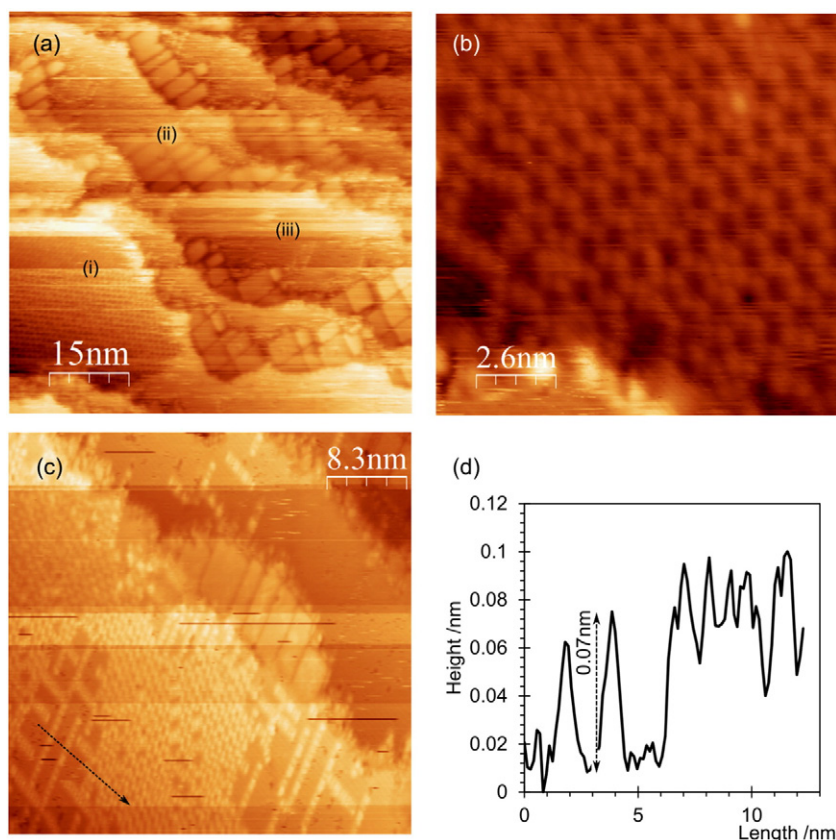


Fig. 6. STM images recorded after exposure of an oxygen saturated Cu(100) to HCl at room temperature. (a) shows the three different structures labeled (i), (ii), and (iii); (b) atomic resolution image of structure (i) assigned to unreacted $(\sqrt{2} \times \sqrt{2})$ -R45°O; (c) high-resolution image of structure (i) after further exposure to HCl at room temperature; (d) line profile from (c) showing the height changes over the reacted structure.

more in evidence after the reaction of the highly oxidized surface. These structures develop at defect sites in grain boundaries in the compact $(\sqrt{2} \times \sqrt{2})$ -R45°O(a) structure but we have not obtained images of sufficient clarity to speculate on the local structure within these islands.

6. Conclusions

Oxygen adsorption at room temperature on Cu(100) forms two distinct domains: a $(\sqrt{2} \times \sqrt{2})$ -R45°O(a) at low coverage and a $(\sqrt{2} \times \sqrt{2})$ -R45°O missing row structure at increased coverage. The latter is the only structure formed by adsorption at elevated temperatures. The $(\sqrt{2} \times \sqrt{2})$ -R45°O(a) surface structure is reactive towards HCl, forming a $(\sqrt{2} \times \sqrt{2})$ -R45°Cl structure; the $(\sqrt{2} \times \sqrt{2})$ -R45°O structure is slightly less reactive towards HCl but is nevertheless rapidly replaced. In contrast to many of the systems previously studied by Madix and others reaction at these surfaces takes place directly between the HCl and the chemisorbed surface without need for clean copper sites.

The presence of oxygen leads to faster reaction kinetics in the reaction with HCl and results in structures with much higher densities of chlorine than reaction with the clean surface. We speculate that this is because the surface is already reconstructed by the chemisorption of oxygen, reducing the barrier to Cl chemisorption and also because of the exothermic formation of water driving the reaction forward. Despite the ability of HCl to react with oxygen-covered surfaces, oxygen was not completely removed from the surface even after extensive exposure to HCl. Multilayers of oxygen react with HCl to give rise to 3D clusters while much of the copper–oxygen planes remain visible.

Acknowledgments

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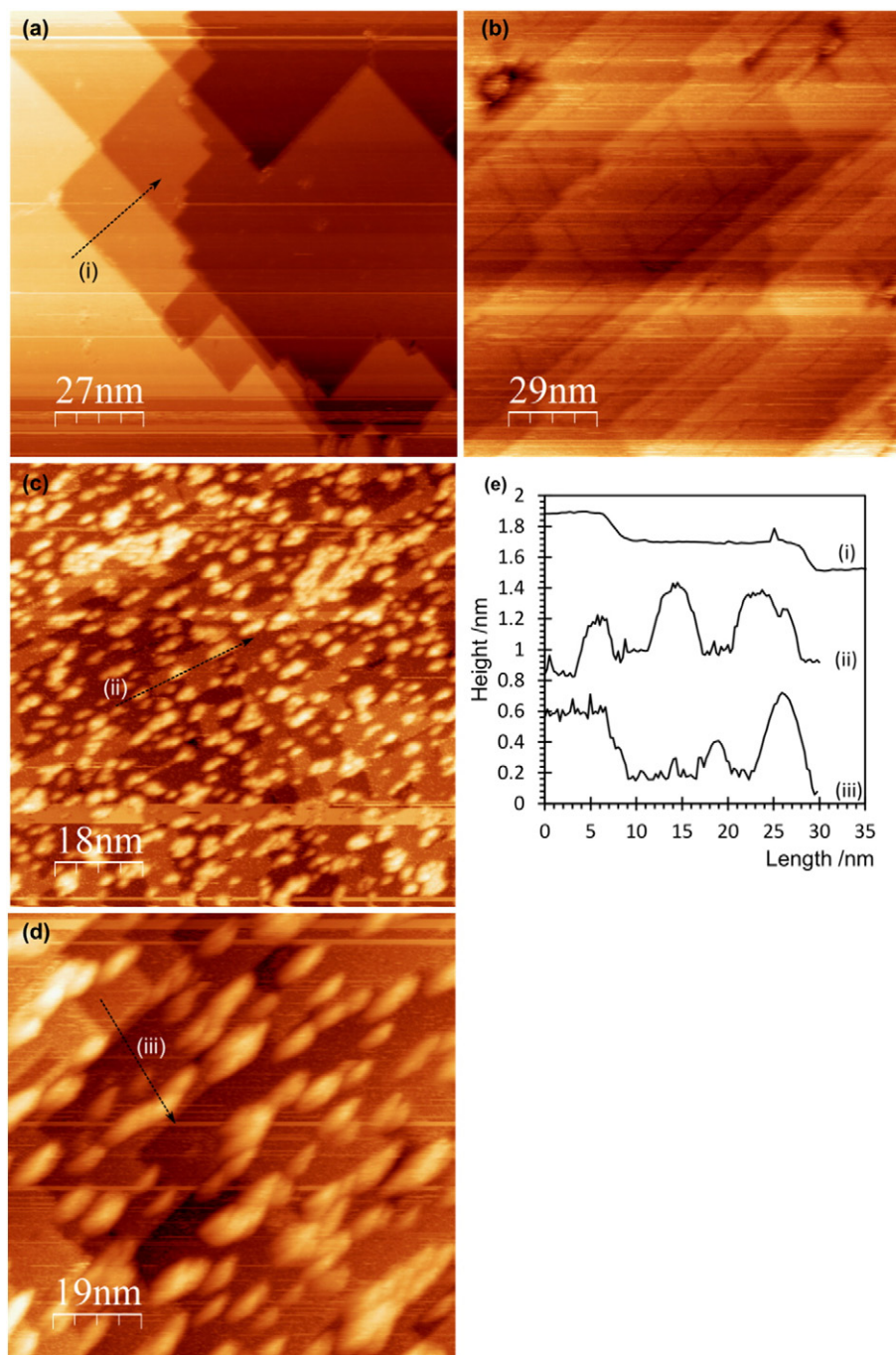


Fig. 7. STM images of a Cu(100) surface oxidized at 523 K and subsequently exposed to HCl at room temperature. (a) Cu(100)/O structure after cooling to room temperature; (b) during initial exposure to HCl showing the formation of grooves in the missing row structures; (c) after exposure of Cu(100)/O(a) surface to 270 L HCl showing copper chloride island formation; (d) close up of the island/terrace structure in (c); (e) line profiles from the images (a), (c), and (d).

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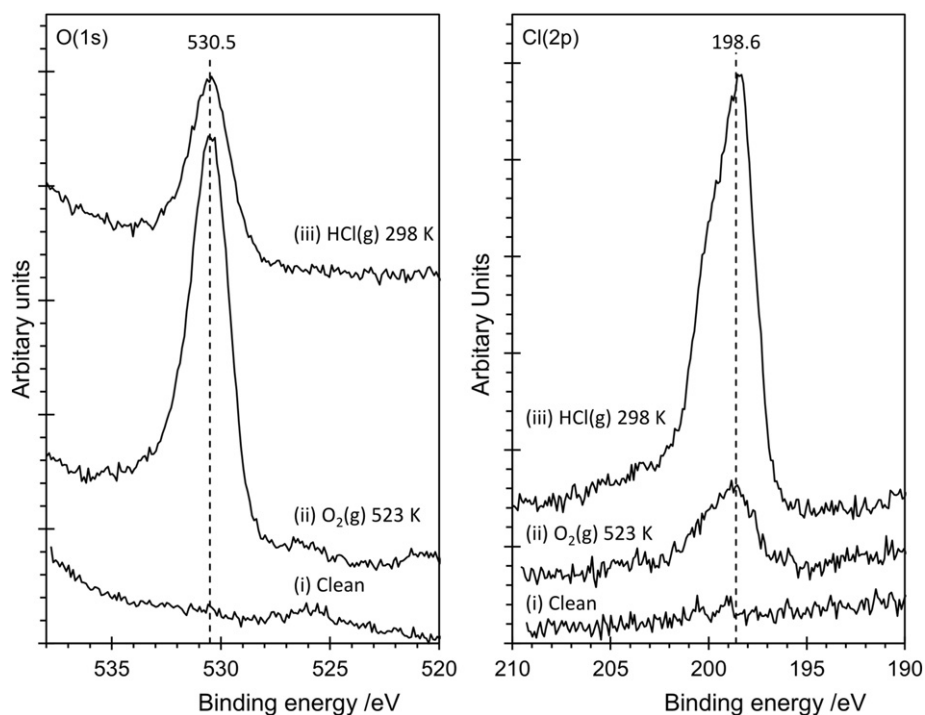


Fig. 8. XPS spectra of the O 1s and Cl (2p) regions after oxidation of the Cu(100) surface at 523 K followed by cooling to room temperature and exposure to HCl at 1×10^{-8} mbar, (270 L).

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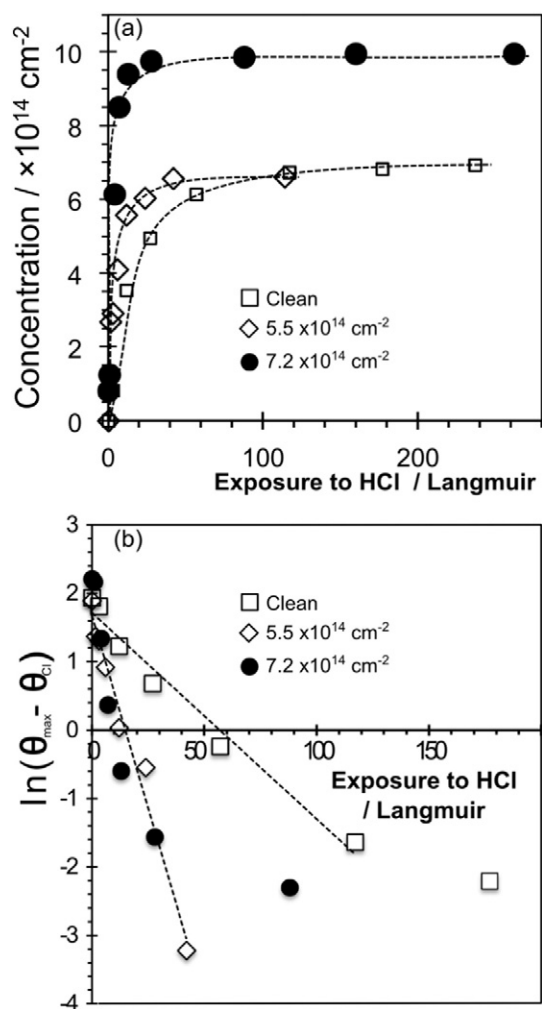


Fig. 9. Comparing the rate of Cl adsorption from the reaction of HCl with clean and oxidized Cu(100) surfaces. Initial oxygen concentrations are indicated on the figures. (a) Shows the surface concentration of the Cl calculated from XP spectra; (b) shows that the rate of adsorption is approximately first order in the number of “reactive sites,” corresponding to empty copper sites in the case of the clean surface and available oxygens in the case of the oxidized surface.