# Controlling oxygen states at a Cu(110) surface: the role of coadsorbed sulfur and temperature

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**Chemisorbed oxygen induces a disorder–order phase change in adsorbed sulfur at Cu(110) to give a c(2 × 2) adlayer at 295 K with oxygen present as isolated (2 × 1)-O strings, while warming a disordered oxygen state present at 80 K to 295 K generates a biphasic oxygen adlayer exhibiting both c(6 × 2) and (2 × 1) structures.**

It is well established that at 295 K the chemisorbed oxygen adlayer at a Cu(110) surface consists of copper–oxygen chains oriented perpendicular to the copper substrate rows.[1a]

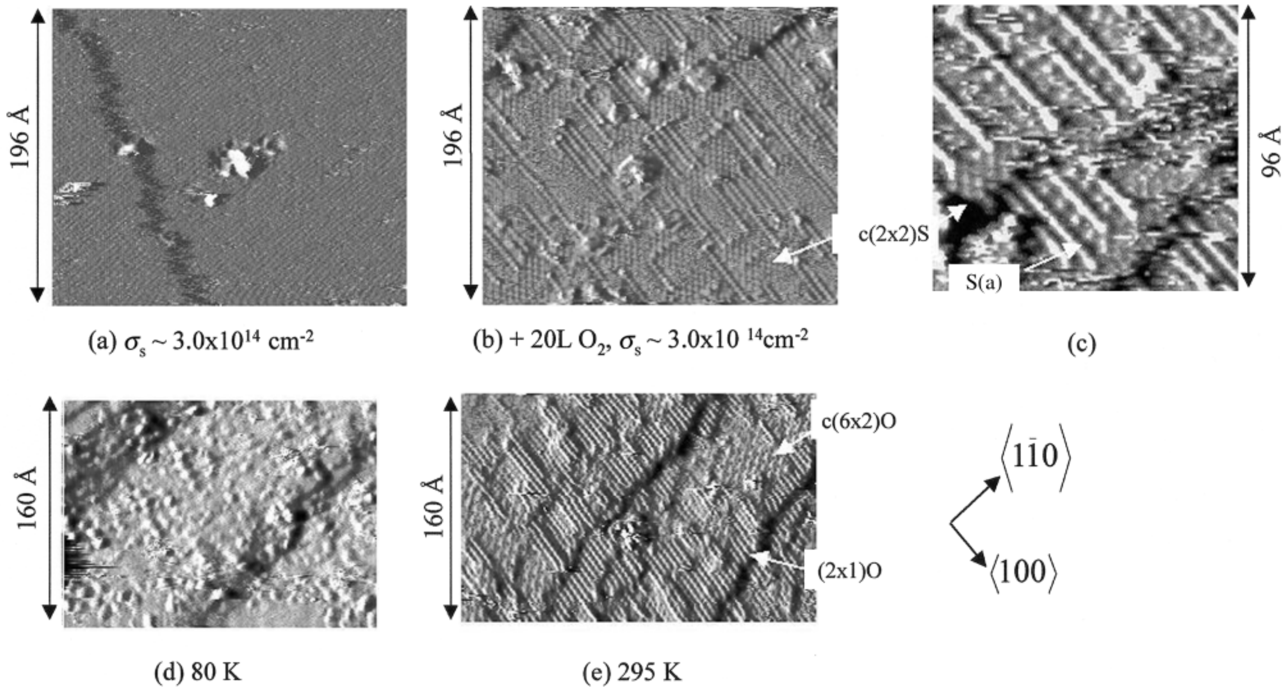
With increasing surface coverage the chains increase in length and coalese to form well ordered close packed islands with a (2 × 1)-O structure. At low oxygen coverages the oxygen chains are short, isolated, mobile and highly reactive to ammonia to form well ordered imide species through an oxydehydrogenation reaction accompanied by desorption of water.[2] By comparison, the oxygen islands are less reactive, with only those oxygen adatoms present at the island peripheries showing comparable dehydrogenation activity.

Here, we establish that a coadsorbate, chemisorbed sulfur, can influence the structure of chemisorbed oxygen states at a Cu(110) surface and how these oxygen states can simultaneously activate a disorder–order transition in the sulfur adlayer. The coadsorbates therefore exhibit cooperative effects which promote within the mixed-adlayer specific structural arrangements of each separate component. We also show that disordered oxygen adatoms present at 80 K are thermally ordered on warming to 295 K to generate a two phase system composed of (2 × 1)-O strings and c(2 × 6)-O structure.

An ultra-high vacuum spectrometer combining facilities for both scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) was supplied by Omicron Vacuum Physik. The Cu(110) crystal was cleaned by argon ion sputtering (0.6 keV beam energy; *ca.* 10 μA ion current) followed by annealing at 750 K for 30 min. The surface was shown to be clean by XPS and the purity of gases checked mass spectrometrically.

A Cu(110) surface was exposed to hydrogen sulfide at 295 K and the intensity of the S 2p binding energy region monitored by XPS. The signal was centred at 162 eV, indicative of chemisorbed sulfur,[3] and corresponded to a concentration of 2.4 × $10^{14}$ S adatoms $\text{cm}^{-2}$. The STM image [Fig. 1(a)] showed no evidence for chemisorbed sulfur although the copper atoms of the Cu(110) surface are resolved. This is consistent with a high surface mobility for the sulfur adatoms, most likely occurring along the $\langle 1\bar{1}0 \rangle$ directed troughs where the activation energy for surface diffusion is least.

However, when the disordered sulfur adlayer corresponding to a surface coverage $\theta \cong 0.28$ ($\sigma_s = 3.0 \times 10^{14}\ \text{cm}^{-2}$) was exposed to oxygen at 295 K, ordered structures were immediately observed in the STM images [Fig. 1(b) and (c)]. A disorder–order phase transition with increasing sulfur coverage



(a) $\sigma_s \sim 3.0\text{x}10^{14}\ \text{cm}^{-2}$ (b) + 20L $O_2$, $\sigma_s \sim 3.0\text{x}10\ ^{14}\text{cm}^{-2}$ (c)

(d) 80 K (e) 295 K

**Fig. 1** STM images of (a) disordered chemisorbed mobile sulfur adatoms ($\sigma_s = 3 \times 10^{14}\ \text{cm}^{-2}$; $\theta = 0.28$) at a Cu(110) surface at 295 K, note the resolved copper atoms in the $\langle 1\bar{1}0 \rangle$ direction; (b) and (c) ordered structures of (2 × 1)-O and c(2 × 2)-S formed by an exposure of (a) to 20 L oxygen at 295 K [1 L (Langmuir) ≡ $10^{-6}$ Torr s]; chemisorbed sulfur adatoms separating (2 × 1)-O strings are visible in image (c); (d) disordered oxygen states present at a Cu(110) surface at 80 K; (e) ordered (2 × 1)-O and (6 × 2)-O states present after warming (d) to 295 K. The tunnelling conditions were typically [image (b)]: sample bias −0.38 V, feedback current 2.5 nA; loop gain 0.19%.

has been observed[1b] previously for Re(0001) but the role of a second adsorbate, in the present case oxygen, has not been reported. There are two distinct structures present at the Cu(110) surface, c($2 \times 2$) structures due to chemisorbed sulfur and ($2 \times 1$) string or chain structures characteristic of chemisorbed oxygen. The presence of chemisorbed oxygen has clearly induced a disorder–order phase transition in the previously mobile disordered sulfur adlayer but with the simultaneous formation of oxygen strings well separated from each other (10 Å or more). The latter are distinctly different from the close packed oxygen island structures characteristic of the chemisorbed oxygen adlayer and more akin to the isolated oxygen chains present at Cu(110) at low oxygen coverage. In view of having established[2] that isolated oxygen chains were highly reactive in oxydehydrogenation reactions at Cu(110), we exposed this mixed sulfur–oxygen adlayer to ammonia at 295 K and confirmed the formation of imide species.

We, therefore, have an unusual phenomenon where during coadsorption two physiochemical processes occur: first chemisorbed oxygen inducing a phase change in the disordered S-adlayer to generate an ordered c($2 \times 2$)-S structure and second the presence of chemisorbed sulfur adatoms acting as a structural promoter of the isolated ($2 \times 1$)-O strings. In some cases we have shown that the oxygen strings are separated from each other by just a single row of chemisorbed sulfur adatoms [Fig. 1(c)], in other cases the strings are well separated and present on terraces occupied predominantly by c($2 \times 2$) S-structures [Fig. 1(b)].

Although oxygen interaction at 295 K results in a well ordered ($2 \times 1$)-O structure, if the Cu(110) is first exposed to oxygen at 80 K and the adlayer warmed to 295 K, the STM image indicates the presence of a biphasic oxygen adlayer [Fig. 1(d) and (e)]. In addition to the ($2 \times 1$) structure there is also a ($6 \times 2$)-O structure.

A c($6 \times 2$)-O structure has previously been reported by Wintterlin and Behm[1a] to exist at a Cu(110) surface when a ($2 \times 1$)-O structure is exposed to 'much higher amounts of oxygen at $T \geqslant 300$ K'. Our STM results indicate that the same structure can develop through warming the chemisorbed adlayer at 80 K to room temperature, which offers a possible explanation for work function studies reported[4] some 30 years ago where the surface potential (change in work function) of chemisorbed oxygen on copper and nickel surfaces at 295 K differed by as much as 1 eV depending on whether or not the oxygen was chemisorbed first at 80 K. An earlier low energy electron diffraction study[5] also drew attention to the role of temperature in controlling the formation of the c($6 \times 2$) structure; Fig. 1(e) however provides atom-resolved evidence for the co-existence of the two phases at 295 K and the disorder–order transition that occurs between 80 and 295 K.

Since it is now well established that the chemical reactivity of oxygen at a Cu(110) surface is dependent on its structural state (isolated oxygen adatoms, isolated oxygen strings or close packed island structures), the ability to control the structural nature of the chemisorbed oxygen state through coadsorbed sulfur offers a novel approach to controlling selectivity in oxygenation catalysis. Sulfur, although more usually considered to be a surface 'poison', can also be a catalytic promoter with lateral interactions controlling surface structural states of oxygen.

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## Notes and references

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