

## Submonolayer coadsorption of chlorine and oxygen on Ag(110) studied by electron energy loss vibrational spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 7699

(<http://iopscience.iop.org/0953-8984/8/41/015>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 04:18

Please note that [terms and conditions apply](#).

# Submonolayer coadsorption of chlorine and oxygen on Ag(110) studied by electron energy loss vibrational spectroscopy

F Stietz<sup>†</sup>, A Elbe, G Meister, J A Schaefer<sup>†</sup> and A Goldmann

Fachbereich Physik der Universität GH Kassel, Heinrich-Plett-Strasse 40, D-34132 Kassel, Germany

Received 23 February 1996, in final form 3 June 1996

**Abstract.** We present a detailed investigation of the submonolayer coadsorption of Cl and O on Ag(110) at room temperature. Our main method is high-resolution electron energy loss spectroscopy (HREELS), supplemented by LEED, XPS and angle-resolved UPS. Preadsorbed chlorine at coverages below about 0.15 monolayer and subsequent exposure to O<sub>2</sub> causes the development of separate domains covered with either Cl or the ( $n \times 1$ )O added row reconstruction. Above 0.2 monolayers of Cl precoverage, oxygen adsorption is inhibited completely. By contrast, oxygen preadsorbed in the ( $n \times 1$ )O structure is almost completely removed by subsequent exposure to chlorine, and the added rows are dissolved.

## 1. Introduction

The coadsorption of chlorine and oxygen on Ag has been studied in several earlier investigations (see e.g. [1–6]). The historical interest in this combination results from the role of chlorine promoters for the catalytic epoxidation of ethylene on Ag [5]. In particular the effect of chlorine precoverage upon the rate of dissociative oxygen on Ag(110) has been investigated in considerable detail. Rovida *et al* [1] observed that adsorbed oxygen is removed by dichloroethane, while different coverages of adsorbed chlorine are not affected when exposed to oxygen. Oxygen adsorption was completely inhibited when the chlorine coverage reached 0.5 monolayers (ML) [1]. In a subsequent study of the Cl–O coadsorption of Ag(331) Marbrow and Lambert [2] examined the interaction of Cl with the oxygen predosed surface and the converse O–Cl reaction. They obtained no conclusive evidence that Cl displaced adsorbed O. This might be related to the presence of surface steps on Ag(331). Later work studied the influence of potassium on the mixed ternary (K + Cl + O) adsorption layer [3] and the effect of a lower substrate temperature ( $T = 80$  K) during exposure [4]. Campbell and Paffett [5] have shown that the role of Cl in the catalytic epoxidation of ethylene can be accurately modelled with atomically chemisorbed Cl on Ag(110). In their studies they used surface analytical tools (XPS, AES, LEED, TDS) under UHV conditions before and after kinetic measurements performed at high pressures (150 torr O<sub>2</sub>) and elevated temperatures ( $T = 490$  K). In agreement with earlier work they observe that atomic oxygen adsorption is completely attenuated by a Cl precoverage of  $c_{\text{Cl}} = 0.25\text{ML}$  under reactor conditions (see above). They also report experiments performed exclusively

<sup>†</sup> Now at Institut für Physik, TU Ilmenau, D-98684 Ilmenau, Germany.

in UHV, which demonstrate that the dissociative adsorption of O<sub>2</sub> on Ag(110) is completely suppressed at a Cl precoverage of  $c_{\text{Cl}} \sim 0.3\text{ML}$ , after O<sub>2</sub> exposures between about 150L and 3800L (1L =  $10^{-6}$  Torr s) and at  $T = 477$  K [5].

Almost nothing is known about the type of interaction between coadsorbed Cl and O atoms on Ag(110). Basically two mechanisms can be proposed. Chlorine, as an electronegative adsorbate, may draw electron density from the Ag surface atoms, thereby changing the interaction with approaching O<sub>2</sub> molecules [5]. On the other hand, a purely steric effect might also be effective: due to the blocked surface area, the number of Ag atoms available to dissociate O<sub>2</sub> is too small to induce atomic adsorption.

The interaction of atomic oxygen with Ag(110) has been studied in the last years by several groups (see e.g. [7–15]). Also some spectroscopic information about atomic chlorine on Ag(110) has been collected (see e.g. [6, 16–20]). In the hope of obtaining further insight into Cl–O coadsorption at submonolayer coverage on Ag(110), we have therefore decided to extend our earlier HREELS studies of the O–Ag(110) system [12, 15] and the Cl–Ag(110) surface [18] to the mixed Cl–O overlayer.

## 2. Experimental

The HREELS experiments were performed using a spectrometer similar to the one used by Ibach and coworkers [21]. It was incorporated into an ultrahigh vacuum system operating at a base pressure of  $5 \times 10^{-11}$  mbar, and was equipped with facilities for low-energy electron diffraction (LEED), X-ray and UV-excited photoelectron spectroscopy (XPS, UPS), and standard sample preparation techniques such as Ar ion bombardment, annealing and exposure to adsorbates. The HREELS spectrometer was operated with an incident electron beam energy of  $E_0 = 3.5$  eV and with a resolution of  $\Delta E = 2.6$  meV (experimentally observed full width at half maximum of the elastic peak). Spectra were obtained with incident and exit angles of  $\theta = 52^\circ$  with respect to the surface normal.

The Ag(110) crystal was oriented to better than  $0.5^\circ$ . No contamination could be detected by XPS and HREELS and an excellent LEED pattern was observed. In addition the UPS detection of a well known surface state at the  $\bar{Y}$ -point of the surface Brillouin zone [22] demonstrated the high quality of the clean Ag(110) surface.

Adsorption of oxygen was performed with the sample at room temperature by admission of molecular oxygen. For the Cl<sub>2</sub> exposure we used an electrochemical Ag–AgCl–graphite solid state cell [23, 24]. This device was operated in a separately pumped UHV preparation chamber, while the sample was at room temperature. Afterwards the crystal was transferred to the analysis chamber without breaking the UHV. The relative chlorine dose emitted by the solid state source was measured in mA s (current through cell times exposure time), a quantity that is directly proportional to the number of Cl<sub>2</sub> molecules emitted. These doses were accurate to at least 5%. Absolute coverages on Ag(110) were monitored by XPS intensities of the chlorine core levels. Their calibration in monolayers assumes a coverage of  $c = 0.5\text{ML}$  for the well-ordered ( $2 \times 1$ )Cl overlayer and  $0.75\text{ML}$  for the saturated  $c(4 \times 2)$ Cl pattern as controlled by LEED. The coverage  $c$  is defined relative to the number of Ag surface atoms ( $c = 1\text{ML}$  is  $8.5 \times 10^{14}$  cm<sup>-2</sup>).

The angle-resolved UPS spectra were excited by HeI radiation ( $\hbar\omega = 21.2$  eV). These data were recorded by a separate spectrometer, also equipped with LEED and XPS, which allows for high intensities by using a position sensitive channel plate detector. Energy and angle resolution were set to  $\Delta E = 100$  meV and  $\Delta\theta = \pm 1.5^\circ$ , respectively. While the angle between the photoelectron and the incident photon was fixed to  $38^\circ$ , the sample normal was rotated in a plane perpendicular to the surface, containing both the electron and

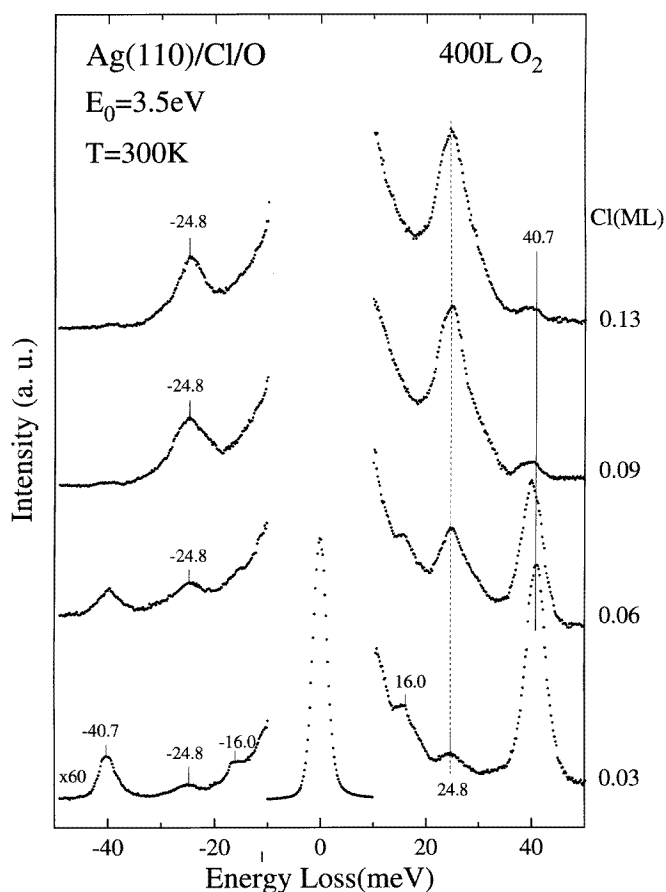
photon directions. In this work results are presented in normal emission geometry ( $\theta = 0^\circ$ , light incident along the [001] bulk lattice direction, along the  $\bar{\Gamma}\bar{Y}$  direction of the surface Brillouin zone) and at the  $\bar{Y}$ -point ( $\theta = 23^\circ$  along [001]). All data were taken at room temperature.

### 3. Results and discussion

Typical HREELS spectra from the Cl–O–Ag(110) coadsorption system are reproduced in figure 1. In all experiments the energy-loss and the energy-gain peaks were recorded. Their intensity ratio is determined by the Bose–Einstein distribution factor and the crystal temperature (always 300 K). The recording of both loss and gain features improves the accuracy with which the vibration energies may be derived from the spectra. The data of figure 1 were assembled as follows: first a Cl precoverage was made, between  $c = 0.03$  and 0.13ML as indicated on the right. Then always the same exposure to 400 L O<sub>2</sub> was made. Subsequently the HREELS data were collected.

Clean Ag(110) shows a phonon resonance at a vibrational loss energy of  $\hbar\omega = 13.2$  meV [12]. Upon exposure to oxygen, this phonon shifts monotonically from  $\hbar\omega = 13.2$  meV to 17 meV [12]. Simultaneously, the O–Ag stretching vibration is observed between  $\hbar\omega = 38.5$  meV at very low coverage and  $\hbar\omega = 40.9$  meV [11, 12, 14] when the well known [7]  $(2 \times 1)$ O ‘added-row’ reconstruction is completed. The Cl–Ag stretching mode vibrates [18] between  $\hbar\omega = 24.7$  meV (extrapolated to  $c \rightarrow 0$ ) and  $\hbar\omega = 25.4$  meV after completion of the well known [6]  $(2 \times 1)$ Cl overlayer at  $c = 0.50$ ML. In contrast to the oxygen overlayer, the clean-surface phonon peak is essentially damped off (at  $\hbar\omega = 13$  meV) at chlorine coverages of  $c = 0.03$ ML. The appearance of a phonon loss around  $\hbar\omega = 16$  meV in the lowest trace of figure 1 is thus not expected from the disordered ‘lattice-gas-like’ chemisorption of atomic Cl as observed without coadsorbed oxygen. Therefore we associate this phonon with the formation of the  $(n \times 1)$  O–Ag–O–Ag added rows which are observed [7] in the absence of chlorine with  $n$  varying from 7 to 2 as the coverage increases up to 0.5ML. Its energy of  $\hbar\omega \approx 16$  meV is a fingerprint of the overlayers with  $n = 3 \pm 1$  [12]. In addition the O–Ag loss energy of  $\hbar\omega = 40.7$  meV observed in figure 1 at  $c_{\text{Cl}} = 0.03$ ML is correlated with  $n \approx 3$  [12], if observed in the absence of coadsorbed Cl. On the clean Ag(110) surface, however, an exposure to O<sub>2</sub> around 1500L was required to observe the  $(3 \times 1)$  overlayer [12], and at 400L O<sub>2</sub> only the  $(4 \times 1)$  reconstruction is built [12]. These results are thus compatible with a compression of the oxygen-covered areas by the presence of chlorine. However, our XPS data (obtained with unmonochromatized MgK <sub>$\alpha$</sub>  radiation) are not accurate enough to distinguish uniquely between  $n = 3$  and  $n = 4$ . In fact the oxygen peak observed at 0.06ML in figure 1 appears both shifted and somewhat broadened when compared to 0.03ML and may be interpreted by a superposition of two peaks corresponding to  $n = 3$  and  $n = 4$  [12].

Our results are also fully consistent with the earlier observations seen using thermal desorption spectroscopy (TDS) in combination with LEED and AES [1]. Roviida *et al* [1] suggest from their data that Cl and O coexist mainly in separate domains. Their results have been questioned in [2] since it was not evident whether dosing with dichloroethane [1] or with gaseous Cl<sub>2</sub> [2] produces identical surfaces. Our data indicate that no basic differences are obtained. Our results also indicate the coexistence of domains with either  $(4 \times 1)$  or  $(3 \times 1)$ O chains—these were identified by us with LEED at a chlorine coverage around  $c = 0.03$ ML, see also [1]—or patches covered essentially with atomic Cl. Increasing the preadsorbed Cl coverage causes both the O–Ag vibration and the correlated phonon to shift to somewhat lower vibration energies and to eventually disappear. In conclusion, while

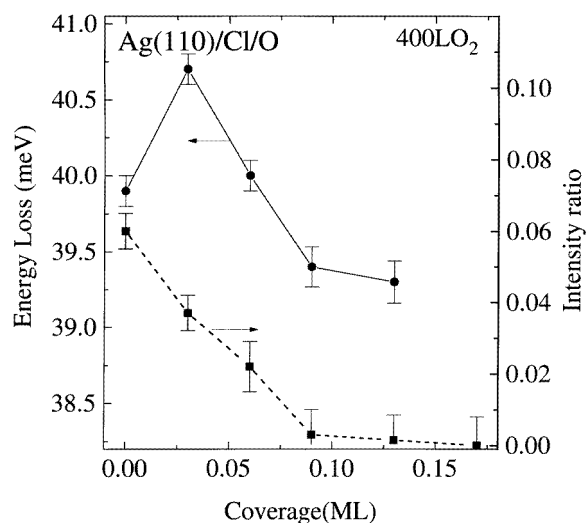


**Figure 1.** High-resolution electron energy loss (and gain) spectra obtained from a Ag(110) surface that was precovered with different amounts of atomic chlorine (see the column on the right-hand side of the frame) and subsequently exposed to 400L of O<sub>2</sub>.

some compression of the oxygen domains appears compatible with the data of figure 1, other explanations of the observed shifts such as lateral interactions or differences between species in the middle and at the boundary of islands have also to be considered. The HREELS data do not allow us to distinguish these cases.

Figure 2 shows how the intensity of the O–Ag vibration (normalized to the elastic peak at  $\hbar\omega = 0$ ) approaches zero at  $c_{\text{Cl}} = 0.17\text{ML}$ . Figure 2 also shows the energy of this vibration. At  $c_{\text{Cl}} = 0$ , as mentioned already,  $\hbar\omega = 39.8\text{ meV}$  corresponds to  $n = 4$  at 400L O<sub>2</sub> [12]. Obviously at  $c_{\text{Cl}} = 0.03\text{ML}$  we already observe  $\hbar\omega = 40.7\text{ meV}$ , which corresponds to  $n = 3$  on the Cl-free Ag(110) surface. Finally at  $c_{\text{Cl}} = 0.13\text{ML}$   $\hbar\omega = 39.3\text{ meV}$  approaches the vibration energy observed around  $n = 6$  at Ag(110) ( $n \times 1$ )O [12]. Now the preadsorbed Cl inhibits the formation of the O–Ag–O chains and no intensity in the O–Ag vibration peak is seen for Cl coverages above  $c_{\text{Cl}} = 0.15\text{ML}$ .

The latter value is in some disagreement with the earlier TDS observation that the oxygen uptake goes to zero at  $c_{\text{Cl}} \approx 0.5\text{ML}$  [1], and is in only reasonable agreement with [5], where the dissociative adsorption of O<sub>2</sub> (as measured by TDS after O<sub>2</sub> exposure at



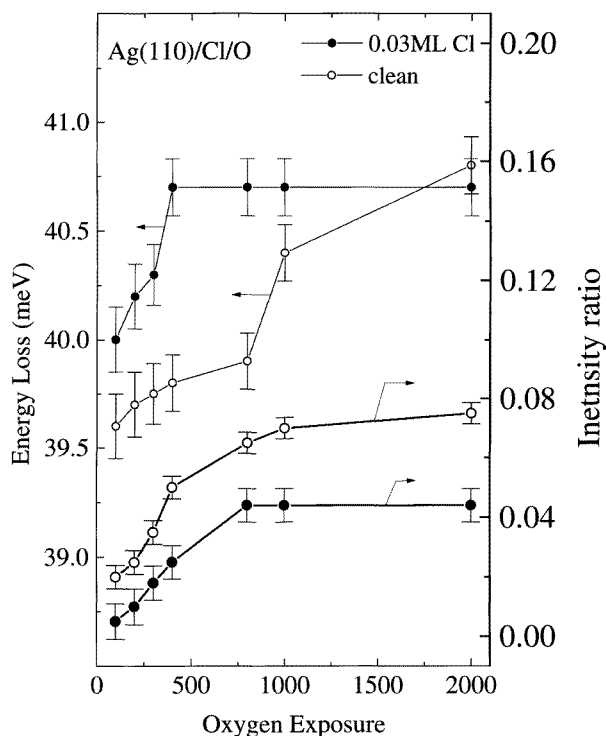
**Figure 2.** Loss energy (circles, left-hand scale) and intensity normalized to the elastic peak (squares, right-hand scale) obtained for the O–Ag vibration after different precoverage of atomic chlorine and subsequent exposure to 400L of O<sub>2</sub>.

$T = 477$  K) is completely suppressed at  $c_{\text{Cl}} = 0.3\text{ML}$ . We can speculate whether (besides possible errors in the calibration of coverages) the TDS results do also register O<sub>2</sub> adsorption on the precovered surface. Without Cl, O<sub>2</sub> does not adsorb at  $T = 300$  K [25]. However, O<sub>2</sub> adsorbed at  $T = 100$  K vibrates at  $\hbar\omega = 30$  meV ( $240\text{ cm}^{-1}$  [25]). We cannot exclude such a contribution, induced e.g. at the boundaries of the different Cl and O domains, in our spectra. In fact, while before exposure to oxygen the Cl–Ag vibration peak is rather symmetric, after oxygen adsorption it exhibits some asymmetry around  $\hbar\omega = 30$  meV (see figure 1). However, our data are not accurate enough to decide on this speculation. In particular, we could not detect an XPS signal characteristic of molecular oxygen, but in this case XPS is at the limits of detectability.

We have also studied the adsorption behaviour of Ag(110) precovered by 0.03ML of Cl to different oxygen exposures. Some results are summarized in figure 3. The data obtained for clean Ag(110) (open symbols) are taken from our earlier study [12]. After precoverage with 0.03ML Cl, the intensity of the O–Ag vibration normalized to the elastic line saturates at exposures  $\geq 400\text{L O}_2$ . Also the peak energy of the O–Ag stretching mode saturates. Obviously all data can be rationalized by assuming that only fractions of the Ag surface are covered by domains of O–Ag chains, and that their line density appears compressed from  $n = 4$  (no Cl) to  $n = 3$  by a Cl coverage of only 0.03ML.

We also refer to the TDS data in [1] which show that the desorption temperature of oxygen is lowered by about 25 K with increasing Cl precoverage. The authors concluded that the presence of Cl affects the Ag–O bond. However, more recent TDS studies of Ag(110) ( $n \times 1$ )O [13] report an almost identical shift of about 23 K between desorption from surfaces with  $n = 3$  and  $n = 8$ . This shift therefore seems to be correlated with repulsive interactions perpendicular to the O–Ag chains, but not with any influence of coadsorbed chlorine atoms. In conclusion, this shift of adsorption temperature gives an additional piece of evidence for domains covered by O–Ag added rows.

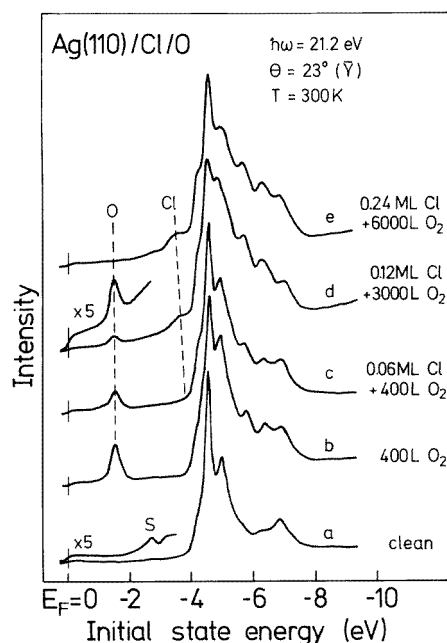
To gain further insight, we have also taken angle-resolved photoelectron spectra. Several



**Figure 3.** Loss energies (two topmost curves, left-hand scale) observed for the O–Ag stretching vibration on clean Ag(110) (open symbols) and after a 0.03ML precoverage with atomic Cl and subsequent adsorption of oxygen at different exposures (filled symbols). The two lowest curves (right-hand scale) indicate the corresponding intensities of the vibrational peak normalized to the elastic line.

earlier studies of the Ag(110) ( $n \times 1$ )O system [8–10] have shown that in normal emission an oxygen-derived occupied orbital (‘antibonding’ with respect to the Ag–O bond) appears at an initial state energy of  $E_i = -2.9$  eV, independent of  $n$ . This feature shows a strong dispersion with  $k_{\parallel}$ , the component of the electron wave vector parallel to the surface, along the  $\bar{\Gamma}\bar{Y}$  direction of the surface Brillouin zone (i.e. along the O–Ag–O chains formed parallel to the [001] bulk crystal axis). At  $\bar{Y}$  the oxygen band appears at  $E_i = (-1.5 \pm 0.1)$  eV in all previous investigations and we have also reproduced the earlier data. It has been shown by Canepa *et al* [10] that the dispersion along  $\bar{\Gamma}\bar{Y}$  is identical for the ( $2 \times 1$ )O, ( $4 \times 1$ )O and ( $6 \times 1$ )O phases. This dispersion is thus a unique fingerprint for the existence of the added-row reconstruction. We have therefore checked for this signature in UPS spectra of the Cl–O coadsorption system.

Typical data are reproduced in figure 4. All spectra were taken at  $\theta = 23^\circ$  along the  $\Gamma K L U$  plane of the bulk reciprocal lattice. This means that the feature at  $E_i = -1.5$  eV lies at the  $\bar{Y}$  point of the surface Brillouin zone. Trace a shows the clean surface result, with the d-band emission at initial state energies  $E_i$  between  $-4$  and  $-8$  eV. Upon exposure to 400L O<sub>2</sub>, the characteristic oxygen-derived peak at  $E_i = -1.5$  eV is observed (see trace b). This sample shows a clear ( $4 \times 1$ )O LEED pattern. Note that the intensity of the O-peak is almost doubled at  $\bar{Y}$  when the ( $2 \times 1$ )O structure is saturated at 2000L O<sub>2</sub>. The spectra labelled c, d and e show the influence of preadsorbed atomic chlorine on the subsequent

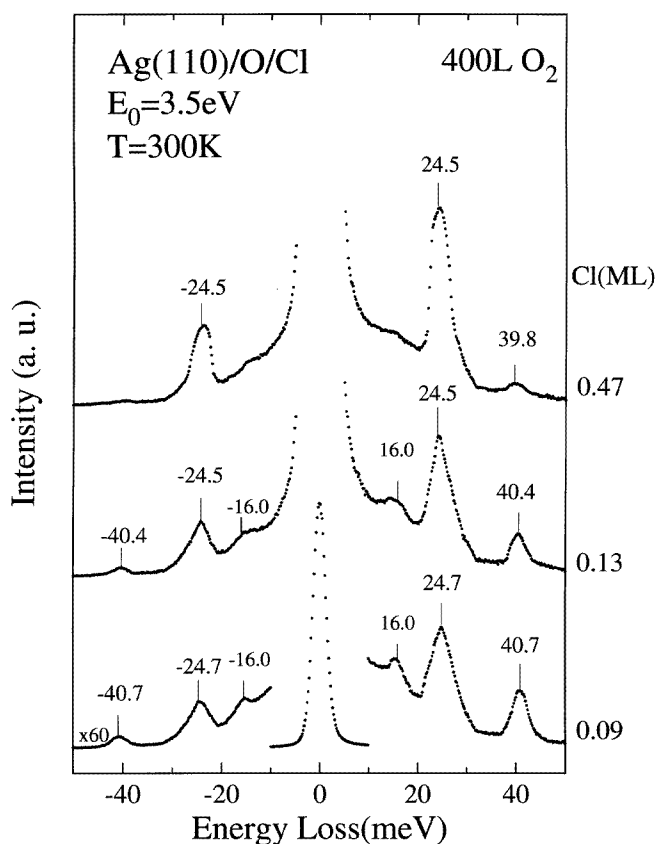


**Figure 4.** Angle-resolved photoelectron spectra collected using HeI photons at an electron emission angle of  $\theta = 23^\circ$  along  $\Gamma\bar{Y}$  (the bulk [001] direction). The initial state energy is referred to the Fermi edge of the Ag(110) substrate. From bottom to top: (a) clean Ag(110), S indicates emission due to a satellite of the light source; (b) after exposure to 400L  $O_2$ , (c,d,e), after different precoverages with atomic chlorine as indicated and subsequent exposure to oxygen as indicated. At  $\theta = 23^\circ$  the feature at  $E_i = -1.5$  eV is located just at the  $\bar{Y}$  point of the surface Brillouin zone.

dissociative chemisorption of oxygen at room temperature. Already 0.06ML of preadsorbed Cl has reduced the intensity of the O peak, although the oxygen exposure was 400L in both cases b and c. Precoverage with 0.12ML of Cl reduces the O-peak further (trace d), even at an exposure to  $O_2$  of 3000L. Finally, at  $c_{Cl} = 0.24$ ML, no oxygen adsorption can be monitored at all. These data therefore strongly support the interpretation given above of the HREELS data: precoverage with Cl above  $c_{Cl} = 0.17$ ML completely blocks dissociative oxygen adsorption. Also, the energy position of the oxygen-derived peak does not shift with  $c_{Cl}$  within the experimental accuracy of  $\pm 0.1$  eV. This is a clear fingerprint of domains exclusively covered by O–Ag–O chains. Simultaneously with decreasing intensity of the O peak in figure 4, we observe the rather broad Cl-derived ‘antibonding’ feature labelled Cl. Its energy shift with Cl coverage and its intensity are not modified by the exposure to  $O_2$ .

We have also tried the reversed sequence. The clean surface was exposed to oxygen first and subsequently to chlorine. Typical HREELS results are summarized in figure 5. In all three spectra the oxygen exposure at 400L produced a well-resolved ( $4 \times 1$ )O LEED pattern. Then different amounts of Cl were adsorbed as indicated on the right of the figure. As is evident from these data, increased Cl coverage causes decreasing intensity of the characteristic oxygen vibration at about 40 meV. We take this as a clear evidence that pre-adsorbed oxygen is removed by chlorine. This is also seen very clearly in the XPS intensities of the O(1s) core level (not reproduced). Our conclusion is in



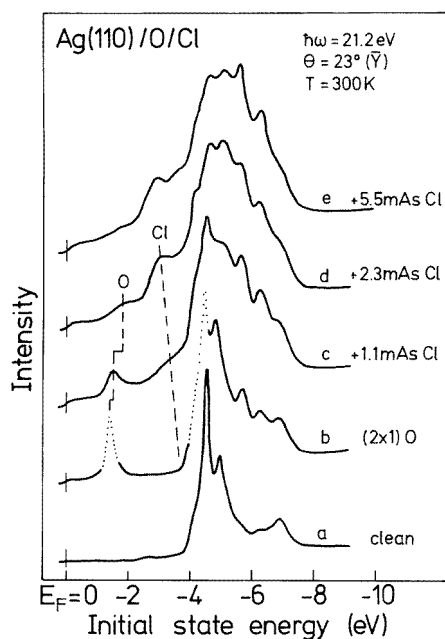


**Figure 5.** High-resolution electron energy loss (and gain) spectra obtained from a Ag(110) surface that was precovered with 400L of O<sub>2</sub>—this induces the (4 × 1)O reconstruction—and subsequent exposure to different amounts of chlorine as indicated at the right side frame.

agreement with the work of Rovida *et al* [1]: these authors first prepared the saturated Ag(110)(2 × 1)O reconstruction. After exposure of this surface to dichloroethane, the same ultimate conditions of the surface were obtained as for the direct exposure of clean Ag(110) to dichloroethane, and no desorption of oxygen could be observed in TDS.

Figure 5 is also compatible with a compression of the oxygen-covered areas as proposed already from the results of figures 1–3. The (4 × 1)O precoverage is characterized by  $\hbar\omega = 39.8$  meV for the O–Ag stretching vibration [12]. The lowest trace in figure 5 indicates a shift to  $\hbar\omega = 40.7$  meV after adsorption of 0.09ML of chlorine. Without coadsorbed Cl,  $\hbar\omega = 40.7$  meV is characteristic [12] for oxygen overlayers between (3 × 1) and (2 × 1). In addition the photon loss, observed around  $\hbar\omega = 16$  meV in figure 5, is a fingerprint of (3 × 2)O [12].

Finally figure 6 reproduces photoelectron spectra, again taken under conditions where the oxygen peak of (2 × 1)O at  $E_i = -1.5$  eV is located just at the  $\bar{Y}$  point ( $\theta = 23^\circ$  along  $\Gamma K L U$ ). The clean surface (trace a) was first covered by a saturated (2 × 1)O overlayer (see trace b). After subsequent exposure to Cl we observe two characteristic features at initial state energies between  $E_F$  ( $E_i = 0$ ) and  $E_i = -4$  eV: First, as expected, a characteristic Cl peak develops. Its energy shift and intensity variation are the same as those observed on



**Figure 6.** Angle-resolved photoelectron spectra collected under the same conditions as for figure 4. From bottom to top: (a), clean Ag(110); (b), after exposure to oxygen and appearance of the  $(2 \times 1)\text{O}$  added row reconstruction; (c,d,e), the Ag(110)  $(2 \times 1)\text{O}$  surface was exposed to different amounts of chlorine. Some data points are reproduced in trace b to indicate the statistical accuracy of all of our spectra. Exposures to chlorine in units of mAs translate to coverage of (trace c) 0.1ML, (d) 0.2ML and (e) 0.4ML, respectively.

Ag(110) which is not precovered. Second, as indicated also in the results of figure 5, the oxygen-peak loses intensity. Third, the oxygen peak broadens and shifts with increasing Cl exposure. This is clearly different when compared with the reverse adsorption sequence, see figure 4. We take the shift of the oxygen peak in figure 6 as a fingerprint for the destruction of the O–Ag–O chains by the adsorption of chlorine. The more electronegative Cl atoms probably attract considerable charge from the Ag atoms in the O–Ag chains. This tends to loosen the bond between O and Ag, oxygen desorbs and the former  $(2 \times 1)\text{O}$  reconstruction is removed.

#### 4. Summary and conclusions

All our experimental results are fully consistent with earlier work of other authors and may be consistently interpreted by some simple assumptions: on Ag(110) at room temperature Ag atoms as well as atoms of both oxygen and chlorine are highly mobile. After the exclusive adsorption of oxygen, the Ag atoms diffuse rapidly over terraces and equally mobile O atoms form linear O–Ag–O–Ag chains along the [001] direction, i.e. the well known  $(n \times 1)\text{O}$  added row reconstruction [7]. Also the dissociative chemisorption of chlorine occurs disordered at coverages below about 0.3ML, while at coverages up to 0.5ML a well-ordered  $(2 \times 1)\text{Cl}$  overlayer is observed [6]. All experimental evidence [18–20] indicates that at all coverages between zero and half a monolayer the Cl atoms sit above the trough atom in a pseudo-four-hole hollow coordination, without induction of a severe

reconstruction of the substrate. Preadsorbed Cl at low coverages leaves a sufficiently large substrate area to dissociate arriving O<sub>2</sub> molecules. After dissociation, the oxygen atoms couple to diffusing Ag adatoms and form O–Ag–O chains of the ( $n \times 1$ ) added-row type. However, as compared with the row-density  $n$  observed at identical exposures in the absence of chlorine, now  $n$  appears to be smaller, i.e. the rows are probably somewhat compressed by preadsorbed Cl. In agreement with earlier information [17] all our results indicate the coexistence of domains with either ( $n \times 1$ )O chains or domains covered with atomic chlorine. Preadsorbed Cl at coverages  $\gtrsim 0.2\text{ML}$  completely blocks oxygen adsorption. We conjecture that two mechanisms are responsible for that: increased Cl coverage does not leave enough Ag atoms free to dissociate O<sub>2</sub>, and simultaneously does not allow sufficient mobility of both the oxygen and silver atoms to meet and form added rows. Our HREELS data do not give evidence for an electronic coupling between Cl and O. In particular we do not see that the presence of Cl significantly affects the Ag–O interactions, as suggested in [1]. We therefore propose purely steric effects to be effective. In the opposite case, the Cl-adsorption on oxygen-precovered Ag(110), we clearly see that the oxygen gets driven off, and the UPS-results indicate a successive dissolution of the ( $2 \times 1$ )O added rows. We suggest that this destructive effect relates to chlorine's role as an electronegative adsorbate in withdrawing electron density from the chains and thereby breaking the O–Ag bonds. With preadsorbed oxygen in chains, diffusion of arriving Cl atoms into separate domains and compression of the O–Ag–O chains is inhibited for steric reasons.

## Acknowledgments

Our work is continuously supported by the Deutsche Forschungsgemeinschaft (DFG). FS thanks the Otto-Braun-Stiftung for a grant. We also thank K Kleinherbers for taking some relevant UPS data in an early stage of this investigation.

## References

- [1] Rovida G, Pratese F and Ferroni E 1976 *J. Catalysis* **41** 140
- [2] Marbrow R A and Lambert R M 1978 *Surf. Sci.* **71** 107
- [3] Kitson M and Lambert R M 1981 *Surf. Sci.* **110** 205
- [4] Au C-T, Singh-Boparai S and Roberts M W 1983 *J. Chem. Soc. Faraday Trans. I.* **79** 1779
- [5] Campbell C T and Paffett M T 1984 *Appl. Surf. Sci.* **19** 28
- [6] Jones R G 1988 Halogen adsorption on solid surfaces *Progr. Surf. Sci.* **27** 25
- [7] Besenbacher F and Norskov J K 1993 *Progr. Surf. Sci.* **44** 5
- [8] Prince K C, Paolucci G and Bradshaw A M 1986 *Surf. Sci.* **175** 101
- [9] Tjeng L H, Meinders M B and Sawatzky G A 1991 *Surf. Sci.* **236** 341
- [10] Canepa M, Cantini P, Mattera L, Terreni S and Valdenazzi F 1992 *Phys. Scr. T* **41** 226
- [11] Vattuone L, Valbusa U and Rocca M 1994 *Surf. Sci.* **317** L1120
- [12] Stietz F, Pantförder A, Schaefer J A, Meister G and Goldmann A 1994 *Surf. Sci.* **318** L1201
- [13] Canepa M, Salvieta M, Traverso M and Mattera L 1995 *Surf. Sci.* **331–333** 183
- [14] Peng M R and Rentt-Robey J E 1995 *Surf. Sci.* **336** L755
- [15] Stietz F, Meister G, Goldmann A and Schaefer J A 1995 *Surf. Sci.* **339** 1
- [16] Kleinherbers K K, Janssen E, Goldmann A and Saalfeld H 1989 *Surf. Sci.* **215** 394
- [17] Hinzert H, Kleinherbers K K, Janssen E and Goldmann A 1989 *Appl. Phys. A* **49** 313
- [18] Stietz F, Elbe A, Meister G, Schaefer J A and Goldmann A *Surf. Sci.* in press
- [19] Holmes D J, Panagiotides N, Dus R, Norman D, Lambie G M, Barnes C J, Della Valle F and King D A 1987 *J. Vac. Sci. Technol. A* **5** 703
- [20] Lambie G M, Brooks R S, King D A and Norman D 1989 *Phys. Rev. Lett.* **62** 2569
- [21] Ibach H 1991 *Electron Energy Loss Spectrometers (Springer Series in Optical Sciences 63)* (Berlin: Springer)

- [22] Landolt-Börnstein 1994 *New Series III* Vol 24b (Berlin: Springer) p 150
- [23] Kramer H M and Bauer E 1981 *Surf. Sci.* **107** 1
- [24] Westphal D and Goldmann A 1983 *Surf. Sci.* **131** 113
- [25] Sexton B A and Madix R J 1980 *Chem. Phys. Lett.* **76** 294
- [26] Stuve E M, Madix R J and Sexton B A 1982 *Chem. Phys. Lett.* **89** 48