Angle-resolved photoemission study of oxygen-adsorbed Cr(110)

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The electronic state of oxygen adsorbed on a Cr(110) surface at 80 K has been studied by angle-resolved photoemission spectroscopy with synchrotron radiation. Dissociative chemisorption occurs up to ~ 2 L, and then oxidation starts at ~ 4 L, leading to the formation of a disordered Cr_2O_3 layer. An emission at ~ 7.5 eV below the Fermi energy, being attributable to a chemisorbed O_2 molecule, was observed at above ~ 20 L. Dispersion effects on the O $2p$-derived levels were found for the Cr(110)p(4×2)-O and faceted Cr(110)-O surfaces produced by annealing.

I. INTRODUCTION

The interaction of oxygen with a Cr(110) surface has been studied extensively by using various surface science techniques.[1-6] Recently, Shinn, and Madey[7,8] reinvestigated this system at 300 and 120 K, and they observed a new p(4×2)-O overlayer and the well-known faceted Cr(110)-O structure,[2-6] but not previously reported c(3×1)-O overlayer.[3] The p(4×2)-O phase, associated with oxygen coverage of $\Theta = \frac{1}{8}$, was reported to be produced after 1.2–1.7 L exposure at 300 K (Ref. 7) or after ~ 1 L exposure at 120 K and subsequent annealing at 300 K.[8]

In our previous paper[1] was reported a study of oxygen chemisorption and initial oxidation of Cr(110) at 300 K by using mainly electron-energy-loss spectroscopy (EELS) (electronic transitions). In the present paper, an angle-resolved photoemission spectroscopy (ARUPS) study of the same system at 80 K is reported. We find (1) dissociative chemisorption up to ~ 2 L, (2) oxidation above ~ 4 L, (3) chemisorption of molecular O_2 above ~ 20 L, and (4) energy-band dispersion in the O $2p$-derived levels for the Cr(110)p(4×2)-O and faceted Cr(110)-O surfaces.

II. EXPERIMENT

Details of the experimental setup and other related procedures were described elsewhere.[1,9-12] The clean Cr(110) surface, showing a sharp p(1×1) low-energy electron diffraction (LEED) pattern, was prepared by the repeated Ar$^+$-ion sputtering (0.6–1.5 kV) and annealing

(870–1150 K) cycles. No impurities were detectable by Auger electron spectroscopy (estimated to be less than ~ 0.01 monolayer). With liquid-N_2 cooling, the sample could be cooled to ~ 80 K. Oxygen was admitted at 1×10^{-8}–5×10^{-7} Torr and at the sample temperature of 80 K into the vacuum chamber through a variable-leak valve. The ARUPS measurements were done at the Photon Factory, National Laboratory for High Energy Physics, using a 150° spherical-sector-type electron energy analyzer with an acceptance angle of ±1°. Total experimental resolution was 0.1–0.2 eV. Throughout the whole experiment, the surface component of the vector potential (A) of the incident light was in the [001] azimuth ($A_{\parallel}$ along [001]). The base pressure in the system was 1×10^{-10} Torr.

III. RESULTS AND DISCUSSION

For 80 K adsorption, LEED shows only the p(1×1) pattern, which becomes weak and diffuse with exposure, but shows no ordered oxygen overlayer structure on Cr(110) throughout the exposure range up to 50 L, in agreement with the results obtained at 120 K by Shinn and Madey.[8]

Figure 1 shows the change in the normal-emission ARUPS spectrum of the Cr(110) surface measured at a photon energy of $h\nu = 30$ eV and at a light incidence angle of $\theta_i = 25°$ (dots) and $\theta_i = 60°$ (solid lines) from the surface normal as a function of oxygen exposure at 80 K. The binding energy (E_B) is referred to the Fermi energy (E_F) of the clean Cr(110) substrate. The clean-surface spectrum shows three peaks at ~ 0.3, ~ 0.9, and ~ 7.0 eV,

which are ascribed to the emission from the Σ_1-symmetry surface resonance, $3d$-like $\Sigma_1 + \Sigma_3$ bulk bands, and $4s$-like Σ_1 bulk band, respectively, as has been discussed in Ref. 12. The 0.3- and 0.9-eV peaks were considerably weakened by oxygen exposure. However, these substrate emission peaks are seen even after 50 L exposure. At this stage, according to Ref. 1, the Cr_2O_3-like oxide with a mean thickness of ~ 20 Å is formed. This suggests that the islands of the oxide overlayer are formed (see also Ref. 7).

For oxygen exposures less than ~ 2 L, the 7-eV $4s$-band emission disappeared, while a new feature came out at ~ 6.2 eV and was developed with increasing exposure. Identical spectra were obtained for the adsorption (< 2 L) at 300 K, where dissociative chemisorption occurs.[1,7] This feature, being attributed to the emission from the O $2p$-derived levels, is characteristic of dissociatively chemisorbed oxygen (simple addition type) on Cr(110). Beyond ~ 4 L, the spectra were significantly changed from those for chemisorption stage below ~ 2 L. That is, a sharp peak at ~ 1.7 eV appeared at ~ 4 L, a broad peak
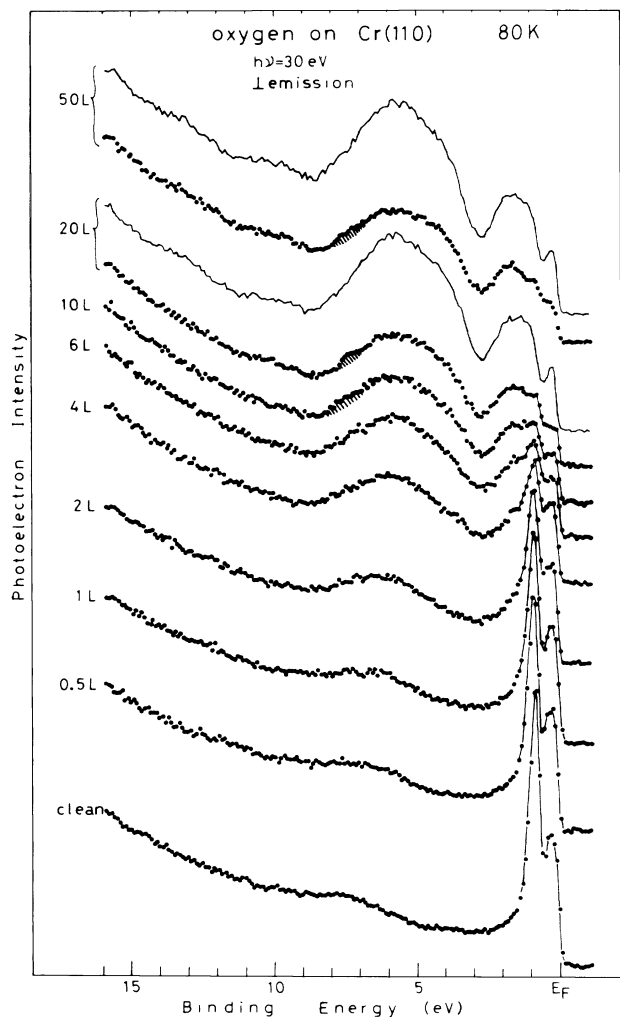

FIG. 1. Change in the normal-emission spectrum of the Cr(110) surface as a function of oxygen exposure at 80 K. The photon energy is $h\nu = 30$ eV and the light incidence angles from surface normal are $\theta_i = 25°$ (dots) and $\theta_i = 60°$ (solid lines).

at ~ 10 eV was developed from ~ 6 L, a shoulder feature at ~ 7.5 eV (shaded area) appeared at ~ 10 L which is clearly seen in the $\theta_i = 25°$ spectra, and a weak and broad peak can be seen at ~ 13 eV above ~ 20 L. In addition, the 6.2-eV feature characteristic of chemisorbed oxygen was replaced by a strong but broad feature centered at ~ 5.5 eV which may contain a shoulder at ~ 4.5 eV. Except for the surviving substrate emission peaks at 0.3 and 0.9 eV and the O-induced features at 7.5 and 13 eV (discussed later), the spectrum obtained at above 20 L is found to be very similar to the previously reported one of Cr_2O_3.[13] Previous studies[1-6] showed that the exposure of Cr(110) to oxygen leads to the formation of Cr_2O_3 oxide as a final product at, typically, ~ 300 K.

Let us discuss the oxide spectrum obtained at above 4 L in Fig. 1. The 1.7-eV feature represents the Cr $3d$-derived emission, the ~ 4.5- and ~ 5.5-eV features represent the O $2p$-derived emission and the 10-eV feature is ascribed to a valence-band satellite in Cr_2O_3 (see Ref. 13 where the spectrum is interpreted in terms of a simple ligand-field theory). Similar satellites have also been observed in NiO,[11,13] CoO,[14] MnO,[14] and Ti_2O_3.[14] The weak feature at ~ 7.5 eV clearly seen above 10 L (shaded area) can be considered to be due to a chemisorbed O_2 molecule, in accord with the results of a vibrational EELS study of oxygen adsorption on Cr(110) at 120 K in Ref. 8 which show the evidence for a superoxidelike molecular O_2 adspecies with a formal bond order of ~ 1.3 even at ~ 0.2 L because of its high surface sensitivity.[15] The 7.5-eV feature was found to disappear after heating to 570–770 K (see below). This is explained by the finding of Ref. 8 that a molecular O_2 adspecies is gone by warming the sample to ~ 200 K. In the 1 L spectrum of Fig. 1 the ~ 6-eV feature reveals a double structure, which might indicate existence of a molecular O_2 adspecies at low exposures in accord with the results of Ref. 8. However, we think that this is not the case. The double structure can be ascribed to noise effect. Note that no evidence for a molecular O_2 adspecies is apparent in the 2–6 L spectra of Fig. 1. It may be concluded that at this temperature dissociative adsorption predominates and that a molecular O_2 adspecies is preferentially formed on top of dissociatively chemisorbed oxygen but not on the bare-metal substrate as has been reported previously,[8] though the present data and those of Ref. 8 are insufficient to determine whether or not a molecular O_2 adspecies exists on Cr(110) at 80~120 K in the limit of zero coverage.

Gland *et al.*[16] has reported a photoemission spectrum of a chemisorbed peroxidelike O_2 species with a bond order of ~ 1.1 on Pt(111) at 100 K, which is characterized by one emission at ~ 8 eV. They attributed the 8-eV emission to the π_g orbital of molecular oxygen which is filled by an electron transfer from the surface to the adsorbed species. The bond order of 1.3 and 1.1 corresponds to ~ 3.4 and ~ 3.8 electrons occupied in the π_g orbital, respectively. For the present purpose, we may neglect the difference between superoxide- and peroxide-like species, then we ascribe the 7.5-eV feature in our spectrum to the π_g orbital of molecular oxygen.

The interpretation of the 13-eV feature is somewhat difficult. There are two possibilities for interperting this feature, i.e., new valence-band satellite in Cr_2O_3 or the $3\sigma_g$ level of a physisorbed O_2 molecule as has been observed on Ni(110).[11]

Figure 2 shows off-normal emission spectra of a Cr(110)p(4×2)-O surface along the [001] azimuth measured at $h\nu=30$ eV and $\theta_i=60°$ (dots). The normal-emission spectrum measured at $\theta_i=25°$ is also shown at the bottom (solid line). The Cr(110)p(4×2)-O surface was prepared by ∼1.5 L exposure at 80 K and subsequent annealing at 300 K. Reference 8 showed that a molecular O_2 adspecies coexists with dissociatively chemisorbed oxygen adatoms on Cr(110) only below ∼200 K. Therefore, no molecular O_2 adspecies should exist on this p(4×2)-O surface. Two O $2p$-derived features are observed at ∼6.2 and ∼7.4 eV for $\theta_i=25°$, while the 7.4-eV feature is reduced in intensity as compared with the 6-eV feature for $\theta_i=60°$. Thus the two features at ∼6.2 and ∼7.4 eV can be ascribed to the emission from the
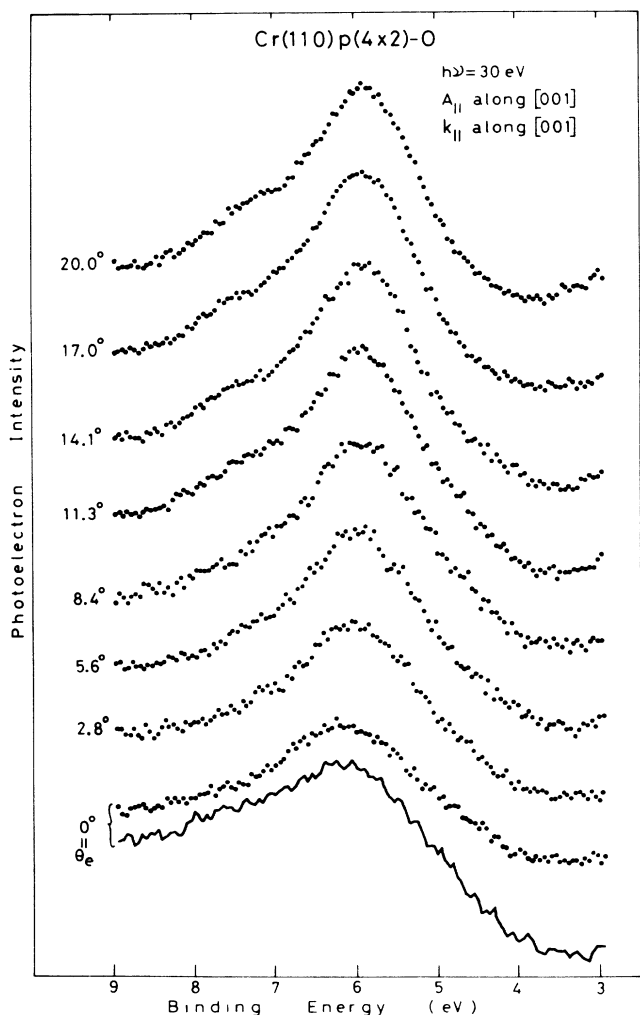
O p_z and O p_x levels, respectively (the z axis is normal to the surface and the x axis is along the [001] azimuth). As seen in Fig. 2, the 7.4-eV feature does not exhibit measurable dispersion along the [001] azimuth, while the 6.2-eV feature shows small dispersion. The measured energies of the O $2p$-derived features for the p(4×2)-O phase could be plotted in an E versus $k_\parallel$ diagram via

$$k_\parallel = [(2m/\hbar^2)E_{kin}]^{1/2}\sin\theta_e ,$$

where E_{kin} is the measured kinetic energy and θ_e the emission angle from the surface normal. The results are shown in Fig. 3(a). In the figure, the surface Brillouin zone of the Cr(110)p(4×2)-O is also shown (the real space model for p(4×2)-O is illustrated in Fig. 11 of Ref. 7). The upper band at ∼6 eV disperses upward by ∼0.3 eV along $\bar{\Gamma}\bar{X}$ and the dispersion is symmetric about $\bar{X}$. This upward dispersion of the O p_z band can be explained by a simple tight-binding-model argument for an isolated oxygen monolayer, since this model predicts upward dispersion for the p_z-type level (see Refs. 9 and 11).

As previously reported,[1-7] streaking parallel to the [1$\bar{1}$0] azimuth was observed by LEED after 10–20 L oxygen exposure at 80 K and subsequent heating at ∼770 K [our LEED pattern is identical with one illustrated in Fig. 13(b) of Ref. 7]. This streaking is caused by the faceting of the Cr(110) surface, arising from the formation of (100) and (010) microfacets.[1-7] Figure 4 shows off-normal emission spectra of the faceted Cr(110)-O surface along the [001] azimuth measured at $h\nu=30$ eV and $\theta_i=60°$ (dots). The $\theta_i=25°$ normal-emission spectrum is also shown (solid line). If the $\theta_e=0°$ spectrum for the faceted Cr(110)-O surface is shifted uniformly by ∼0.8 eV towards higher binding energies, energies of the
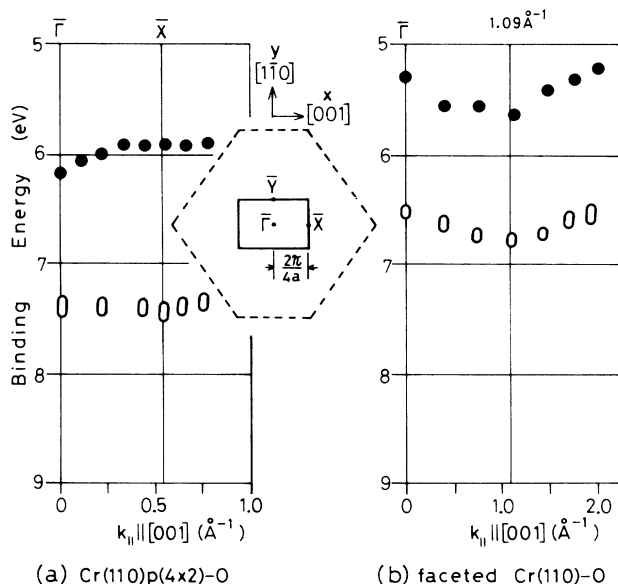

FIG. 2. Off-normal emission spectra for Cr(110)p(4×2)-O in the [001] azimuth measured at $h\nu=30$ eV and 80 K: $\theta_i=60°$ (dots) and $\theta_i=25°$ (solid line).

FIG. 3. Measured dispersion $E(k_\parallel)$ of the O $2p$-derived bands for (a) Cr(110)p(4×2)-O and (b) faceted Cr(110)-O (see text) in the [001] azimuth. The surface Brillouin zone for Cr(110)p(4×2)-O is also shown.
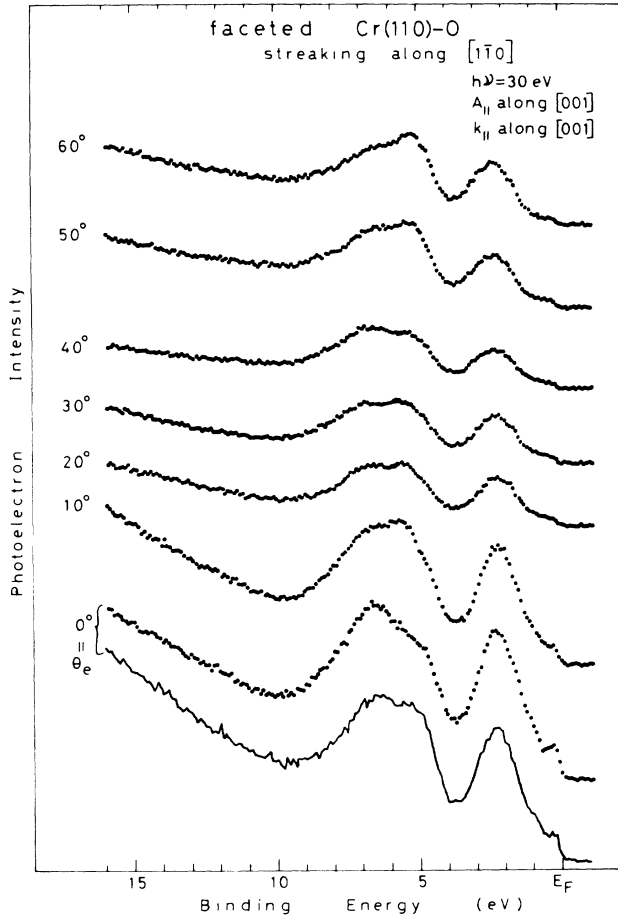
FIG. 4. Off-normal emission spectra for the faceted Cr(110)-O surface (see text) in the [001] azimuth measured at $h\nu = 30$ eV and 80 K: $\theta_i = 60°$ (dots) and $\theta_i = 25°$ (solid line).

dence of the normal-emission spectra, two O $2p$-derived features at ~ 5.3 and ~ 6.6 eV can be assigned to the p_x and p_z emissions, respectively. Furthermore, from Fig. 4 we can directly obtain the energy dispersion $E(k_\parallel)$ of the O $2p$-derived bands along the [001] azimuth (perpendicular to the streaks) for the faceted surface, as shown in Fig. 3(b). We find that along the [001] azimuth the upper band (p_x type) disperses downward by ~ 0.4 eV with increasing $k_\parallel$ up to 1.09 Å^{-1} and then upward from $k_\parallel = 1.09$ Å^{-1} to $k_\parallel = \sim 2$ Å^{-1}. Note that the dispersion of the upper band is symmetric about $k_\parallel = 1.09$ Å^{-1} which is 2π times the inverse streaking spacing (i.e., π/a, where a is the lattice constant of 2.884 Å). The lower band (p_z type) shows similar but smaller dispersion along the same azimuth. Since satellite features characteristic of Cr_2O_3 oxide are absent in the spectrum of the faceted surface, we can say that this surface does not possess the character of Cr_2O_3 oxide, but possibly of CrO-like oxide. CrO has formally four $3d$ electrons per cation, resulting in a large $3d$ contribution as compared with the case of Cr_2O_3 which contains only Cr^{3+} ($3d^3$) ions. The change in the $3d$ electron number influences the satellite energy as has been observed in Cu compounds.[17]

IV. CONCLUSION

Angle-resolved photoemission spectra of oxygen adsorbed on Cr(110) at 80 K indicate the presence of both atomic and molecular oxygen adspecies, in agreement with a very recent study of the same system.[8] For the Cr(110)p(4×2)-O and faceted Cr(110)-O surfaces produced by annealing, we measured the band dispersion of the O $2p$-derived levels along a symmetry direction of each surface Brillouin zone. The UPS spectra suggest that the faceted Cr(110)-O surface does not possess the character of Cr_2O_3 oxide, but possibly of CrO-like oxide.

oxygen-induced features at lower E_B (i.e., except for the surviving substrate emission at ~ 0.3 and ~ 0.9 eV) are in agreement with the values in the oxide spectrum obtained after 20–50 L oxygen exposures at 80 K (see Fig. 1). The major difference between the two is that features corresponding to the 7.5-, 10-, and 13-eV peaks in the oxide spectrum are absent in the present case. Note also that the $3d$ emission feature is increased in this case than in the Cr_2O_3 case (see Figs. 1 and 4). From the θ_i depen-

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