

Ultrathin Chromium Oxide Films on the W(100) Surface

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Ultrathin chromium oxide films were prepared on a W(100) surface under ultrahigh-vacuum conditions and investigated in situ by X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and low-energy electron diffraction. The results show that, at Cr coverage of less than 1 monolayer, CrO₂ is formed by oxidizing pre-deposited Cr at 300–320 K in $\sim 10^{-7}$ mbar oxygen. However, an increase of temperature causes formation of Cr₂O₃. At Cr coverage above 1 monolayer, only Cr₂O₃ is detected.

1. Introduction

Research on metal oxide surfaces has been carried out extensively due to their importance in various areas and applications such as gas sensors, heterogeneous catalysis, metal ceramic interfaces, and solid-state electronic devices. For example, chromium(III) oxide (Cr₂O₃) is widely used as a catalyst in many applications and as a constituent of anti-corrosive materials.^{1–4} Chromium dioxide (CrO₂) is a half-metallic ferromagnetic material with a Curie temperature of about 390 K. These electronic and magnetic properties have been predicted by band-structure calculations^{5,6} and have also been demonstrated by spin-resolved photoemission⁷ and superconducting point-contact experiments,⁸ which have shown additionally that CrO₂ has a spin polarization at the Fermi level of close to 100%. Furthermore, according to local-density calculations, the CrO₂(001) surface has the same half-metallic characteristics as the bulk.⁹ These studies also suggest that CrO₂ films maintain the spin polarization character of the bulk. Due to its special spin polarization properties, CrO₂ is an attractive material for spin transport. One novel application of CrO₂ as a source for spin injection was demonstrated by its use as a tip material in the earliest substantial report of spin-polarized scanning tunneling microscopy.¹⁰ On the other hand, a recent study shows that the proposed half-metallic materials such as chromium dioxide suffer from fundamental limitations.¹¹

Unfortunately, CrO₂ is metastable at atmospheric pressure and has been shown to irreversibly reduce to Cr₂O₃ at temperatures between 250 and 460 °C.^{7,12–14} This imposes the demand for rigorous synthesis conditions and also limits the potential applications of CrO₂. For example, suitable growth conditions were not obtained for preparation of single-phase CrO₂ by molecular beam epitaxy.¹⁵ However, CrO₂ films were prepared successfully on TiO₂ and Al₂O₃ by high-pressure thermal decomposition¹² and by chemical vapor deposition^{16,17} using CrO₃ or CrO₂Cl₂ as a precursor. Laser-initiated chemical vapor deposition was also used to grow chromium oxide films on Si(111) and Al₂O₃(0001) substrates by oxidation of Cr(CO)₆ in oxygen and argon environments,^{18,19} respectively. Very few

studies of the growth of CrO₂ on metals have been reported. To address this problem, we note that ultrathin films of TiO₂ have been prepared on a W(100) surface²⁰ in ultrahigh vacuum. This suggests the possibility of growing other technologically important rutile oxides, e.g., CrO₂, which are not readily available.

In this paper, we report on the growth, transformation, and decomposition of ultrathin chromium oxide films on a W(100) substrate. Cr films were grown at room temperature (RT) by metal vapor deposition in ultrahigh vacuum with subsequent oxidation at low pressure. Previously, Cr was found to grow pseudomorphically on the W(100) surface between 100 and 400 K.²¹ The chromium and chromium oxide films that are formed here were characterized in situ by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and low-energy electron diffraction (LEED). We find that CrO₂ or Cr₂O₃ can be formed at Cr coverage of 1 monolayer or less on W(100), depending upon the oxidation conditions. However, only Cr₂O₃ is formed when a Cr coverage of more than 1 monolayer is oxidized.

2. Experimental Details

The experiments were carried out in an ultrahigh-vacuum system (ESCA-LAB 5, VG Scientific Ltd., U.K.) consisting of two chambers. The analysis chamber is equipped with reverse view optics for LEED, dual-anode X-ray sources (Mg and Al) for XPS, and a He(I) source for UPS. The preparation chamber contains an Ar⁺ sputtering gun, an electron-beam heater for sample annealing, and various metal deposition and gas sources. The base pressure was 5×10^{-9} mbar in the analysis chamber and 2×10^{-8} mbar in the preparation chamber. The XP spectrometer was carefully calibrated by a standard method using pure metallic Au (4f_{7/2}, 84.0 eV), Ag (3d_{5/2}, 368.3 eV), and Cu (2p_{3/2}, 932.7 eV).

The W(100) sample (10 mm diameter disk with a thickness of 0.5 mm) was fixed to a Mo holder with Ta foil. The W substrate could be heated to 2000 K using electron bombardment. A W–5% Re/W–26% Re thermocouple was spot-welded on a support close to the sample holder for monitoring temperature. Prior to Cr deposition, the W(100) substrate was cleaned by heating to ~ 2000 K and then annealed at ~ 1200 K in 8×10^{-8} mbar O₂ to remove impurities, predominantly

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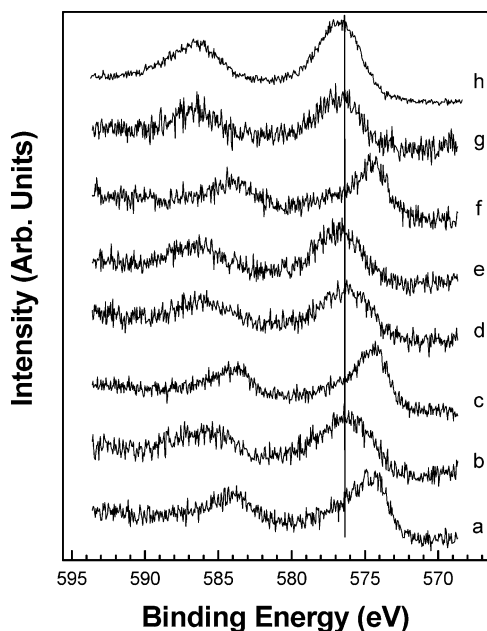


Figure 1. XPS of Cr $2p_{3/2}$ and Cr $2p_{1/2}$: (a) 1 monolayer of Cr on W(100) at RT; (b) after oxidation at $\sim 10^{-7}$ mbar O_2 and ~ 320 K for 5 min; (c) after annealing to 1100 K for 5 min; (d) after oxidation at $\sim 10^{-7}$ mbar O_2 and ~ 320 K for 5 min; (e) after oxidation at $\sim 10^{-7}$ mbar O_2 and 800 K for 5 min; (f) after annealing to 1100 K for 5 min; (g) after oxidation at $\sim 10^{-7}$ mbar O_2 and 800 K for 5 min; (h) analytically pure Cr_2O_3 powder. The solid line indicates the peak position for Cr_2O_3 .

carbon, followed by flashing to ~ 2000 K to remove surface oxides. After several repeated cycles of this treatment, a well-ordered sharp (1×1) LEED pattern was obtained, and no impurities were detected with XPS except a small amount of residual oxygen.

The chromium source was made from a pure Cr ($>99.9\%$) block tightly wrapped with a tungsten wire and was thoroughly degassed before deposition. Chromium oxide films were grown on the W(100) surface by evaporation of Cr at 320 K followed by oxidation of the pure Cr film at 10^{-7} – 10^{-8} mbar oxygen pressure at several indicated temperatures. In agreement with earlier work,²¹ we find that Cr growth at 320 K produces only a (1×1) LEED pattern, indicating pseudomorphic films. The Cr deposition rate was determined to be 0.2 monolayer/min from measurements of the Cr/W XPS intensity ratio versus the Cr deposition time.

3. Results and Discussion

The oxidation of Cr films of various thickness on W(100) was carried out at 320 and 800 K. Figures 1–4 show the XPS and UPS results at various stages of oxidation of 1 monolayer Cr films. Initially, the XP spectrum of the substrate shown in Figure 2a matches the characteristics of metallic tungsten quite well.^{15,22} However, a very small amount of residual oxygen on the tungsten surface is detected before Cr deposition. After 1 pseudomorphic monolayer of Cr is deposited on the W(100) surface at RT, the Cr $2p_{3/2}$ core level peak is observed with the binding energy (BE) of 574.3 eV and the distance between the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks is 9.8 eV (Figure 1a), suggesting characteristics of metallic Cr.^{23,24} After exposing ~ 1 monolayer Cr/W(100) to $\sim 10^{-7}$ mbar oxygen at 320 K for 5 min, the Cr $2p_{3/2}$ and $2p_{1/2}$ peaks are shifted to 576.3 and 585.8 eV, respectively (Figure 1b). The peak shape after oxidation is asymmetric and consists of two features at least, which indicates a mixture of chromium oxides. However, the dominant peak at

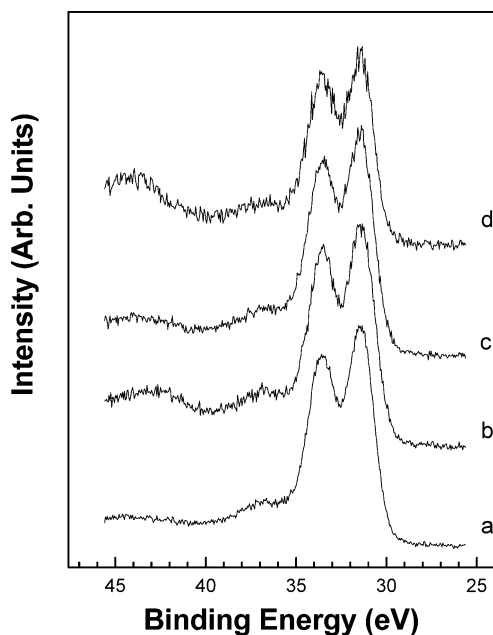


Figure 2. XPS of W 4f: (a) clean W(100) surface; (b) 1 monolayer of Cr on W(100); (c) ultrathin film of Cr_2O_2 on W(100) surface; (d) ultrathin film of Cr_2O_3 on W(100) surface.

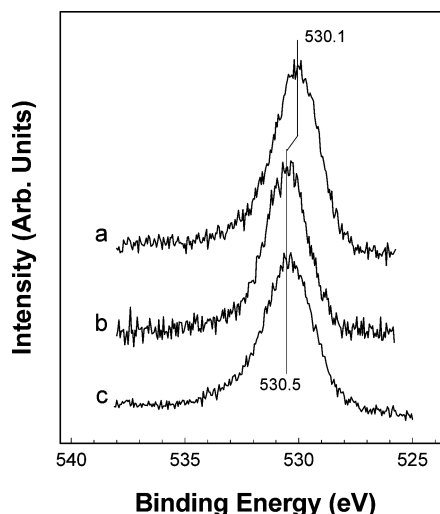


Figure 3. XPS of O 1s: (a) after oxidation of 1 monolayer of Cr on W(100) at $\sim 10^{-7}$ mbar O_2 and ~ 320 K for 5 min; (b) after deposition of ~ 1 monolayer of Cr in $\sim 10^{-8}$ mbar O_2 at RT; (c) from analytically pure Cr_2O_3 powder sample.

576.3 eV reveals mainly the formation of CrO_2 .^{15,24,25} Formation of the CrO_2 film produced no new features in the LEED pattern. The Cr $2p_{3/2}$ and $2p_{1/2}$ peaks shift back to 574.3 and 584.1 eV, respectively, upon annealing the oxidized Cr film at 1100 K for 5 min without oxygen (Figure 1c). This identifies the emergence of pure Cr after the decomposition of CrO_2 . Desorption of Cr from W(100) is known to occur at higher temperatures.²¹ Interestingly, Cr could be oxidized to CrO_2 again at 320 K in $\sim 10^{-7}$ mbar oxygen, as shown in Figure 1d. Further annealing of the ultrathin CrO_2 film in $\sim 10^{-7}$ mbar oxygen at about 800 K for 5 min causes the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks to shift to 576.8 and 586.3 eV (Figure 1e), respectively, resulting from the formation of Cr_2O_3 .^{23,26,27} When the Cr_2O_3 film is annealed at 1100 K for 5 min without oxygen, it decomposes and reverts to pure Cr (Figure 1f). Cr_2O_3 can be formed again by reoxidizing the Cr film at $\sim 10^{-7}$ mbar oxygen and 800 K, as shown in Figure 1g. For comparison, we performed XPS of Cr_2O_3 powder with analytical purity and found the BE of the

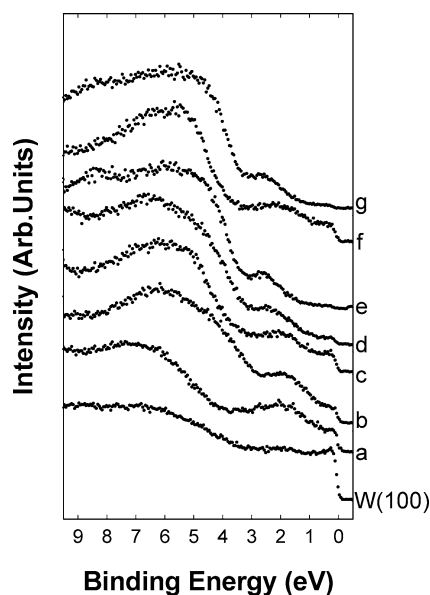


Figure 4. UP spectra following Figure 1: (a) 1 monolayer of Cr on W(100) at RT; (b) after oxidation at $\sim 10^{-7}$ mbar O_2 and ~ 320 K for 5 min; (c) after annealing to 1100 K for 5 min; (d) after oxidation at $\sim 10^{-7}$ mbar O_2 and ~ 320 K for 5 min; (e) after oxidation at $\sim 10^{-7}$ mbar O_2 and 800 K for 5 min; (f) after annealing to 1100 K for 5 min; (g) after oxidation at $\sim 10^{-7}$ mbar O_2 and 800 K for 5 min. The spectrum of a clean W(100) is also given.

Cr $2p_{3/2}$ peak to be 576.8 eV, as shown in Figure 1h. This confirms that the film that was prepared by oxidizing 1 monolayer of Cr/W(100) at 800 K is Cr_2O_3 (Figure 1g). It is noteworthy that bulk Cr_2O_3 is quite stable, with a melting point of 2602 K,²⁸ but the ultrathin Cr_2O_3 film formed on W(100) apparently decomposes or reduces to Cr easily at considerably lower temperature, as indicated in Figure 1f.

The XP spectra of the W 4f core levels are shown in Figure 2 for the various films. No shift of the W 4f peaks is caused by deposition of 1 monolayer of Cr at RT or by the formation of ultrathin films of CrO_2 at 320 K and Cr_2O_3 at 800 K on W(100). This suggests that there is no interaction between chromium or chromium oxides and the substrate or that the interaction is too weak to detect in our experimental setup.

An alternative approach to forming chromium oxides would be to deposit Cr in an oxygen-ambient pressure. Chromium oxide films were grown on the W(100) surface by evaporating Cr in an O_2 ambient of 10^{-6} to 10^{-8} mbar at different temperatures and were also investigated with XPS. The results show that only Cr_2O_3 can be obtained by depositing Cr in ambient oxygen. Figure 3 gives the O 1s XP spectra for the chromium oxide films prepared by the different methods. For the CrO_2 film, the BE of the O 1s core level is 530.1 eV (Figure 3a). This compares to an O 1s BE of 530.5 eV for the film prepared by deposition of ~ 1 monolayer of Cr in $\sim 10^{-8}$ mbar oxygen at RT (Figure 3b). The BE values reported in the literature for Cr_2O_3 range from 530 to 531 eV,²⁹ which brings an uncertainty for qualitative analysis. However, the O 1s BE for the pure Cr_2O_3 powder sample (Figure 3c) measured in our system is 530.4 eV, suggesting that the film prepared by evaporating Cr in an oxygen ambient is Cr_2O_3 (Figure 3b).

UPS is particularly suited to the study of bonding at surfaces. Therefore, the valence bands of the various films were investigated using UPS after each XPS acquisition in order to further distinguish the chromium oxides and to characterize their properties (Figure 4). The UPS of a clean W(100) surface is also shown in Figure 4. The BE in Figure 4 is given with respect

to the Fermi level, E_F . A very broad peak can be seen around 7 eV due to the 2p level of residual oxygen on an otherwise clean W(100) surface. After 1 monolayer of Cr is deposited on the W(100) surface at RT, the Cr 3d peak can be seen with a BE of about 1.9 eV (Figure 3a). A sharp edge at E_F suggests that the Cr film is metallic.^{30,31} After oxidation of ~ 1 monolayer of Cr on W(100) in $\sim 10^{-7}$ mbar oxygen pressure at 320 K for 5 min, a pronounced O 2p peak appears which is shifted toward lower BE compared to the residual oxygen and the Cr 3d peak is shifted to 1.7 eV. The density of states (DOS) at E_F is also diminished, while a sharp edge is retained at E_F after oxidation (Figure 4b), indicating formation of CrO_2 .^{7,9,32} After annealing at 1100 K for 5 min without oxygen, the Cr 3d peak shifts back from 1.7 eV to about 1.9 eV and the DOS at E_F returns to the value of the initially pure Cr film (Figure 4c), indicating the decomposition of CrO_2 to Cr. However, a significant O 2p signal remains in the UPS at ~ 6 eV after annealing at this high temperature. This indicates that the residual surface oxygen is not removed by annealing to 1100 K. Interestingly, the metallic Cr that is regenerated by the decomposition of CrO_2 could be reoxidized at 10^{-7} mbar at 320 K to partially form CrO_2 again as shown in Figure 4d. Further annealing of the ultrathin CrO_2 film in $\sim 10^{-7}$ mbar oxygen at 800 K for 5 min causes the Cr 3d peak to shift to about 2.4 eV (Figure 4e), signaling the formation of Cr_2O_3 .^{23,33} Note that the DOS at E_F is much lower for Cr_2O_3 (Figure 4e) compared to CrO_2 (Figure 4b). Annealing the ultrathin Cr_2O_3 film at 1100 K for 5 min without oxygen resulted in the formation of a film (Figure 4f) that resembles the initially pure Cr film. Further UPS studies proved that this Cr film can be reoxidized to Cr_2O_3 , as seen in Figure 4g. The XPS and UPS spectra presented above suggest that an ultrathin film of CrO_2 can be prepared by oxidizing ~ 1 monolayer of Cr on W(100) at 320 K.

An important question concerns the fate of the oxygen in the CrO_2 films that are formed at RT when these films are decomposed by heating to high temperature. Note that CrO_2 is not thermally stable, having a melting point of ~ 470 K and the onset of decomposition via oxygen loss at ~ 530 K.³⁴ Therefore, it is possible that oxygen is lost from the CrO_2 films directly to the vacuum during heating. It is also possible that the oxygen migrates to the W substrate during heat treatments. The heats of formation of CrO_2 , Cr_2O_3 , WO_2 , and WO_3 are -598 , -1139.7 , -589 , and -842.9 kJ/mol,²⁸ respectively. The difference of heat of formation between CrO_2 and WO_2 is not very big. However, since no change of the W 4f peak was observed in XPS measurements, we conclude that the production of tungsten oxide is not the dominant process. This means that most of the oxygen that is lost during the decomposition of the CrO_2 films escapes to the vacuum.

We have also investigated the effect of varying the initial Cr coverage upon chromium oxide formation. Figures 5 and 6 show the XP and UP spectra, respectively, after oxidation of 0.7–3.5 monolayers thick Cr films in 10^{-7} mbar O_2 at RT. At the lowest coverage, 0.7 monolayer, the BE of the Cr $2p_{3/2}$ peak before oxidation is 574.3 eV (Figure 5a), characteristic of metallic Cr. After oxidation in $\sim 10^{-7}$ mbar O_2 for 5 min at RT, the BE of the Cr $2p_{3/2}$ peak is located at 576.3 eV (Figure 5b). Comparison of these results to the BE of the Cr $2p_{3/2}$ core level reported in the literature^{15,24} indicates that the formation of Cr^{4+} cations occurs upon oxidation of 0.7 monolayer of Cr on W(100). This is the same result that was obtained for oxidation of 1 monolayer of Cr, as discussed above. Oxidation of increasing Cr coverages was performed sequentially in 0.7 monolayer increments. After depositing a coverage increment,

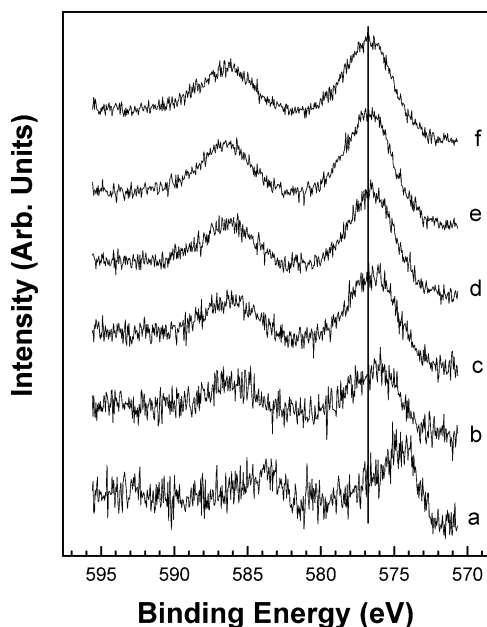


Figure 5. XPS of Cr $2p_{3/2}$ and Cr $2p_{1/2}$: (a) 0.7 monolayer of Cr on W(100); (b) after oxidation at $\sim 10^{-7}$ mbar O_2 and RT for 5 min; (c–f) after oxidation of Cr coverages of 1.4, 2.1, 2.8, and 3.5 monolayers at $\sim 10^{-7}$ mbar O_2 and RT for 5 min, respectively. The solid line indicates the peak position for Cr_2O_3 .

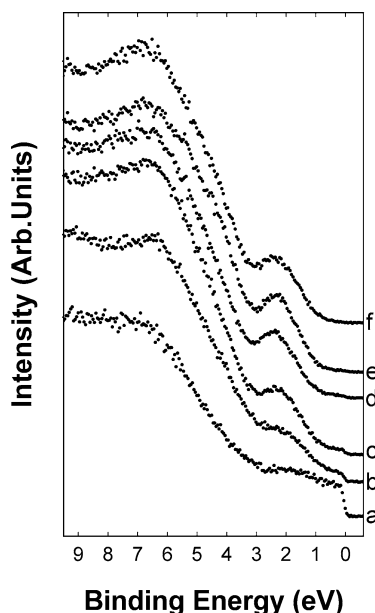


Figure 6. UPS of Cr/W(100): (a) 0.7 monolayer of Cr on W(100); (b) after oxidation at $\sim 10^{-7}$ mbar O_2 and RT for 5 min; (c–f) after oxidation of Cr coverages of 1.4, 2.1, 2.8, and 3.5 monolayers at $\sim 10^{-7}$ mbar O_2 and RT for 5 min, respectively.

oxidation was carried out in $\sim 10^{-7}$ mbar oxygen for 5 min at RT. After each oxidation step, an additional coverage increment was deposited. At 1.4 monolayer Cr coverage, the Cr $2p_{3/2}$ peak is shifted to higher BE, as seen in Figure 5c, indicating formation of Cr_2O_3 . The Cr $2p_{3/2}$ peak is also more symmetric, indicating a more uniform oxide composition. For higher Cr coverages, 2.1, 2.8, and 3.5 monolayers on W(100), the BE of the Cr $2p_{3/2}$ peak clearly indicates formation of Cr_2O_3 (Figure 5d–f, compare to Figure 1h).

UPS was employed after each XPS measurement to monitor the change of the valence band of the films with different Cr coverages. After deposition of about 0.7 monolayer of Cr on the W(100) substrate, the Cr 3d peak is broad with a sharp edge

at E_F (Figure 6a), indicating metallic Cr on W(100). The UP spectra after oxidation of 0.7, 1.4, 2.1, 2.8, and 3.5 monolayers at RT are given in Figure 6b–f. One can see that the Cr 3d peak is initially around 1.9 eV (Figure 6b) for the oxidized 0.7 monolayer Cr film and is gradually shifted to higher BE as the increasing Cr coverages are oxidized. At 1.4 monolayer Cr coverage, the DOS at E_F is still noticeably nonzero. This indicates that a portion of the chromium oxide film remains CrO_2 as part of, possibly, a mixture of CrO_2 and Cr_2O_3 . This result is consistent with the XPS results discussed above. However, Figure 6 clearly reveals a change from metallic Cr to Cr_2O_3 with increasing Cr coverage. On the basis of previous studies,^{7,9,23,33} these results suggest the transformation from the Cr^{4+} (CrO_2) to the Cr^{3+} (Cr_2O_3) oxidation state with increasing Cr coverage on the W(100) surface.

It is difficult to comment on the film morphology on the basis of the present studies. It is known that 1 monolayer of Cr wets the surface to form a continuous pseudomorphic film at room temperature.^{21,35} In our separate low-energy electron microscopy (LEEM) and LEED experiments, oxidation of a 1 monolayer Cr film at elevated temperature causes the Cr film to dewet and form three-dimensional (3D) islands. The tendency for the Cr film to dewet during oxidation decreases below 800 K. Therefore, we believe that the Cr film remains largely two-dimensional while it is oxidized at RT. While we can provide no direct evidence of the Cr film morphology in the present experiments, we believe that annealing an oxidized Cr film to 1100 K in the absence of oxygen ambient also tends to dewet the Cr film, possibly forming nanoparticles. Annealing of the 1 monolayer Cr film in oxygen at 800 K in the present investigation likely creates 3D chromium oxide islands, in accordance with our separate LEEM/LEED investigations.³⁵

4. Conclusion

Ultrathin chromium oxide films have been prepared on the W(100) surface by oxidizing predeposited Cr films. The film stoichiometry is found to depend on the initial Cr coverage and annealing temperature during oxidation. CrO_2 is formed by oxidizing 1 monolayer of Cr or less at 300–320 K in 10^{-7} mbar oxygen. Cr_2O_3 is formed when 1 monolayer of Cr is oxidized at 800 K or for oxidation of higher initial coverages at RT. Chromium oxide formation may depend also upon many other factors that we have not yet explored, such as O_2 pressure and exposure time, as well as the relative Cr deposition rate and O_2 pressure during co-deposition. More detailed study of these factors may guide the reliable preparation of various chromium oxides on the W(100) surface in the future.

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