

# Epitaxial Growth of $\text{CrO}_2$ Thin Films on $\text{TiO}_2(110)$ Surfaces

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Chromium dioxide films on  $\text{TiO}_2(110)$  single crystals have been grown by using chemical vapor deposition. The average growth rate was  $\sim 1.8 \text{ nm} \cdot \text{min}^{-1}$ . Powder X-ray diffraction indicated that the films were highly (110) textured. X-ray photoelectron spectroscopy showed that the  $\text{CrO}_2$  films were continuous and no other chromium oxides were present. The  $\text{CrO}_2$  films were composed of grains typically 200–300 nm in diameter and appeared consistent with the rutile crystal structure. Atomic force microscopy suggested that the films were relatively rough, with a root-mean-square roughness of  $\sim 114 \text{ nm}$  for an 850 nm thick film. The resistivity at room temperature was found to be  $\sim 137 \mu\Omega \cdot \text{cm}$  which decreased to  $\sim 16 \mu\Omega \cdot \text{cm}$  at 5 K, consistent with metallic behavior. The films were ferromagnetic with a Curie temperature of 398 K.

## Introduction

Transition metal oxides exhibit a wide range of physical, chemical, and structural properties and are important in various technological applications, including electronic materials, catalysis, and corrosion inhibition. As such, the surface properties and reactivities of these materials are an active area of research.<sup>1</sup> While considerable efforts have been made to understand the surface chemistry of these metal oxides, many of the fundamental atomic-level properties still remain poorly understood. This is largely due to the difficulty in the preparation of high-quality oxide surfaces and the experimental difficulties associated with the insulating properties of many of these oxides.

One solution to these problems is to grow thin films of the metal oxides on conductive substrates. In this way, the films may be sufficiently conductive without modifying the surface by doping or creating defects. Thin film techniques also allow the preparation of model metal oxide surfaces without the growth and preparation of large single crystals. Some examples include the growth of thin films of  $\beta\text{-MnO}_2$ ,<sup>2</sup> anatase  $\text{TiO}_2$ ,<sup>3,4</sup> and  $\alpha\text{-Cr}_2\text{O}_3$ <sup>5–7</sup> where pure large single crystals are not commercially available. Further reviews on the growth and properties of metal oxide thin films can be found in two recent articles.<sup>8,9</sup>

We present here the results of using a thin film approach, via chemical vapor deposition, to prepare an ordered chromium dioxide  $\text{CrO}_2(110)$  surface on rutile  $\text{TiO}_2(110)$ . Chromium dioxide is a ferromagnetic metallic black solid that adopts the rutile crystal structure and has similar lattice parameters to rutile ( $\text{CrO}_2$ ,  $a = 4.41$  and  $c = 2.91 \text{ \AA}$ ;  $\text{TiO}_2$ ,  $a = 4.59$  and  $c = 2.96 \text{ \AA}$ ). It has attracted significant attention due to its commercial importance as a particulate recording medium for data storage applications.<sup>10</sup> Although the metallic and magnetic properties of  $\text{CrO}_2$  have been studied extensively, the surface properties and reactivities of this metallic oxide are still not well understood.

Chromium dioxide is difficult to synthesize because it is metastable at atmospheric pressures. It is often synthesized under high oxygen pressure conditions ( $P > 10 \text{ bar}$ ) by thermal decomposition of  $\text{CrO}_3$ . This process produces a fine powder with crystals no larger than  $\sim 0.5 \text{ mm}$ .<sup>11,12</sup> Approaches to create larger ordered  $\text{CrO}_2$  surfaces via high pressure, epitaxial film syntheses have been investigated on rutile  $\text{TiO}_2(100)$ , (110), (210), and (001) surfaces as well as on the (0001) and (110) planes of  $\text{Al}_2\text{O}_3$ . X-ray diffraction (XRD) has indicated that the substrates induced a texture in the  $\text{CrO}_2$  layer, producing epitaxially orientated  $\text{CrO}_2$  films on the  $\text{TiO}_2$  surfaces.<sup>12,13</sup>

Chromium dioxide films on  $\text{TiO}_2$  surfaces have also been grown by using a chemical vapor deposition (CVD) method developed by Ishibashi et al. as an alternative to high-pressure routes.<sup>14</sup> In that work, scanning elec-

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(1) Henrich, V. E.; Cox, P. A. *The Surface Science of Metal Oxides*; Cambridge University Press: Cambridge, 1994.

(2) Chambers, S. A.; Liang, Y. *Surf. Sci.* **1999**, *420*, 123.

(3) Chen, S.; Mason, M. G.; Gysling, H. J.; Paz-Pujalt, G. R.; Blanton, T. N.; Castro, T.; Chen, K. M.; Fictorie, C. P.; Gladfelter, W. L.; Franciosi, A.; Cohen, P. I. *J. Vac. Sci. Technol., A* **1993**, *11*, 2419.

(4) Herman, G. S.; Gao, Y.; Tran, T. T.; Osterwalder, J. *Surf. Sci. 2000*, *447*, 201.

(5) Maurice, V.; Cadot, S.; Marcus, P. *Surf. Sci.* **2001**, *471*, 43.

(6) Henderson, M. A.; Chambers, S. A. *Surf. Sci.* **2000**, *449*, 135.

(7) Zhang, L.; Kuhn, M.; Ulrike, D. *J. Vac. Sci. Technol., A* **1997**, *15*, 1576.

(8) Street, S. C.; Xu, C.; Goodman, D. W. *Annu. Rev. Phys. Chem.* **1997**, *48*, 43.

(9) Chambers, S. A. *Surf. Sci. Rep.* **2000**, *39*, 105.

(10) Chamberland, B. L. *Crit. Rev. Solid State Mater. Sci.* **1977**, *7*, 1.

(11) Kubota, B. *J. Am. Ceram. Soc.* **1961**, *44*, 239.

(12) Devries, R. C. *Mater. Res. Bull.* **1966**, *1*, 83.

(13) Ranno, L.; Barry, A.; Coey, J. M. *J. Appl. Phys.* **1997**, *81*, 5774.

(14) Ishibashi, S.; Namikawa, T.; Satou, M. *Mater. Res. Bull.* **1979**, *14*, 51.

tron microscopy and reflection electron diffraction suggested that  $\text{CrO}_2$  films up to about 500 nm thick were deposited with epitaxial control on the  $\text{TiO}_2$  (100), (110), (111), and (001) substrate surfaces. However, the surface of the  $\text{CrO}_2$  produced by this method was not examined in detail. Amorphous thin films of  $\text{CrO}_2$  have been grown on glass and Si(110) substrates by using oxidized Ti as a buffer layer. XRD indicated the presence of textured, polycrystalline  $\text{CrO}_2$  films.<sup>15,16</sup> Li and co-workers have applied this CVD method to grow  $\text{CrO}_2$  films on  $\text{TiO}_2$ (100) for magnetic measurements<sup>17–19</sup> and observe epitaxial  $\text{CrO}_2$  films on  $\text{TiO}_2$ (110).<sup>20</sup>

In this work, we present an examination of the surface morphology of  $\text{CrO}_2$  grown on  $\text{TiO}_2$ (110) single crystals using a modified version of Ishibashi et al.'s CVD approach. We have successfully grown epitaxial thin films of  $\text{CrO}_2$  on  $\text{TiO}_2$ (110) single-crystal substrates at atmospheric pressure. Our studies provide insight into the growth characteristics, composition, and morphology of these films as indicated by scanning electron microscopy (SEM), powder XRD, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). Additionally, the magnetic (magnetization) and transport (resistivity) properties of the  $\text{CrO}_2$  films were examined and the results are compared to previously published work.

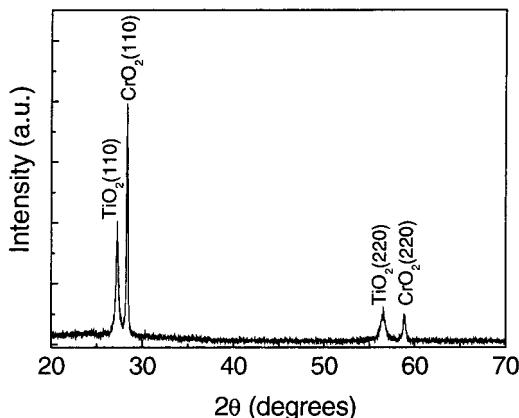
## Experimental Section

**Film Deposition.** Chromium dioxide films were prepared by using CVD inside a dual-zone programmable furnace. The starting material,  $\text{CrO}_3$  (99% purity, Aldrich Chemical Co., Inc., Milwaukee, WI), was placed in the first zone at 260 °C. Titanium dioxide (110) single-crystal substrates (7 × 7 × 1 mm, 99.99% purity, Superconductive Components, Inc., Columbus, OH) were ultrasonically cleaned in acetone, rinsed in  $\text{H}_2\text{O}$ , heated in oxygen at 400 °C for 24 h, and then placed in the second zone of the furnace at 400 °C. Oxygen flowing at a rate of ~0.1 L·s<sup>-1</sup> was used as the carrier gas for the decomposition products of  $\text{CrO}_3$ , which would subsequently form films of  $\text{CrO}_2$  ( $\text{CrO}_3 \rightarrow \text{CrO}_2 + \frac{1}{2}\text{O}_2$ ) on the  $\text{TiO}_2$ (110) substrates. Typical depositions ran for 8 h.

**Electron Microscopy.** Thickness analyses of the  $\text{CrO}_2$  films were performed with a JSM-6400V SEM incorporating a  $\text{LaB}_6$  electron source. Data were acquired with an accelerating voltage of 20 kV.

**Powder XRD.** Analyses of the films were performed by using a calibrated Rigaku-Denki/RW400F2 (Roflex) rotating anode powder diffractometer operating at 50 kV/100 mA with a 1°/min scan rate, employing Ni-filtered Cu radiation in a Bragg–Brentano geometry.

**XPS Analyses.** A Perkin-Elmer  $\Phi$  spectrometer (base pressure =  $2.0 \times 10^{-10}$  Torr) with an unmonochromatized  $\text{Al K}\alpha$  ( $h\nu = 1486.6$  eV) source operating at 300 W was used to acquire XP spectra. The spectrometer was calibrated by using the binding energy (BE) of the  $\text{Au 4f}_{7/2}$  line at 84.0 eV with respect to the Fermi level. All XPS spectra were collected by using a hemispherical mirror analyzer operating at a pass energy of 44.7 eV and acquired at normal takeoff angle (90° from the surface plane). After a Shirley-type background subtraction, the spectra were fitted using simple Gaussian–Lorentzian peak shapes. Observed BE's were referenced to the adventitious C 1s photoemission line at 285.0 eV and compared



**Figure 1.** Powder XRD pattern of an 850 nm thick  $\text{CrO}_2$  film on  $\text{TiO}_2$ (110).

to reference XP spectra of  $\text{CrO}_2$  powder (99.9% purity, EMTEC Magnetics GmbH) acquired under the same experimental conditions. Reference spectra of  $\text{Cr}_2\text{O}_3$  (98% purity, Aldrich) and  $\text{Na}_2\text{Cr}_2\text{O}_7$  (prepared by heating  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (99.5% purity, Fisher Scientific) to 100 °C in a vacuum) were also acquired for comparison. The atomic compositions were evaluated by using sensitivity factors provided by the instrument manufacturer ( $\text{Cr 2p} = 2.427$  and  $\text{O 1s} = 0.711$ ).

**AFM Analysis.** Images were obtained by using a Digital Instruments Nanoscope AFM operating in contact mode in air using a standard silicon nitride probe. Micrographs were collected at several different positions on the surface to confirm that the  $\text{CrO}_2$  layer was uniform on a macroscopic scale. The root-mean-square (rms) roughness of the films was calculated by using Nanoscope 4.1 software.

**Magnetic and Transport Analysis.** The magnetic susceptibility of the  $\text{CrO}_2$  films was measured as a function of temperature by using a Quantum Design MPMS magnetometer with an applied field of 500 G. All measurements were made with the magnetic field oriented in the plane of the film. Resistivity measurements were made at a temperature range of 5–400 K, using conventional four terminal methods on the samples which were mounted on a probe that was inserted into the same instrument.

## Results and Discussion

The  $\text{CrO}_2$  films produced were black and highly reflective. SEM cross-sectional images of a typical  $\text{CrO}_2$  film on a  $\text{TiO}_2$ (110) substrate indicated an average thickness of approximately 850 nm, consistent with an average deposition rate of 1.8 nm·min<sup>-1</sup>. Supporting thickness measurements were also determined by AFM. While film deposition took place, small areas at the edge of the  $\text{TiO}_2$  single crystal were covered by retaining clips. Once the deposition was completed and the films were removed from the furnace, the supporting clips were removed and the atomic force microscope was used to examine the "height" of the steps produced. The thicknesses of the films determined by AFM were consistent with the SEM analyses. All the powder XRD patterns, a typical example of which is presented in Figure 1, showed features associated with both  $\text{TiO}_2$  and  $\text{CrO}_2$  (110) and (220) reflections. There is no evidence for orientations other than  $\text{CrO}_2$ (110) or other chromium oxides.

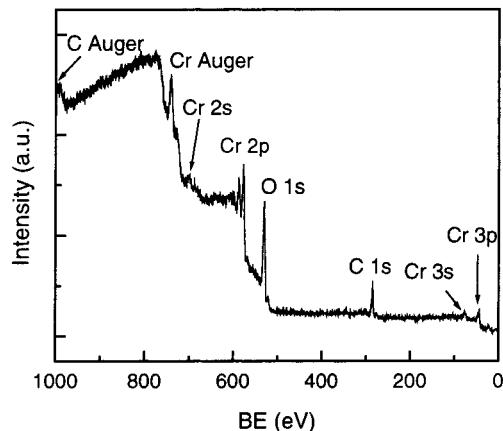
**XPS Analyses.** The composition and purity of the  $\text{CrO}_2$  films on  $\text{TiO}_2$ (110) were studied by XPS. Survey spectra, as shown in Figure 2, indicated that only chromium, oxygen, and carbon were present on the surface of the films. Peaks associated with titanium are

- (15) Suzuki, K.; Tedrow, P. M. *Phys. Rev. B* **1998**, *58*, 597.
- (16) Suzuki, K.; Tedrow, P. M. *Solid State Commun.* **1998**, *107*, 583.
- (17) Li, X. W.; Gupta, A.; Xiao, G. *Appl. Phys. Lett.* **1999**, *75*, 713.
- (18) Li, X. W.; Gupta, A.; Xiao, G. *J. Appl. Phys.* **1999**, *85*, 5585.
- (19) Yang, F. Y.; Chien, C. L.; Ferrari, E. F.; Li, X. W.; Xiao, G.; Gupta, A. *Appl. Phys. Lett.* **2000**, *77*, 286.
- (20) Gupta, A.; Li, X. W.; Xiao, G. *Appl. Phys. Lett.* **1999**, *75*, 2996.

**Table 1. XPS Binding Energies (eV) Obtained for  $\text{CrO}_2/\text{TiO}_2(110)$  Film and Other Chromium Oxides<sup>a</sup>**

	$\text{CrO}_2/\text{TiO}_2(110)$	$\text{CrO}_2$	$\text{Cr}_2\text{O}_3$	$\text{CrO}_3$	$\text{Na}_2\text{Cr}_2\text{O}_7$
Cr 2p <sub>3/2</sub>	576.6	576.4 (576.3) <sup>b</sup>	576.7 (576.8) <sup>c</sup>	578.3	579.6 (579.4) <sup>c</sup>
Cr 2p <sub>1/2</sub>	586.2	586.0 (586.0) <sup>b</sup>	586.4 (586.5) <sup>c</sup>	586.0	588.7 (588.5) <sup>c</sup>
O 1s	529.3	529.2 (529.3) <sup>b</sup>	530.3 (530.5) <sup>c</sup>	529.9	530.4 (530.0) <sup>c</sup>

<sup>a</sup> All values except those in parentheses were determined in the present study. <sup>b</sup> Data from the work of Ikemoto et al.<sup>22</sup> <sup>c</sup> Data from the work of Allen et al. (their results have been corrected to the Au 4f<sub>7/2</sub> as 84.0 eV).<sup>23</sup>

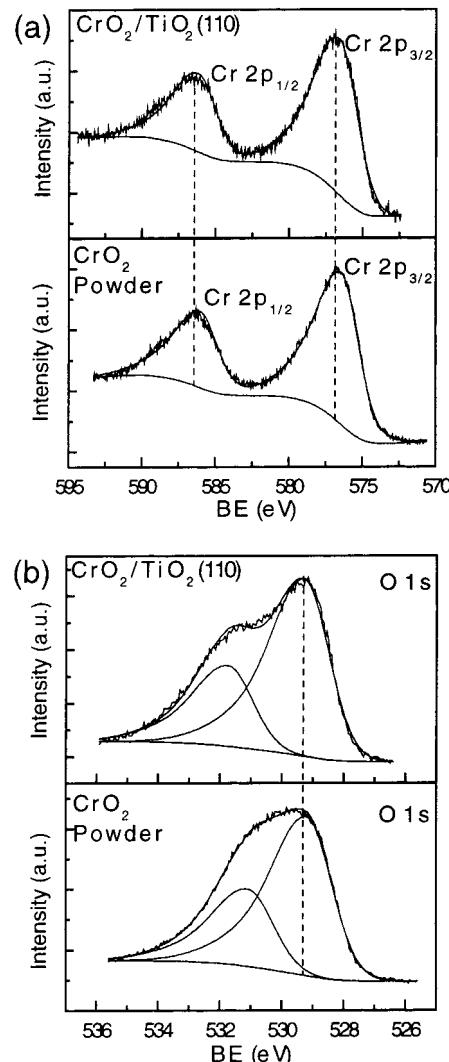


**Figure 2.** XPS survey scan of  $\text{CrO}_2$  film on  $\text{TiO}_2(110)$  (Al K $\alpha$  radiation). Note the absence of any features associated with  $\text{TiO}_2$  substrate.

not evident, indicating that the films are continuous and, based on an estimate for the inelastic mean free path for the Ti 2p photoelectrons of 2.0 nm,<sup>21</sup> at least 6.0 nm thick. The minimum thickness inferred from the XPS measurements supports the AFM and SEM thickness values.

High-resolution scans of the Cr 2p and O 1s regions of the  $\text{CrO}_2$  film on  $\text{TiO}_2(110)$  and a standard  $\text{CrO}_2$  powder were acquired as shown in Figure 3. The peaks connected by a dashed line are those associated with  $\text{CrO}_2$ . The BE's for Cr 2p and O1s peaks in the film and powder are in excellent agreement with each other and with values reported by Ikemoto et al.<sup>22</sup> as given in Table 1. Also shown in Table 1 are the BE's determined for other chromium oxide species, confirming that the oxide produced on our  $\text{TiO}_2$  substrate could be uniquely identified. The measured BE's and spin-orbit splittings for  $\text{Cr}_2\text{O}_3$  (Cr(III)) and  $\text{CrO}_3$  and  $\text{Na}_2\text{Cr}_2\text{O}_7$  (Cr(VI)) reported here are generally within 0.2 eV of analogous values in the literature.<sup>22–24</sup> It is interesting to note that the chromium(IV) 2p peaks for  $\text{CrO}_2$  do not follow a simple trend of increasing BE with increasing formal oxidation state. These effects have been remarked upon previously and attributed to differences in the crystal structure, ionic character, and electronic properties of these oxides.<sup>22,25</sup>

The Cr 2p peaks of the  $\text{CrO}_2$  film and powder, as shown in Figure 3a, were noticeably asymmetric and broadened to the high binding energy side when compared with the Cr 2p peaks for  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{Cr}_2\text{O}_3$  (data



**Figure 3.** XPS comparison between  $\text{CrO}_2/\text{TiO}_2(110)$  film and  $\text{CrO}_2$  powder: (a) Cr 2p region and (b) O 1s region. For the Cr 2p region, dashed lines are drawn at 576.5 and 586.1 eV BE. For the O 1s region, a dashed line is drawn at 529.2 eV BE. The features connected by dashed lines correspond to  $\text{CrO}_2$ .

not shown). Attempts were made to fit the Cr 2p peak envelope to simple symmetric peaks located at the BE's expected for Cr(IV) ( $2p_{3/2} = 576.4$  eV) with a minor component attributable to Cr(VI) ( $2p_{3/2} = 579.6$  eV). However, the quality of the fit was substantially worse than a single asymmetric peak due to Cr(IV). We therefore conclude that the  $\text{CrO}_2$  peak shape is intrinsic to the material and is likely to be associated with small energy electron-hole pair excitation across the Fermi level of this metallic material (so-called Doniach-Sunjic line shape).<sup>26</sup>

The oxygen photoemission peaks for both  $\text{CrO}_2/\text{TiO}_2(110)$  film and  $\text{CrO}_2$  powder (Figure 3b) showed the presence of two components. These two components were fit with the same peak shape and fwhm (1.9 eV).

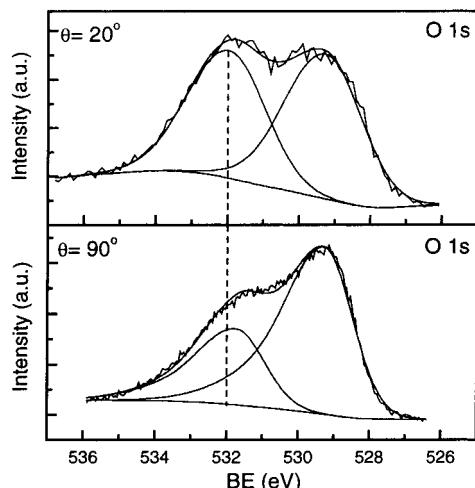
(21) Woodruff, D. P.; Delchar, T. A. *Modern Techniques of Surface Science*, 2nd ed.; Cambridge University Press: Cambridge, 1994.

(22) Ikemoto, I.; Ishii, K.; Shuichi, K.; Kuroda, H.; Alario Franco, M. A.; Thomas, J. M. *J. Solid State Chem.* **1976**, *17*, 425.

(23) Allen, G. C.; Curtis, M. T.; Hooper, A. J.; Tucker, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, *16*, 1675.

(24) Hassel, M.; Hemmerich, I.; Kuhlenbeck, H.; Freund, H.-J. *Surf. Sci. Spectra* **1998**, *4*, 246.

(25) Hanafi, Z. M.; Ismail, F. M.; Mohamed, A. K. *Z. Phys. Chem. (Munich)* **1996**, *194*, 61.

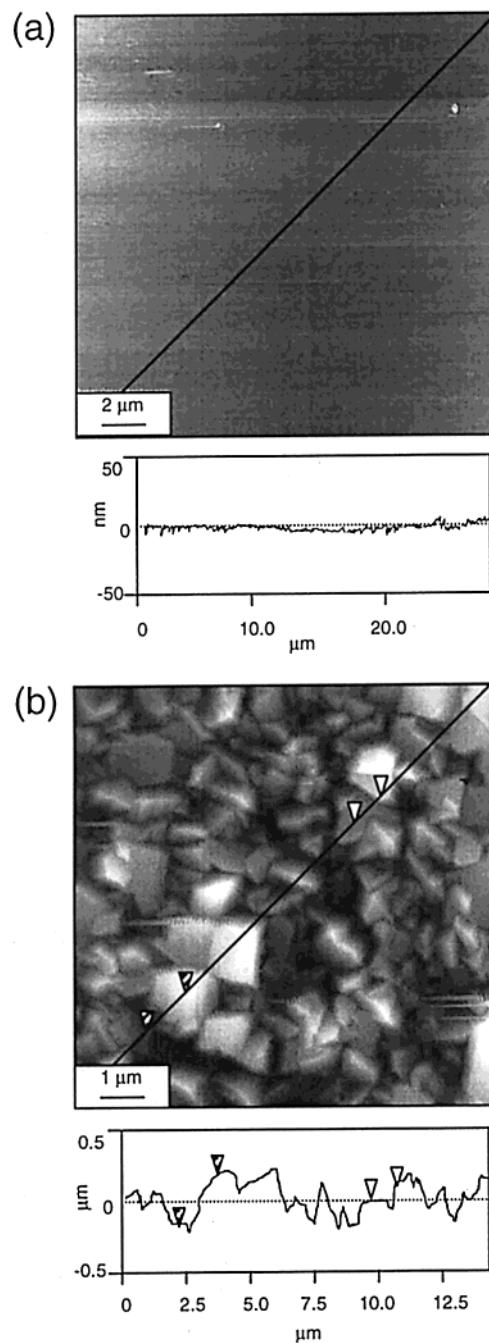


**Figure 4.** XPS comparison of O 1s region for  $\text{CrO}_2/\text{TiO}_2(110)$  film at two different take off angles ( $\theta$ ). Takeoff angle is defined as the angle between the surface plane and the electron energy analyzer acceptance axis. The dashed line is drawn at 532.0 eV BE and is associated with surface  $\text{H}_2\text{O}$ .

The lower BE component, at  $529.25 \pm 0.05$  eV BE, is associated with the chromium oxide species based on comparison to literature values.<sup>22</sup> The Cr/O ratio was calculated by using the peak area for Cr 2p and the lower BE O 1s component and was found to be 0.52 for the film and 0.60 for the powder. We estimate the error in these calculated ratios to be about  $\pm 0.05$ , determined largely by the errors associated with peak fitting. The calculated Cr/O ratios for the film and powder are in reasonable agreement with the theoretical value for  $\text{CrO}_2$  of 0.50.

The higher BE oxygen component in the  $\text{CrO}_2$  film and powder (Figure 3b), located at about 532 eV BE, can be attributed to a surface contaminant. This was established by examining the O 1s region as a function of the XPS analyzer takeoff angle. When the takeoff angle is changed from 90 to 20° (Figure 4), the sampling depth is effectively decreased from approximately 4.5 to 1.5 nm. The intensity of the high BE component of the O 1s envelope relative to the low BE  $\text{CrO}_2$  O 1s peak is greater at 20 than at 90°, indicating that this feature is localized in the near-surface region. Similar broadening of the O 1s region to higher BE for oxides of chromium has been reported previously, and this feature is believed to be associated with adsorbed  $\text{H}_2\text{O}^{23}$  and  $\text{O}_2^{22}$ .

Many metal oxides readily form a hydroxide layer on the surface when exposed to ambient air.<sup>27</sup> One example is  $\text{Cr}_2\text{O}_3$ , where  $\text{H}_2\text{O}$  dissociatively chemisorbs and forms surface-bridging and terminal OH groups even on a nondefective surface.<sup>5,6,28</sup> Adsorbed OH and  $\text{H}_2\text{O}$  on the surface can be distinguished by the magnitude of the XPS chemical shift from the  $\text{O}^{2-}$  peak associated with the oxide. The peak positions of OH and  $\text{O}^{2-}$  are usually  $+(1.1-1.5)$  eV BE apart. However,  $\text{H}_2\text{O}$  creates higher BE shifts, typically  $>+3$  eV from the oxide



**Figure 5.** AFM surface morphology and sectional height analysis of (a)  $\text{TiO}_2(110)$  single crystal ( $400 \mu\text{m}^2$  area) and (b) 850 nm  $\text{CrO}_2$  film on  $\text{TiO}_2(110)$  surface ( $100 \mu\text{m}^2$  area).

peak.<sup>29</sup> For the  $\text{CrO}_2$  film and powder studied here, the BE difference between the two O 1s peaks is about 2.7 eV. Based on this BE difference, we propose that the second oxygen component on the surface of the film and the powder is likely a surface  $\text{H}_2\text{O}$  species.

**Morphology Investigation.** AFM was used to investigate the morphology of the  $\text{CrO}_2/\text{TiO}_2(110)$  films. It is known that the  $\text{TiO}_2$  substrate is important in providing epitaxial stabilization of the  $\text{CrO}_2$  phase.<sup>12,14,20</sup> In Figure 5a, a  $400 \mu\text{m}^2$  AFM image of a clean  $\text{TiO}_2(110)$  single crystal is shown. The surface is uniform, and a sectional height analysis across the surface

(26) Barr, T. L. *The Principles and Practice of X-ray Photoelectron Spectroscopy*; CRC Press: Boca Raton, 1994.

(27) Brown, G. E.; Henrich, V. E.; Casey, W. H.; Clark, D. L.; Eggleston, C.; Felmy, A.; Goodman, D. W.; Grätzel, M.; Maciel, G.; McCarthy, M. I.; Nealon, K. H.; Sverjensky, D. A.; Toney, M. F.; Zachara, J. M. *Chem. Rev.* **1999**, 99, 55.

(28) Maurice, V.; Cadot, S.; Marcus, P. *Surf. Sci.* **2000**, 458, 195.

(29) McIntyre, N. S.; Chan, T. C. In *Practical Surface Analysis*; Briggs, D., Seah, M. P., Eds.; Wiley: New York, 1990; Vol. 1, p 501.

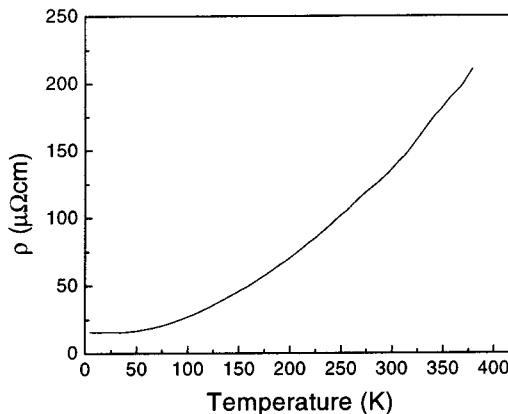
indicates a flat substrate devoid of any noticeable surface features. The rms roughness of the  $\text{TiO}_2(110)$  substrate was calculated to be 1.5 nm for a  $10 \mu\text{m}^2$  area within this image.

A typical AFM image of a  $100 \mu\text{m}^2$  area of an 850 nm thick  $\text{CrO}_2$  film on  $\text{TiO}_2(110)$  is shown in Figure 5b. Individual grains on the surface can be resolved, and their appearance is generally consistent with the rutile crystal structure of  $\text{CrO}_2$ . Sectional height analysis of the film shows that the grains vary in size and height along the surface. The markers indicate the relationship between the topographical image and the section height analysis. On the  $\text{CrO}_2$  film, grain sizes as large as  $\sim 1000$  nm exist. However, typical grain sizes found on the surface are approximately 200–300 nm in size. These grain sizes are larger or equal to those in the reported literature for  $\text{CrO}_2$  films on  $\text{TiO}_2(100)$ .<sup>17,30,31</sup> The calculated rms roughness of the film was 114 nm, which reflects an increase of 2 orders of magnitude compared to the initial  $\text{TiO}_2$  substrate. Ranno et al. also noted large surface roughness of  $\text{CrO}_2$  films grown by high-pressure synthesis and reported variations of 20–30% in film thickness,<sup>13</sup> which are somewhat larger than our values of 10–15%.

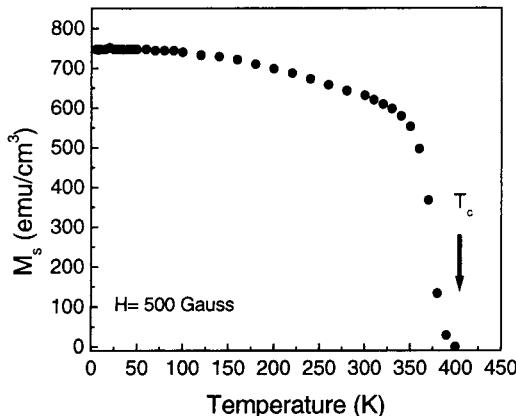
The surface roughness of the  $\text{CrO}_2$  films may be a reflection of the deposition method. From the AFM images, it may be concluded that many nucleation sites are present on the  $\text{TiO}_2(110)$  crystal surface, which would lead to the growth of grains of various sizes and ultimately a roughened surface. Alternatively, strain energy can accumulate rapidly with increasing film thickness, which might also result in an increase in surface roughness.<sup>32</sup>

Methods to decrease the surface roughness, such as annealing the film or changing the deposition temperature of the substrate, were not investigated in this study. The temperature of the substrate must fall within 390–400 °C to allow for  $\text{CrO}_2$  growth. Deposition at higher or lower temperatures will lead to the formation of other chromium oxides.<sup>14</sup> Postannealing of the film after deposition at higher temperatures is also not possible: chromium dioxide decomposes to  $\text{Cr}_2\text{O}_3$  at temperatures above 400 °C.<sup>12,14</sup> Future investigations are underway to better control the surface roughness of  $\text{CrO}_2$  films.

**Electrical and Magnetic Properties.** The magnetic and electrical properties of these  $\text{CrO}_2/\text{TiO}_2(110)$  films are discussed briefly here but will be addressed in more detail in a subsequent publication.<sup>33</sup> Figure 6 shows the electrical resistivity,  $\rho$ , for an 850 nm thick  $\text{CrO}_2$  film on  $\text{TiO}_2(110)$  as a function of temperature. The gross properties of  $\text{CrO}_2$  films on  $\text{TiO}_2(110)$  are similar to those of  $\text{CrO}_2$  films grown on the  $\text{TiO}_2(100)$  surface, by CVD using  $\text{CrO}_3$ <sup>18,30</sup> and  $\text{CrO}_2\text{Cl}_2$ <sup>31</sup> as precursors, and also films formed by high-pressure synthesis on  $\text{TiO}_2(110)$ <sup>34</sup> surfaces. Resistivity increased from  $\sim 16 \mu\Omega\cdot\text{cm}$  at 5 K to  $\sim 137 \mu\Omega\cdot\text{cm}$  at 300 K. An increase of resistivity



**Figure 6.** Resistivity vs temperature of an 850 nm thick  $\text{CrO}_2$  film on a  $\text{TiO}_2(110)$  surface.



**Figure 7.** Spontaneous magnetization as a function of temperature for an 850 nm (110) orientated  $\text{CrO}_2$  film in a 500 G field.

of this magnitude is consistent with metallic behavior. These resistivity values are similar to those reported for  $\text{CrO}_2$  films on  $\text{TiO}_2(110)$  by high-pressure synthesis.<sup>34</sup> However, it should be noted that our resistivity values should be regarded as approximate due to errors associated with measurement of the cross-sectional area of the  $\text{CrO}_2/\text{TiO}_2$  film and the unknown effects of surface roughness.

Measurements of the magnetic properties of the films indicated a clear ferromagnetic hysteresis and anisotropy along the  $c$ -axis of the films,<sup>33</sup> which is consistent with the assumption of a collinear relation between the crystallographic  $c$ -axis and the magnetic easy axis of  $\text{CrO}_2$  single crystals<sup>35</sup> and  $\text{CrO}_2(100)$  films.<sup>17,18,31,36</sup> The spontaneous magnetization determined as a function of temperature in an applied field of 500 G, is presented in Figure 7. From these data, the Curie temperature was found to be  $\sim 398$  K, which is in agreement with published results of  $\text{CrO}_2$  films<sup>16–18,31,34</sup> and bulk  $\text{CrO}_2$ .<sup>10</sup> Similar magnetization behavior has been also observed in  $\text{CrO}_2(100)$  films grown by CVD<sup>17,18,31,34</sup> but cannot be directly compared to our  $\text{CrO}_2(110)$  films due to different crystallographic orientations. To our knowledge, spontaneous magnetization measurements in (110) films have not been reported.

(30) Rabe, M.; Dressen, J.; Dahmen, D.; Pommer, J.; Stahl, H.; Rüdiger, U.; Gündtherodt, G.; Senz, S.; Hesse, D. *J. Magn. Magn. Mater.* **2000**, *211*, 314.

(31) DeSisto, W. J.; Broussard, P. R.; Ambrose, T. F.; Nadgorny, B. E.; Osofsky, M. S. *Appl. Phys. Lett.* **2000**, *76*, 3789.

(32) Uchitani, T.; Maki, K. *J. Vac. Sci. Technol., A* **2000**, *18*, 2706.

(33) Bullen, H. A. et al. In preparation.

(34) Watts, S. M.; Wirth, S.; von Molnar, S.; Barry, A.; Coey, J. M. D. *Phys. Rev. B* **2000**, *61*, 9621.

(35) Rodbell, D. S. *J. Phys. Soc. Jpn.* **1966**, *21*, 1224.

(36) Spinu, L.; Srikanth, H.; Gupta, A.; Li, X. W.; Xiao, G. *Phys. Rev. B* **2000**, *62*, 8931.

### Conclusions

Metallic chromium dioxide (110) films on  $\text{TiO}_2$ (110) have been successfully deposited. To the best of our knowledge, this is the first specific investigation of the growth, morphology, and bulk/surface composition of  $\text{CrO}_2$ (110) films grown by simple chemical vapor deposition. The films were highly oriented with the (110) plane parallel to the  $\text{TiO}_2$ (110) surface plane but exhibit a granular structure with grain sizes up to about  $1\text{ }\mu\text{m}$ . Both powder XRD and XPS confirmed that no other bulk oxides are formed, but the surface is probably covered by a water-like layer. This CVD method has proven successful in growing  $\text{CrO}_2$ (110) thin films, and it is

experimentally more accessible than a high-pressure synthesis technique.

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