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# MOCVD Route to Stable, Oxygen-Rich, Chromium Oxide Films and Their Conversion to Epitaxial $Cr_2O_3$

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Using $Cr(acac)_3$ as a precursor, deposition of chromium oxide onto silicon and $Al_2O_3$ by MOCVD produced 800 Å to 2 $\mu$m thick films, which were characterized by IR, UV–vis spectroscopies, XPS, oxygen and carbon resonance RBS, and XRD, as well as optical and electron microscopies. Optimization of deposition conditions such as precursor temperature, carrier gas type and flow rate, substrate type and temperature, and postdeposition anneal yielded smooth, crystalline, epitaxially oriented films of $Cr_2O_3$ on single crystalline $Al_2O_3$ substrates. Deposition under flowing $O_2$ at 400–900 °C produced discontinuous $Cr_2O_3$ films comprised of 1–20 $\mu$m diameter crystallites the orientation of which was dependent on the substrate. Deposition at 300–350 °C under $O_2$ and at 300–500 °C under $N_2$ produced very smooth films of $Cr_2O_x$ ($3.2 \le x \le 4.9$); such films contained some crystalline $Cr_2O_3$. XPS analysis of these oxygen-rich films revealed the presence of chromium in oxidation states, III (major), IV, and VI. The $Cr_2O_{3.5}$ films did not lose oxygen upon firing to 1100 °C under argon, but were cleanly converted to smooth, epitaxial $Cr_2O_3$ at 1300 °C.

## Introduction

Chromium oxides are important technological materials because of their intrinsic properties such as resistance to chemical attack, high-temperature stability, very high hardness and dielectric strength, useful magnetic properties, and more. $Cr_2O_3$ has been used as a protective coating on high-temperature battery electrodes,[1] as corrosion-resistent layers on semiconductors[2] and metals,[3] as isolation layers on high output klystron tubes,[4] and as wear-resistant layers on magnetic particles.[5] $Cr_2O_3$ sublayers have been found to promote epitaxial growth of gold on sapphire.[6] $CrO_2$ is widely used in magnetic media applications.[7–9] Mixtures of chromium metal and its oxides (black chrome) have found application as solar absorber coatings.[10–13] Bulk $Cr_2O_3$ is widely used as a green pigment, and amorphous bulk chromia, in high surface area configurations, is found in catalytic applications.

Films of $Cr_2O_3$ have been made by a variety of methods including evaporation[5,14] or sputtering[1,13,15] of the oxides, oxidation of chromium metal,[4,6,16–18] electrochemical deposition,[11,19] CVD,[2,3,9,10,20–23] spray pyrolysis,[24,25] and dip coating.[26] One recurrent problem in the deposition of such films is retention of stoichiometry, particularly with sputter deposition. Often, substoichiometric oxides are formed that exhibit different conductivity and wear characteristics than $Cr_2O_3$.[1,5,15] Although the use of tris(2,4 pentanedionato)chromium(III), $Cr(acac)_3$, as a precursor for MOCVD derived $Cr_2O_3$ films has previously been reported,[2,3,23,27] no systematic study concerning the influence of deposition temperature or carrier gas type on film composition has been reported. Additionally, some questions exist concerning the true stoichiometry of the as-deposited films.

In this paper, the MOCVD deposition of $Cr_2O_3$ films using $Cr(acac)_3$ is presented. The influence of CVD

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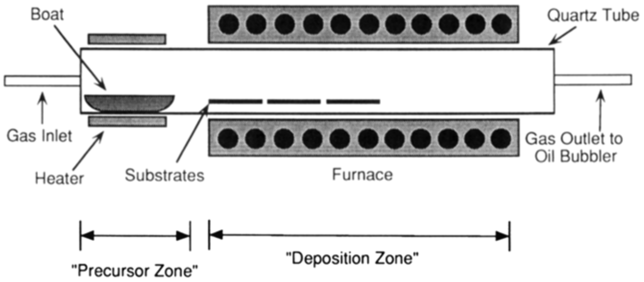

**Figure 1.** Schematic diagram (not to scale) of the apparatus used for deposition of chromium oxide films from Cr(acac)$_3$.

deposition atmosphere on chromium oxide film quality and composition is systematically examined. Analyses of deposited thin films demonstrated that they contain oxygen-rich chromium oxide phases, which are stable at much higher temperatures than corresponding bulk powders.

## Experimental Section

**Film Deposition and Firing.** Cr(acac)$_3$ (98%) was obtained from Alfa and was used as received. Prepurified grade oxygen, nitrogen, and forming ($N_2$ 93%, $H_2$ 7%) gases were used as supplied from the manufacturer. Prepurified grade argon was passed over reduced BASF R3-11 catalyst and Aquasorb (Mallinckrodt) for removal of residual oxygen and water, respectively. Humidification of deposition gases was achieved by bubbling them through a fritted glass tube in deionized water. Gases humidified in this manner were saturated with water vapor at room temperature as measured by a Fisher Scientific hygrometer. Film depositions were carried out at atmospheric pressure and 350−900 °C in a tube furnace (type 70, Hevi-Duty Heating Equip.) fitted with a fused silica tube (25 mm o.d. by 60 cm). All length dimensions in the experimental setup (Figure 1) were measured from the gas inlet end of the tube. The furnace was 32 cm in length and was positioned starting 18 cm from the gas inlet end of the silica tube. The tube was heated to 140−170 °C by means of a heating tape, controlled by a Variac, in a region 13 cm long (designated as the "precursor zone"), 3 cm from the tube's end. Polycrystalline alumina (99%, IBM) and silicon wafer (Unisil) substrates were placed horizontally, end-to-end in the furnace-heated tube starting 18 cm from the tube end, (designated as the "deposition zone"). The native oxide on silicon wafer substrates was not removed prior to deposition. Unoriented disks of single crystalline $Al_2O_3$ (Meller Optics, 1 cm diameter), and (0001) oriented squares of single crystalline $Al_2O_3$ (Union Carbide, 1 cm$^2$), were supported on silicon wafer pieces placed horizontally in the tube. Some "unoriented" $Al_2O_3$ disks were shown to be only 1−2° misoriented from the (110) axis by XRD analysis. The furnace controller thermocouple was calibrated with an external thermocouple (Omega). There was a temperature gradient of 200−400 °C at 18−21 cm from the front of the tube (from the end to 3 cm into the furnace). Thus, samples at the very front of the deposition zone were deposited at temperatures 200−400 °C lower than the indicated furnace temperature. There was no measurable temperature gradient in the center of the deposition zone, from 21 to 47 cm from the front end of the tube.

The precursor was weighted into a tared alumina boat (5 × 1 × 1 cm) and placed in the "precursor zone" approximately 16 cm from the end. Precursor weights ranged from 5 to 170 mg. Gas flow rates, ranging from 150 to 750 cm$^3$/min, were calibrated with a gas flow meter (Rotameter 4331, Linde) and were generally monitored by an oil bubbler placed after the gas outlet of the furnace tube. Small variations in gas flow rate did not change the deposition process.

In a typical deposition, furnace and precursor zone temperatures were allowed to equilibrate for 30 min after reaching their set points, 500 and 150 °C, respectively. Oxygen gas flow was set at 300−350 cm$^3$/min. Two pieces of silicon, 1 cm by 6 cm, were cleaved from a silicon wafer and inserted into the deposition zone of the furnace, end to end with the edge of the first wafer placed 18 cm from the end. The substrates were allowed to equilibrate at the furnace temperature for 10 min. A tared alumina boat containing Cr(acac)$_3$ (0.1013 g) was inserted into the "precursor zone" 16 cm from the end, and deposition was started. After 29 h there was no precursor left in the boat, and heating was discontinued while oxygen flow continued during cool down. The two coated silicon wafer pieces were removed at room temperature. The resultant deposit was gray along the first 4.5 cm after which a short region, <1 cm, of black material was deposited. The rest of the film, >8 cm in length, was green and nonreflective. The first silicon wafer piece was cleaved into two pieces, sample 1B, containing the gray region of the film, and sample 2B, containing a green region of the film. The second silicon wafer piece, with a completely green deposit, was labeled 3B. The temperature of deposition for sample 1B was estimated from calibration profiles of the furnace to be 300−350 °C. The alumina boat, used to hold the precursor, was within 0.2 mg of the tare weight.

Firing of films was carried out in a tube- or muffle-furnace equipped with a ramp and soak controller. Except where noted, firings were done under argon. In all cases, the controller's thermocouple was calibrated against an external thermocouple (Omega). A high-purity alumina tube (Vesuvius McDaniel, 99.8%) was used for firings at 1300 °C.

**Analysis.** Environmental scanning electron microscopy (ESEM) was performed on an Electro-Scan, E-3 microscope. A water saturated air environment of $(5-7) \times 10^{-3}$ mmHg pressure was used for all samples. Environmental SEM allowed the examination of nonconductive samples without the use of a conductive coating. Rutherford backscattering spectroscopy at the carbon and oxygen resonance energies (CRRBS and ORRBS) was done at Cornell's MSC ion beam facility. Samples were coated with a 20 Å layer of Au/Pd to prevent charging. Modeling of the spectra was performed with a modified version of the RUMP code[28] for RBS spectral analysis developed at Cornell.[29,30] X-ray diffraction (XRD) was performed on Scintag PADX and PADY diffractometers in both normal $2\theta$ and pole figure configurations using Cu K$\alpha$ radiation ($\lambda = 1.5406$ Å).

Ellipsometry was performed on a Rudolph Auto-El ellipsometer. The wavelength of light used for analysis was 632.8 nm and the angle between the source and detector, $\phi$, was set at 70°. Calibration was performed using a thermal oxide covered silicon standard. Profilometry measurements were made on a Tencor Instruments Alpha Step profilometer with a 12.5 $\mu$m radius diamond tip stylus. Samples on silicon substrates were scribed, and the average thickness from several measurements was taken. Full scale deflection was set at 5000−25 000 Å. UV−vis spectra was scanned from 800 to 200 nm at 200 nm/min on a Cary 05 UV−vis−NIR spectrometer; an uncoated single crystalline sapphire substrate was used in the reference beam. Transmission IR spectra were taken at a resolution of 4 cm$^{-1}$ on a Mattson Galaxy 4020 FTIR spectrometer using a silicon substrate reference.

X-ray photoelectron spectroscopy (XPS) was performed on a Surface Science Lab SSL-100-03 instrument using monochromatic Al K$\alpha$ radiation at an energy of 1486.6 eV. The beam spot size was 600 $\mu$m$^2$, and the operating pressure was less than $1 \times 10^{-9}$ mmHg. An electron flood gun, operated at 3 V, was used to compensate for charging of nonconductive samples. As-deposited films were dried in static air at 250−500 °C for 1−3 h to remove adsorbed surface water. All samples were stored over $CaSO_4$ (Drierite) prior to analysis. Peak positions were referenced to the C1s peak of adventitious surface carbon. Samples that were calcined at 750 °C gave slight shifts in peak positions to higher energy, indicating a

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decrease in surface conductivity with respect to the dried films. Qualitative peak deconvolution was performed using the manufacturer's program. The quality of the individual curve fits was evaluated by the $\chi^2$ test and by the position of the resulting component peaks.

The sample numbering scheme used in the discussion is the following: sample number, substrate type (A is oriented (0001) $Al_2O_3$, B is silicon, C is unoriented single crystalline $Al_2O_3$), and a counter number to distinguish samples deposited under the same conditions but fired at different temperatues.

## Results and Discussion

**Deposition.** $Cr(acac)_3$, which has been previously used for MOCVD of chromium oxide films,[2,3,23] is air and water stable and has a vapor pressure of 0.1 and 1.0 mmHg at 150 and 180 °C, respectively.[31-33] Having a decomposition temperature in excess of 200 °C and relatively low toxicity, $Cr(acac)_3$ is an excellent precursor for low-temperature MOCVD. The apparatus used is shown in Figure 1.

The length of the deposited film was unaffected by furnace temperature; depositions at 400, 500, and 600 °C all yielded 3 cm long, green $Cr_2O_3$ films. Lower precursor temperatures required longer deposition times but the deposited film length was unchanged. Faster carrier gas flow rates, on the other hand, yielded green $Cr_2O_3$ films of 9−12 cm in length. The thickness of the film ranged from 300 to 30 000 Å; greater precursor masses yielded thicker films. Some of the films were not continuous (i.e., they formed microscopic "islands" of material on the surface), so a direct comparison of precursor weight with amount of material deposited was not possible. For the deposition of stoichiometric $Cr_2O_3$ (see below), optimum conditions were precursor zone temperature of 150 °C, precursor weight of 100 mg, $O_2$ gas flow of 300−450 cm$^3$/min, and furnace temperature of 500 °C, which yielded a total deposition length of 8 cm after 32 h. No residue was left in the alumina boat after deposition, indicating that there was no decomposition of the precursor during sublimation.

Dry and humidified oxygen atmospheres at furnace temperatures of 400−500 °C yielded tan, black, or gray material at the front of the deposition zone, where temperatures were 200 to 300 °C, in contrast to the green films deposited in the middle of the furnace. At deposition temperatures above 600 °C, all of the deposited film was green. The use of dry and humidified $O_2$ atmospheres at 350 °C yielded smooth tan or gray films throughout the deposition zone. In contrast, a dry nitrogen atmosphere at 350 °C, did not produce any film at all, whereas a humidified $N_2$ atmosphere at 350 °C, yielded a smooth gray film. Deposition at 500 °C, under both dry and humidified $N_2$, yielded smooth gray films as did a reducing atmosphere ($H_2/N_2$, forming gas) at 500 °C. These observations indicated that the type of carrier gas and the furnace temperature had considerable influence on film deposition.

**XRD Analysis.** The only crystalline phase seen in the X-ray analysis of any of the samples was $Cr_2O_3$; any contamination from other phases (e.g., carbides or other oxides) was in the form of amorphous material. The XRD data are summarized below according to substrate type and are presented in Table 1 for selected samples.

**Table 1. RBS and XRD Analyses of Chromium Oxide Films**

| sample[a] | deposition[b] | firing[g] (°C/h) | XRD[c] | thickness (Å) | RBS analysis[d] |
|---|---|---|---|---|---|
| 1B1 | 300/$O_2$ | ad | vw rand | 10 000 | $Cr_2O_{3.5}C_{0.0}$ |
| 1B2 | 300/$O_2$ | 1100/24 | m (110), w (006) | | $Cr_2O_{3.5}C_{0.0}$ |
| 2B | 500/$O_2$ | ad | vw rand, m (110) | 16 000 | $Cr_2O_{3.0}C_{0.0}$ |
| 3B | 500/$O_2$ | ad | w rand, m (110) | 8 800 | |
| 4C | 600/$O_2$ | ad | s (**110**) | 2 500 | |
| 5C | 900/$O_2$ | ad | s (**110**) | 10 000 | |
| 6B1 | 350/$O_2$ | ad | m (006) | 2 500 | $Cr_2O_{3.3}C_{0.22}$ |
| 6B3 | 350/$O_2$ | 750/24 | w (006) | 2 100 | $Cr_2O_{3.3}C_{0.09}$ |
| 7B1 | 350/h$N_2$ | ad | am | 600−800 | $Cr_2O_{4.9}C_{0.08}$ |
| 7B3 | 350/h$N_2$ | 750/24 | am | 500−700 | $Cr_2O_{3.7}C_{0.0}$ |
| 8B | 500/$N_2$ | ad | vw rand | 2 900 | $Cr_2O_{3.3}$[f] |
| 9A | 900/$O_2$ | ad | s (006) | 20−40 000 | |
| 10C1 | 350/$O_2$ | ad | vs (**110**), vw (006) | | |
| 10C2 | 350/$O_2$ | 1300/12 | vs (**110**), w (006) | | $Cr_2O_{3.08}$[f] |
| 11B | 350/h$O_2$ | ad | am | 2 500 | $Cr_2O_{3.9}$[f] |
| 12B | 500/h$N_2$ | ad | am | 2 800 | $Cr_2O_{3.5}$[f] |
| 13B1 | 500/$N_2$, $H_2$ | ad | am | 1 100 | $Cr_2O_{4.0}C_{0.90}$ |
| 13B2 | 500/$N_2$, $H_2$ | 700/12[e] | w rand | 1 050 | $Cr_2O_{3.5}C_{0.26}$ |
| 14B | 500/h$O_2$ | ad | w rand | 10 000 | $Cr_2O_{3.0}C_{0.0}$ |
| 15A | 350/$O_2$ | 1300/12 | w (110), m (**006**) | 2 200−2 800 | |
| 16A | 350/$O_2$ | 750/12 | vw (110), s (**006**) | 2 200−2 800 | |

[a] Sample numbering scheme: sample number, substrate type (A is (0001) $Al_2O_3$, B is silicon, C is unoriented single crystalline $Al_2O_3$), counter number (to distinguish different sample firing temperatures). [b] Deposition zone temperature and atmosphere, where h is humidified gas. Forming gas is identified as $N_2$, $H_2$. [c] $Cr_2O_3$ orientations for films with preferred orientation are given in parentheses. Orientations in bold are epitaxial, as indicated by pole figure analysis. Abbreviations: vw = very weak, w = weak, m = medium, s = strong, rand = randomly oriented, am = amorphous. [d] Stoichiometry was determined by modeling of CRRBS and ORRBS spectra. [e] Sample fired in air. [f] No CRRBS was performed. [g] ad = as deposited.

*Polycrystalline $Al_2O_3$ Substrates.* Deposition at 400−600 °C under oxygen onto polycrystalline alumina yielded green, crystalline $Cr_2O_3$. Gray or tan films, deposited at 200−350 °C, were largely amorphous. Calcination of the amorphous films at 700 °C resulted in an increase in crystallinity of $Cr_2O_3$, as monitored by overall XRD peak intensity, but no change in color. Firing at 1100 °C did not increase crystallinity but did change the color of very thin sections of gray films to green.

*Silicon Substrates.* Preferred orientation of crystalline $Cr_2O_3$ on silicon has been reported by others[25] in coatings made by spray pyrolysis of solutions containing $Cr(acac)_3$. In this work, as-deposited chromium oxide films on silicon showed a strong preferred orientation of crystalline $Cr_2O_3$. There was some indication of an influence on crystallinity by deposition gas; comparison of the XRD patterns of films deposited at 500 °C, under dry $O_2$ (sample 2B1) and humidified $O_2$ (sample 14B, see Figure 2) shows strong preferred orientation of (110) $Cr_2O_3$ at 36.19° ($2\theta$) in the former and randomly oriented $Cr_2O_3$ in the latter.[34] Deposition at 350 °C under humidified $O_2$ produced only amorphous material,

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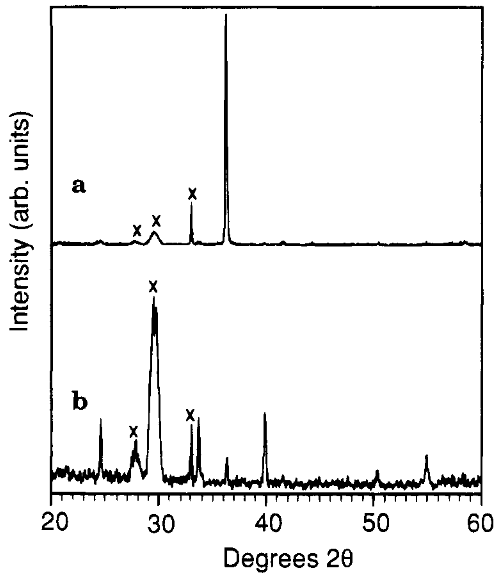

**Figure 2.** XRD patterns of chromium oxide films deposited on silicon at 500 °C under (a) dry oxygen and (b) humidified oxygen, showing preferentially oriented (110) $Cr_2O_3$ and randomly oriented $Cr_2O_3$ patterns, respectively. Silicon substrate and detector fluorescence peaks are marked with an ×.

whereas deposition under dry $O_2$ (sample 6B1) produced completely oriented (006) $Cr_2O_3$.

Pole figure analysis of sample 6B1 demonstrated that the film showed preferred orientation of the basal plane of $Cr_2O_3$, but the crystallites were not epitaxially oriented to the silicon substrate. Deposition under humidified or dry $N_2$ at 500 °C yielded randomly oriented $Cr_2O_3$. The use of a reducing environment, sample 13B1, produced only amorphous material, unlike any other deposition at 500 °C. The overall results show a clear link between deposition atmosphere and film crystallization on silicon, but the cause of this influence is not known.

*Single Crystalline $Al_2O_3$ Substrates.* $Cr_2O_3$ has been deposited on single crystalline $Al_2O_3$ by reactive sputtering of Cr metal,[6] but no such deposition by CVD has been reported. Deposition onto sapphire substrates at 600–900 °C under dry $O_2$ resulted in oriented (110) $Cr_2O_3$ on slightly off-axis (110) $Al_2O_3$ substrates ("unoriented" from the manufacturer; samples 4C and 5C). Pole figure XRD analysis of the films showed that they were epitaxially oriented to the substrate. Calcination at 1100 °C under argon for 24 h did not change the crystallinity, as judged by diffraction peak width and intensity. The composition of the chromium oxide phase was determined to be pure $Cr_2O_3$ from the (110) $Cr_2O_3$ peak position[34] (with the substrate (110) $Al_2O_3$ peak serving as an internal standard), indicating that there was no substantial interdiffusion of the $Cr_2O_3$ and $Al_2O_3$ phases.[35] XRD analyses of films that were deposited onto sapphire substrates at 350 °C under dry $O_2$ also showed epitaxially oriented (110) $Cr_2O_3$ as well as less intense (006) and randomly oriented $Cr_2O_3$. Calcination of these samples at 750 °C under argon yielded an increase in the (110) peak intensity but no decrease in any of the other peaks. Firing at 1300 °C resulted in a disappearance of all peaks except the (110) and (006) peaks. No interdiffusion of the film and the substrate could be detected from shifts in the $Cr_2O_3$ or $Al_2O_3$ (110) peaks, but a small interfacial reaction zone, ≤150 Å, would be below the limits of detection of the XRD analysis.

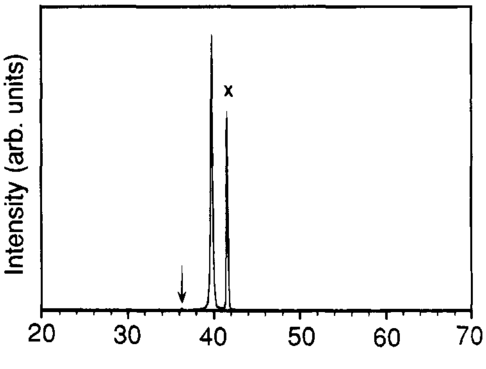

**Figure 3.** XRD pattern of epitaxially oriented (006) $Cr_2O_3$ deposited at 350 °C under $O_2$ and calcined at 750 °C for 12 h. The substrate is (0001) $Al_2O_3$, and the (006) $Al_2O_3$ peak is marked with an ×. The arrow indicates the position of a very low intensity (110) $Cr_2O_3$ peak.

Depositions at 900 °C under dry $O_2$ onto (0001) $Al_2O_3$ substrates gave (006) $Cr_2O_3$. Films deposited at 350 °C under dry $O_2$ onto (0001) $Al_2O_3$ substrates and calcined at 750 and 1300 °C under argon, yielded epitaxially oriented (006) $Cr_2O_3$, (samples 15 A and 16A; see Figure 3), as well as a much weaker (110) $Cr_2O_3$ peak in some patterns.

No evidence of interdiffusion of the film and substrate was seen. Thus, although completely epitaxially oriented films are deposited at 600–900 °C under dry $O_2$, the conversion of partially crystalline $Cr_2O_3$ films deposited at 350 °C under $O_2$, to fully crystalline $Cr_2O_3$ by high-temperature firing resulted in a small amount of oriented (110) $Cr_2O_3$ in addition to the epitaxially oriented (006) $Cr_2O_3$.

**IR Spectroscopic Analysis.** Samples on silicon substrates were analyzed by transmission IR spectroscopy for which an uncoated silicon substrate was used as a reference. The IR spectra of chromium oxides have been reported for powders; the Cr–O stretching modes of $Cr_2O_3$ absorb between 710 and 400 $cm^{-1}$.[36–39] The five resolved peaks and shoulders in the crystalline $Cr_2O_3$ spectrum are replaced by a single, broad absorbance centered around 600 $cm^{-1}$ for the amorphous oxide.[38] Our as-deposited films that contained crystalline $Cr_2O_3$ (as seen in the XRD), exhibited distinct IR absorbances at 652, 540, 445, and 407 $cm^{-1}$ with shoulders at 613 and 586 $cm^{-1}$ which correspond well with the reported spectra for powder.[36–39] Amorphous films gave single broad absorbances centered at 600 $cm^{-1}$. None of the IR spectra showed absorbances at 900–1000 $cm^{-1}$, which would be indicative of crystalline chromium oxide phases of composition $CrO_x$ ($x > 1.5$).[37] The absence of absorbances in the O–H stretching region, 3000–3500 $cm^{-1}$, confirmed the absence of any

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trapped $H_2O$ or Cr−OH from deposition in humidified atmospheres. No absorbances from the precursor were detected.

Thus, IR spectroscopy indicated that the precursor decomposed cleanly at temperatures above 300 °C to give films that were free of organic residues, hydroxides or water.

**UV−Vis Spectroscopy.** The ultraviolet and visible absorption spectra obtained from reflectivity measurements of single crystals and thin films[4,40] and powders[39] of $Cr_2O_3$ have been reported. Both the thin-film and powder spectra show absorbances at 600, 460, 370−355, and 250 nm. The UV−vis spectra of $Cr_2O_3$ powder is also reported[39] to contain a weak absorbance at 700 nm due to a forbidden transition that has not been reported for $Cr_2O_3$ thin films. The data of Kirby *et at.*[4] and Misho *et al.*[24] indicate that very thin films of $Cr_2O_3$ do not show any of the expected $Cr^{3+}$ absorbances. No doubt the diffuse nature of the peaks contributes to a lower sensitivity of UV−vis spectroscopy. In the present work, films of $Cr_2O_3$, deposited at 350 °C under dry oxygen onto single crystalline sapphire substrates, showed absorbances at 600 and 470 nm with shoulders at 370 and 500 nm, and a very broad charge-transfer band centered at 250 nm. No absorbance at 550 nm, indicative of $CrO_2$,[7] was seen. No changes in the UV−vis spectra were seen for samples fired to 1100 or 1300 °C under argon. The main features of the spectra correspond to the expected d−d transitions of $Cr^{3+}$ but the cause of the small shoulder at 500 nm is not known.

Thus, in spite of the observed color differences in films as-deposited at 350 °C and films fired at 1300 °C after deposition, gray and green, respectively, no significant differences were seen in their UV−vis spectra. Although no strong evidence of chromium species other than $Cr^{3+}$ was seen, due to the relatively low sensitivity of UV−vis spectroscopy for thin films, we cannot rule out the existence of other chromium oxidation states in the films based on these spectra.

**Profilometry and Optical and Electron Microscopy.** Profilometry showed that thickness usually varied along the length of the deposition. Typically, a very thin film formed at the front of the deposition zone and film thickness rapidly increased along the deposition length. The center portion of the deposited film was of constant thickness and the film ended abruptly. Films deposited at 500 °C under $O_2$ onto silicon were comprised of close packed, 0.2−0.5-μm-sized grains completely covering the surface. Profilometry indicated surface roughness on the order of 1000 Å. Films deposited at higher temperatures, viz., 600−900 °C, on single crystalline $Al_2O_3$ substrates contained well-faceted crystallites of $Cr_2O_3$. At low coverages (deposition starting with less than 20 mg of precursor), the crystallites were well separated and ranged in size from 5 to 10 μm wide (Figure 4a). Profilometry revealed that the crystals were 1−3 μm thick. Deposition from larger amounts of $Cr(acac)_3$ yielded surfaces that were more densely covered with crystallites, as seen in Figure 4b. Crystallite thicknesses of 2−4 μm suggest that $Cr_2O_3$ formed in an island growth mode rather than a layer by layer mode. A small number of nucleation sites on the surface produced small single crystals. Subsequently deposited material added to these small crystals rather than to the uncovered surface.

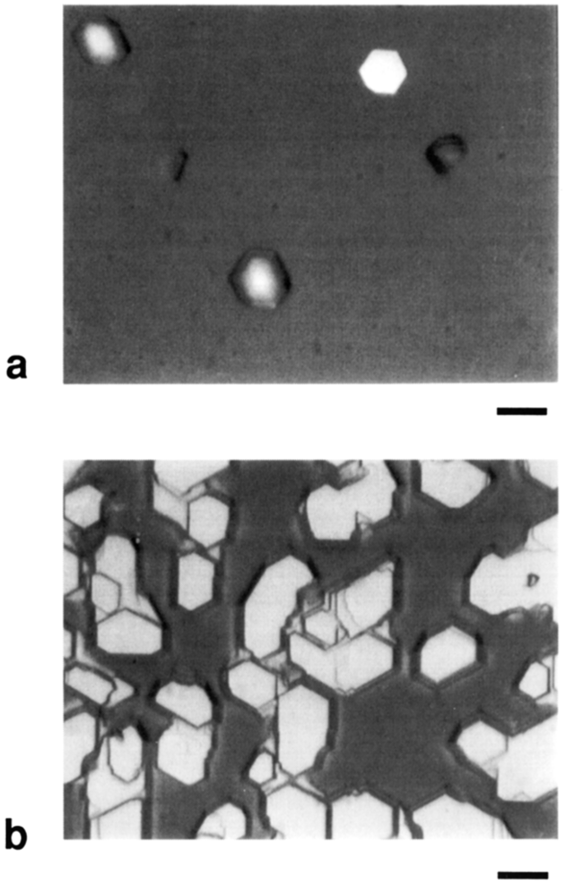

**Figure 4.** Optical micrographs of $Cr_2O_3$ films at 900 °C in $O_2$ on (0001) $Al_2O_3$: (a) at low coverage showing well-faceted crystallites; (b) at higher coverage showing intergrowth of crystallites. The bar is 10 μm.

Chromium oxide films deposited under $O_2$ or humidified $N_2$ at 350 °C and under $N_2$ or forming gas at 500 °C were very smooth. The surfaces of the as-deposited films were featureless at magnifications greater than 20 000× on silicon and single crystalline $Al_2O_3$. Firing at 750 °C under argon did not produce any change in the surface features. Firing at 1300 °C yielded some poorly resolved surface features, seen at 10 000×. Profilometry showed an increase in surface roughness from <50 Å (for the as-deposited films) to 300−600 Å for films fired at 1300 °C. Therefore, deposition at 350 °C and subsequent annealing yielded films that did not show crystalline $Cr_2O_3$ islands on the surface and were substantially smoother than those deposited at 500−900 °C.

**Rutherford Backscattering Spectroscopy.** Carbon content is difficult to assess quantitatively by most surface analysis techniques. Rutherford backscattering spectroscopy performed at the carbon and oxygen resonance energies, CRRBS and ORRBS, respectively, is a powerful technique for quantitative analysis of 1000 Å to 10 μm thick films, giving carbon and oxygen concentrations. This relatively new analytical method exploits the phenomenon of nuclear "resonance", which enhances the backscattered $He^{3+}$ ion yield from light nuclei 10−

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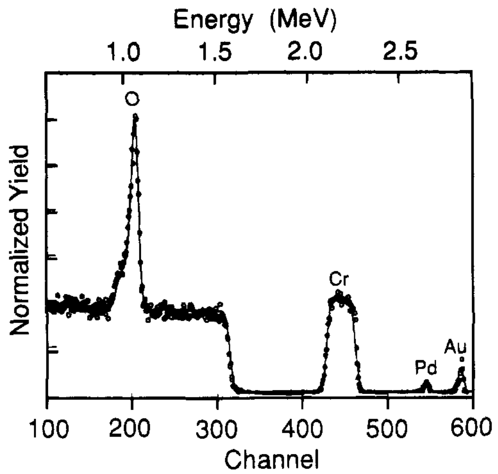

**Figure 5.** Oxygen resonance RBS spectrum of an oxygen-rich chromium oxide film, deposited on silicon at 350 °C under $O_2$ and fired at 750 °C for 24 h. The Au and Pd signals are from a 20 Å layer sputtered on the surface to prevent charging. The film's composition of $Cr_2O_{3.3}$ is derived from the modeled spectrum given by the solid line.

100-fold.[41,42] This resonance phenomenon is seen at an incident ion energy of 4.28 MeV for carbon and at 3.06 MeV for oxygen.[29,30]

CRRBS and ORRBS data are presented in Table 1. Analysis of films on silicon, deposited at 500 °C under dry $O_2$, indicated a composition of $Cr_2O_3$ consistent with their green color. Smooth, gray films deposited at 350–500 °C under $N_2$ or below 400 °C under $O_2$ were richer in oxygen with film compositions of $Cr_2O_x$ where $3.2 \leq x \leq 4.9$ (see Figure 5). All of these films contained less than 4 atomic % carbon. The oxygen content of as-deposited films *increased* as follows: dry and humidified $O_2$ at 500 °C < dry $O_2$ at 350 °C < dry and humidified $N_2$ at 500 °C < humidified $O_2$ at 350 °C < humidified $N_2$ at 350 °C. From this ranking we can deduce the following:

1. The oxygen present in the oxygen-rich films may not necessarily come from the deposition atmospheres as illustrated by depositions under dry $N_2$ at 500 °C where very little oxygen was present. The acetylacetonate ligands contain two oxygens each, or six oxygens per chromium. Therefore, there are more than enough oxygens contained in the precursor to provide the observed film stoichiometry. Tracer experiments, needed to settle this question, are planned.

2. In both $O_2$ and $N_2$ deposition atmospheres, the addition of water at 500 °C does not substantially change the stoichiometry of the film. The addition of water at 350 °C increases the oxygen content for films deposited under $O_2$ and is necessary to obtain any film at all under $N_2$. These observations indicate that the role of gaseous $H_2O$ in the decomposition of the precursor is important at lower temperatures.

3. Overall, contrary to what might be expected, films deposited under $N_2$ contained more oxygen than those formed in $O_2$ under comparable conditions. The only exception is deposition at 350 °C under dry $N_2$ in which no film is formed at all. An atmosphere of $O_2$ seems to change the decomposition mechanism of the precursor and yields stoichiometric $Cr_2O_3$ films at 500 °C, a lower temperature than that of any other deposition environment.

Deposition under a reducing atmosphere (forming gas) yielded an oxygen-rich film, further supporting the hypothesis that the oxygen in the films may come from the ligand and not from the deposition atmosphere. These depositions showed that a reducing atmosphere at 500 °C is not sufficient to convert oxygen-rich films to stoichiometric $Cr_2O_3$. CRRBS showed that the films (sample 13B1) also contained a significant amount (13 atomic %) of residual carbon. Firing for 12 h at 750 °C under oxygen, (13B2), yielded films with excess oxygen and residual carbon; $Cr_2O_{3.5}C_{0.26}$. Although the firing did remove some excess oxygen and carbon, their continued presence after 12 h at 750 °C suggests that diffusion of oxygen or carbon within the film is quite slow.

Films of composition $Cr_2O_{3.5}$, deposited under dry $O_2$ at 350 °C, were calcined at 700, 750, and 1100 °C under argon. ORRBS analysis revealed that the films did not lose any oxygen but CRRBS showed a loss of carbon upon firing at 750 °C (from 4 to 1.7 atomic % carbon). Films deposited under wet $N_2$ at 350 °C exhibited a loss of oxygen upon firing, changing from $Cr_2O_{4.9}$ to $Cr_2O_{3.7}$. Films deposited under dry $O_2$ at 350 °C and fired under argon at 1300 °C for 12 h, yielded a composition of $Cr_2O_{3.08}$ when analyzed. This corresponds to a 96–97 mol % conversion to $Cr_2O_3$ with the remaining 3–4 mol % calculated as $CrO_3$ or $CrO_2$, respectively.

The present work represents the first use of ORRBS and CRRBS in the analysis of chromium oxide films. Ajayi and co-workers[27] used conventional RBS for the examination of chromium oxide films produced by direct pyrolysis of $Cr(acac)_3$; films deposited under argon at 420 °C, designated "$Cr_2O_3$", may have been oxygen-rich. The nonstoichiometry would be consistent with the films' reported black color.[27]

**X-ray Photoelectron Spectroscopy.** X-ray photoelectron spectra of various chromium oxides have been reported.[4,19,43,44] The shift in the core Cr $2p^{3/2}$ peak with change in oxidation state of the chromium is relatively small, <5 eV, and the XPS spectra of oxides with multiple chromium oxidation states contain overlapping $2p^{3/2}$ peaks. XPS analysis was used to qualitatively determine the oxidation states of chromium in oxygen-rich films deposited at 350 °C under dry $O_2$ and humidified $N_2$ (samples 6B and 7B, respectively). The resistivities of the films were low enough to prevent charging of the surface during measurement. Samples that were calcined at 750 °C gave slight shifts in peak positions to higher energy, indicating a decrease in surface conductivity with respect to the dried films. All the spectra from oxygen-rich films had multiple peaks for Cr and indicated the presence of chromium in oxidation states III, IV, and VI (see Figure 6). Assignments of peaks were made by comparison of peak energies to those reported from spectra of $Cr_2O_3$, $CrO_2$, and $CrO_3$.[19,43,44] Although films, deposited on single crystalline $Al_2O_3$ and fired at 1300 °C (sample 10C2)

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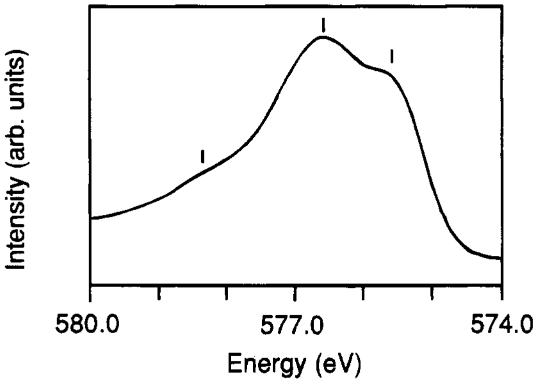

**Figure 6.** XPS spectrum of the Cr $2p^{3/2}$ peak of a chromium oxide film deposited under dry $O_2$ at 350 °C and dried at 250 °C for 2 h. The peaks at 578.4, 576.5, and 575.3 eV, (indicated with vertical slashes), are assigned to Cr(VI), Cr(III) and Cr(IV), respectively (see text).

suffered from significant charging, and required the use of an electron flood gun, the corrected peak centroid position at 576.6 eV corresponded well to that of reported values for $Cr^{3+}$.

Although no chromium oxide phase, other than $Cr_2O_3$, is thermodynamically stable above 500 °C, the existence of $Cr^{6+}$ at high temperatures during the oxidation of chromium metal has been reported.[45,46] Clearly, the existence of oxidation states other than $Cr^{3+}$ in films fired to 1100 °C is indicative of a non-equilibrium condition. Formation of a very thin layer of $Cr_2O_3$ on the oxide surface could act as a diffusion barrier due to the very low self diffusion rate of $Cr_2O_3$.[17,18,47] A thin layer of $Cr_2O_3$ on the surface could account for the observed increase in the surface resistivity for samples fired at 750 °C. Firing at 1300 °C for 12 h in argon is sufficient to convert oxygen-rich films to the thermodynamically stable $Cr_2O_3$ phase.

## Summary and Conclusions

MOCVD of chromium oxide, using $Cr(acac)_3$ as a precursor, is dramatically affected by deposition temperature and carrier gas. Films of epitaxially oriented $Cr_2O_3$ were deposited on single crystalline $Al_2O_3$ substrates under $O_2$ at temperatures above 500 °C. Depositions under $O_2$ or humidified $N_2$ at 350 °C, and $N_2$ or forming gas at 500 °C, produced oxygen-rich films, $Cr_2O_x$ ($3.2 \leq x \leq 4.9$) as analyzed by carbon and oxygen resonance RBS. All deposition atmospheres, other than forming gas, yielded films with very little carbon. In contrast to the relatively rough films of $Cr_2O_3$ deposited at 600–900 °C, all oxygen-rich, largely amorphous $Cr_2O_x$ ($3.2 \leq x \leq 4.9$) films were very smooth. IR spectroscopy indicated that the as-deposited films did not contain water, hydroxide, or precursor residues. XRD showed that the only crystalline phase present in the films was $Cr_2O_3$. Multiple, high oxidation states of chromium were indicated by XPS analysis of oxygen-rich films. Firing of the oxygen-rich films at 750–1100 °C for 24 h under argon was not sufficient to convert them to the thermodynamically stable $Cr_2O_3$ phase. Firing at 1300 °C for 12 h under argon yielded epitaxially oriented $Cr_2O_3$ on single crystalline $Al_2O_3$ substrates in >96% conversion. Deposition under a reducing atmosphere produced oxygen-rich films that contained a substantial amount of residual carbon. These films contained excess oxygen and some residual carbon after firing at 750 °C under oxygen. All of the as-deposited oxygen-rich films were stable at much higher temperatures than analogous chromium oxide powders, perhaps due to a very low diffusivity within the films.

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