

May 2000

SELECTIVE AREA CHEMICAL VAPOR DEPOSITION OF CHROMIUM OXIDES

Ruihua Cheng

University of Nebraska - Lincoln

C.N. Borca

University of Nebraska - Lincoln

Peter A. Dowben

University of Nebraska-Lincoln, pdowben@unl.edu

Follow this and additional works at: <http://digitalcommons.unl.edu/physicsdowben>



Part of the [Physics Commons](#)

Cheng, Ruihua ; Borca, C.N.; and Dowben, Peter A., "SELECTIVE AREA CHEMICAL VAPOR DEPOSITION OF CHROMIUM OXIDES" (2000). *Peter Dowben Publications*. 166.

<http://digitalcommons.unl.edu/physicsdowben/166>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

SELECTIVE AREA CHEMICAL VAPOR DEPOSITION OF CHROMIUM OXIDES

Ruihua Cheng, C.N. Borca, and P.A. Dowben

Department of Physics and Astronomy and the Center for Materials Research and Analysis (CMRA), Behlen Laboratory of Physics, University of Nebraska-Lincoln, NE 68588-0111, USA, pdowben@unlserve.unl.edu

ABSTRACT

We demonstrate that two-phase CrO_2 and Cr_2O_3 thin films can be grown by using selective organometallic chemical vapor deposition through the oxidation of $\text{Cr}(\text{CO})_6$ in an oxygen environment. While the magnetization measurements show that both chromium oxides are present, the relative weight of each phase depends on the oxygen partial pressure. Changes of the Curie temperature, T_c , and the saturation magnetization field may be possible by controlling the stoichiometry.

INTRODUCTION

Chromium oxides have been seriously considered as spin-polarized electron injectors to spin-tunnel junctions [1] and other magnetoresistive devices [2,3]. The insulating antiferromagnetic chromium oxide Cr_2O_3 has a Néel temperature of 307K and is suitable as a tunnel junction barrier [3] both below and above the Néel temperature. The ferromagnetic chromium oxide CrO_2 with T_c of 397K [4], has been predicted half-metallic (metallic for one spin direction while insulating for the other spin direction) by band structure calculations [5-9], though Kulatov and Mazin found CrO_2 to be insulating in both spin directions [10]. Evidence of nearly 100% polarization, consistent with the half metallic character of CrO_2 , were observed in spin-polarized photoemission [11], vacuum tunneling [12], and Andreev scattering [13], though some discrepancies from perfect half metallic character remain unresolved. The high electron polarization, in addition to the half metallic character of the surface [9] (and by extension, one hopes the interface as well) makes CrO_2 an attractive material for spin-polarized electron tunneling, and very large tunneling magnetoresistance (TMR) is expected.

It is difficult to fabricate CrO_2 films using conventional methods because CrO_2 is metastable. This is not altogether bad, as the two-phase $\text{CrO}_2/\text{Cr}_2\text{O}_3$ system exhibits higher magnetoresistance than the pure material [3]. The oxidation of the organometallic complex hexacarbonyl $\text{Cr}(\text{CO})_6$ has the potential for selective deposition of CrO_2 [14-17]. These studies have established that chromium oxides are the thermodynamic sinks of chromium hexacarbonyl decomposition [16], and the oxidation is further aided by the presence of an ambient oxygen background [14,15]. By modifying this organometallic chemical vapor deposition (OMCVD) procedure, we have been able to fabricate the ferromagnetic and antiferromagnetic chromium oxides. Here we describe both the growth and the magnetic properties of these films.

EXPERIMENTAL APPROACH

Film growth was carried out on Si (111) substrates in an ultra high vacuum chamber with maintained base pressure of 1.0^{-9} Torr. This chamber was designed for laser-initiated chemical vapor deposition, as described elsewhere [18-19]. The prevalent source compound was $\text{Cr}(\text{CO})_6$.

During the deposition the photolytic decomposition of $\text{Cr}(\text{CO})_6$ was performed by a commercial nitrogen laser with the main emission line at 337 nm (corresponding to 3.69 eV) and running at a repetition rate of 10 Hz. A quartz lens was used to focus the radiation onto the substrate.

The laser-initiated decomposition and oxidation was aided by the ambient oxygen (O_2) atmosphere ranging from 2×10^{-7} to 1×10^{-6} Torr, relative to the $\text{Cr}(\text{CO})_6$ partial pressure of 1×10^{-5} Torr. Purity of the gases introduced was monitored with a quadruple mass spectrometer operated in pulse counting mode.

The films were examined by scanning electron microscopy (SEM) and x-ray emission spectroscopy (XES or EDAX). Magnetic measurements have been carried out by using a superconducting quantum interference device (SQUID) magnetometer.

RESULTS

Figure 1 shows the SEM image of the film fabricated with 1×10^{-6} Torr O_2 partial pressure and 1×10^{-5} Torr $\text{Cr}(\text{CO})_6$ partial pressure. The topology of the film is relatively uniform, with only a fine microstructure visible on an 800 nm scale.

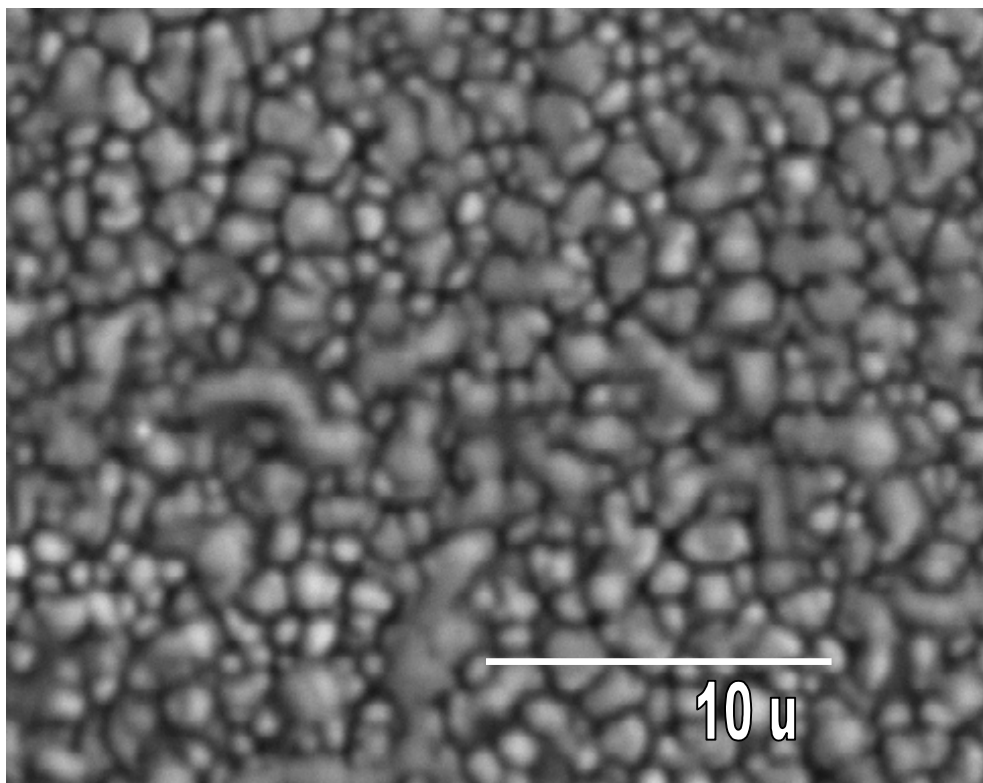


Figure 1: The scanning electron microscope image of a chromium oxide film fabricated on a Si (111) substrate by laser-initiated decomposition of $\text{Cr}(\text{CO})_6$ (pressure 1×10^{-5} Torr) in an ambient O_2 (1×10^{-6} Torr) background.

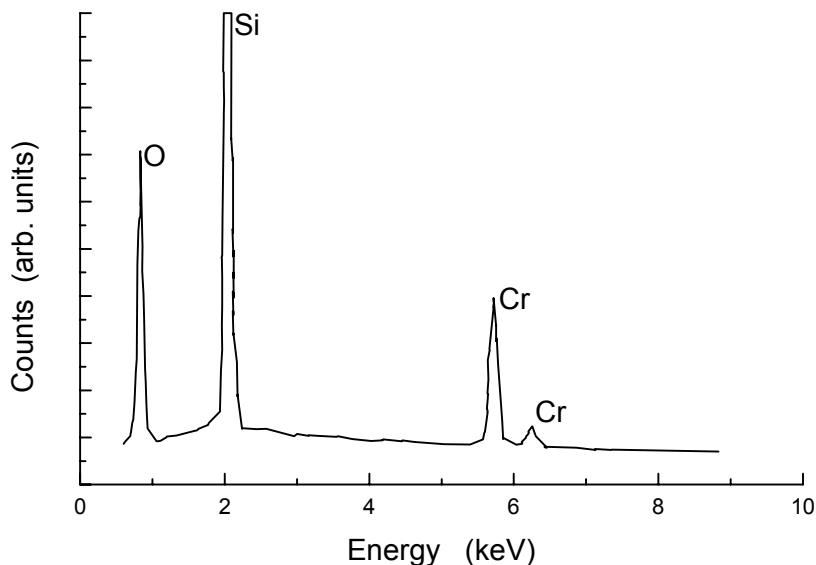


Figure 2: The EDAX spectra of the film shown in Figure 1. Note the strong oxygen and chromium signals in addition to the silicon signal from the Si(111) substrate.

As seen in Figure 2, the EDAX spectra of the same film shown in Figure 1, provides evidence for the desirable oxygen and chromium signal in addition to the strong Si signal from the substrate.

Figure 3 shows the magnetization versus temperature obtained from SQUID. The critical temperature clearly depends upon the oxygen partial pressure at the time of film fabrication. At low oxygen partial pressure (an O_2 pressure of 2×10^{-7} Torr relative to the $Cr(CO)_6$ partial pressure of 1×10^{-5} Torr) the Curie temperature was 345 ± 10 K. At higher oxygen partial pressure (an O_2 pressure of 1×10^{-6} Torr relative to the $Cr(CO)_6$ partial pressure of 1×10^{-5} Torr) the Curie temperature was 390 ± 10 K.

The hysteresis loop, shown in the inset to Figure 3, was obtained at 100 K with the applied magnetic field in the plane of the film. The curve shown is for the sample with the lower O_2 partial pressure (an O_2 pressure of 2×10^{-7} Torr relative to the $Cr(CO)_6$ partial pressure of 1×10^{-5} Torr). We find that the saturation field for this film is about 1.5 T.

DISCUSSION

The absence of a sharp T_c and the presence of a long tail in the magnetization curves (Figure 3) near the critical temperature, are suggestive of a two-phase system. This is supported by indications of both ferromagnetic and antiferromagnetic behavior in the hysteresis loops.

The fact that the coercive fields for these films are often not symmetric in our films suggests uniaxial antiferromagnetism, in addition to the more conventional antiferromagnetic behavior. In the hysteresis loop obtained for the film at the lower oxygen partial pressure, for the left half of the loop the coercivity is 250 Oe while for the right half of the loop the coercivity is 150 Oe, in addition to having other characteristics of antiferromagnetism: strong hysteresis at higher fields.

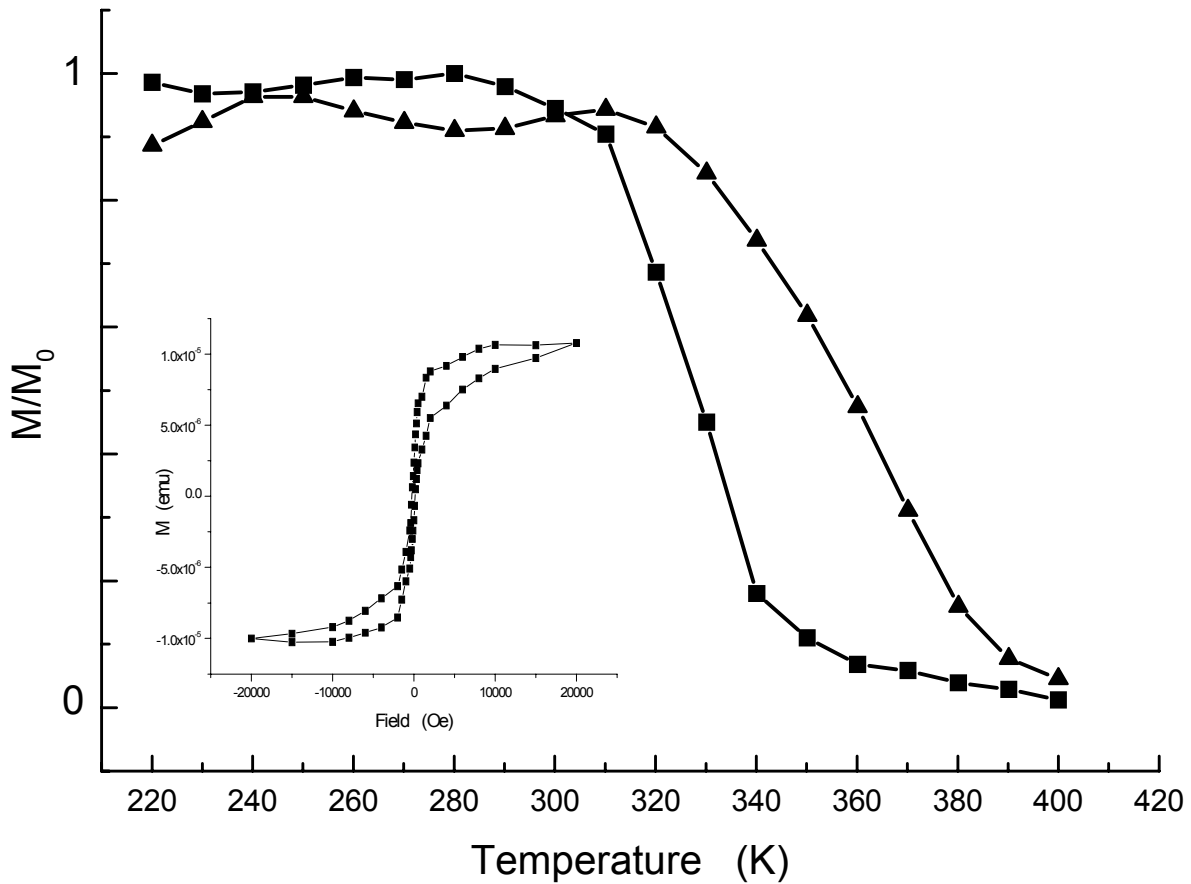


Figure 3: The magnetization (M/M_0) versus temperature (T) at an applied field of $H=500$ Oe. Data are shown for two films: at low oxygen partial pressure (▲), i.e. (an O_2 pressure of 2×10^{-7} Torr relative to the $Cr(CO)_6$ partial pressure of 1×10^{-5} Torr) and at higher oxygen partial pressure (■), i.e. (an O_2 pressure of 1×10^{-6} Torr relative to the $Cr(CO)_6$ partial pressure of 1×10^{-5} Torr). The hysteresis loop, shown as an inset, was taken at 100K for the film with an O_2 pressure of 2×10^{-7} Torr.

We believe that our films contain both ferromagnetic CrO_2 and antiferromagnetic Cr_2O_3 phases. At lower oxygen partial pressures, CrO_2 becomes less dominant, compared with Cr_2O_3 , and the Curie temperature is suppressed to lower temperatures than the expected 397 K of CrO_2 (the Néel temperature of Cr_2O_3 is 307 K). When we increased the O_2 partial pressure, the amount of CrO_2 phase increased, and the critical temperature approached the expected T_c of 397 K.

In any case, deposition of our two-phase chromium oxide films is restricted to the area of the substrate illuminated with the light, so that the process is clearly a selective area deposition process.

CONCLUSIONS

We have used laser-assisted chemical vapor deposition and oxidation of $\text{Cr}(\text{CO})_6$ to make chromium oxide thin films. The advantage of this technique is selective area deposition. The resulting films exhibit behavior consistent with a two-phase system containing both Cr_2O_3 and CrO_2 domains in the films, and the relative weight of each phase appears to depend on the O_2 partial pressure. If we choose the appropriate oxygen partial pressure, we should be able to obtain pure Cr_2O_3 and CrO_2 phases respectively.

ACKNOWLEDGEMENTS

This work was supported by NSF through grant # DMR-98-02126, the Center for Materials Research and Analysis (CMRA) and the Nebraska Research Initiative at the University of Nebraska.

BIBLIOGRAPHY

1. A.M. Bratkovsky, *Phys. Rev. B.* **56** (1997) p. 2344.
2. S.S. Manoharan, D. Elefant, G. Reiss and J.B. Goodenough, *Appl. Phys. Lett.* **72** (1998) p. 984; X.W. Li, A. Gupta, T.R. McGuire, P.R. Duncombe, and Gang Xiao, *J. Appl. Phys.* **85** (1999) p. 5585; K. Suzuki and P.M. Tedrow, *Phys. Rev. B.* **58** (1998) p. 11597.
3. J.D.M. Coey, A.E. Berkowitz, Ll Balcells, F.F. Putris and A. Barry, *Phys. Rev. Lett.* **80** (1998) p. 3815.
4. J. S. Kouvel and D. S. Rodbell, *J. Appl. Phys.* **38** (1967) p. 979.
5. K. Schwarz, *J. Phys.* **16** (1986) p. L211.
6. S. Matar, G. Demazeau, J. Sticht, V. Eyert, and J. Kübler, *J. de Physique I* **2** (1992) p. 315.
7. M.A. Korotin, V.I. Anisimov, D.I. Khomskii and G.A. Sawatzky, *Phys. Rev. Lett.* **80** (1998) p.4305.
8. S.P. Lewis, P.B. Allen, T. Sasaki, *Phy. Rev. B* **55** (1997) p. 10 253.
9. H. van Lueken and R.A. de Groot, *Phys. Rev. B* **51** (1995) p. 7176.
10. E. Kulatov and I.I. Mazin, *J. Phys. Condens. Matter*, **2** (1990) p. 343.
11. K.P. Kämper, W. Schmitt, G. Güntherodt, R.J. Gambino, and R. Ruf. *Phys. Rev. Lett.*, **59** (1987) p. 2788.
12. R. Weisendanger, H.-J. Güntherodt, G. Güntherodt, R.J. Gambino, and R. Ruf. *Phys. Rev. Lett.*, **65** (1990) p. 247.
13. R.J. Soulen, et al., *Science*, **282** (1998) p. 85; R.J. Soulen, M.S. Osofsky, B. Nadgorny, T. Ambrose, P. Boussard, S.F. Cheng, C.T. Tanaka, J. Nowack, J.S. Moodera, G. Laprade, A. Barry and M.D. Coey, *J. Appl. Phys.*, **85** (1999) p. 4589.
14. P. A. Dowben, Yoon Gi Kim, S. Baral-tosh, G. O. Ramseyer, Chanyong Hwang and M. Onellion, *J. Appl. Phys.*, **67** (1990) p. 5658.
15. K. Perkins, C. Hwang, M. Onellion, Yoon-Gi Kim, and P.A. Dowben, *Thin Solid Films* **198** (1991) p. 317–329.
16. D.C. Mancini, S. Varma, J.K. Simons, R.A. Rosenberg, and P.A. Dowben, *J. Vac. Sci. Technol.* **B8** (1990) p.1804–1807.

17. P.A. Dowben and M. Onellion, "Fabrication of CrO₂ and Cobalt Doped CrO₂ Films from Organometallic Complexes", U.S. Patent Number 4,980,198 issued December 25, 1990.
18. D. Welipitiya, C. N. Borca, P. A. Dowben, I. Gobulukoglu, H. Jiang, B. W. Robertson and J.D. Zhang, *Mat. Res. Soc. Symp. Proc.*, **475** (1997) p. 257.
19. C. N. Borca, D. Welipitiya, S. Adenwalla and P. A. Dowben, *Phys. Low-Dim. Struct.*, **11/12** (1997) p.173.