

Structural and Microanalytical Studies of CrO₂ Thin Films on c-Sapphire by High Resolution Electron Microscopy Methods

M.I. Ortiz ^a, P.M. Sousa ^b, C. Ballesteros ^a, A.J. Silvestre ^c, L.F. Cohen ^d and O. Conde ^{b,*}

^a Universidad Carlos III, EPS, Departamento de Física, 28911 Leganés (Madrid), Sp

^b Universidade de Lisboa, Departamento de Física e ICEMS, 1749-016 Lisboa, PT

^c Instituto Superior de Engenharia de Lisboa e ICEMS, 1959-007 Lisboa, PT

^d Imperial College, Department of Physic, Blackett Laboratory, London SW7 2AZ, UK

* oconde@fc.ul.pt

Chromium dioxide (CrO₂) has been extensively used in the magnetic recording industry. However, it is its ferromagnetic half-metallic nature that has more recently attracted much attention, primarily for the development of spintronic devices. CrO₂ is the only stoichiometric binary oxide theoretically predicted to be fully spin polarized at the Fermi level. It presents a Curie temperature of ~ 396 K, i.e. well above room temperature, and a magnetic moment of 2 μ_B per formula unit [1-5]. However an antiferromagnetic native insulating layer of Cr₂O₃ is always present on the CrO₂ surface which enhances the CrO₂ magnetoresistance and might be used as a barrier in magnetic tunnel junctions.

Here we report on high resolution electron microscopy structural and analytical studies of CrO₂ films deposited onto Al₂O₃ (0001) by atmospheric pressure CVD from CrO₃ precursor. As reported previously [6] films were grown within a broad range of deposition temperatures from 320 to 410 °C, and oxygen carrier gas flow rates of 50 – 500 sccm. Herein we will show the results obtained for two films grown at 340 and 360 °C with 100 sccm oxygen.

Cross-sectional specimens for TEM were prepared by mechanical grinding, dimpling and argon ion-milling of the samples in a liquid-nitrogen-cooled holder with an acceleration voltage of 5 keV and an incidence angle of 8°. Analytical TEM and HREM studies were carried out using a Philips Tecnai 20F FEG microscope operating at 200 keV, equipped with an Energy Dispersive X-Ray (EDX) analysis system and a scanning transmission electron microscopy modulus (STEM) with a high angle annular detector (HAAD) for Z-contrast imaging and composition mapping. Electron diffraction pattern (EDP) and simulations using Fast Fourier transform (FFT) of the HREM images were used to analyze the crystal structure.

Bright field images of the sapphire substrate and of the chromium oxide film deposited at 360 °C are shown in figure 1. Two different growth areas were identified. At the first stages of deposition a three-dimensional (3D) growth forming pyramidal structures of Cr₂O₃ is observed. Defects and distortions at the substrate-film interface can be seen. The corresponding high resolution image is also shown in figure 1, as well as the simulated patterns using FFT which indicate that both aluminium and chromium oxides show corundum structure with an orientation relationship between the substrate and the 3D layer of the type (0001) Al₂O₃ || (0001) Cr₂O₃. The top part of the layer that appears with a clear contrast is a mixture of Cr₂O₃ and tetragonal rutile CrO₂. The observed contrast in the top layer suggests a columnar growth and the defects observed along the layer indicate epitaxial stress during growth.

When the films are grown at a lower temperature of 340 °C a different interfacial structure is observed. The substrate/film interface appears sharp and free of defects, as can be seen in the high resolution image of figure 2, no Cr₂O₃ 3D interlayer structure is formed, and only a mixture of CrO₂ and Cr₂O₃ crystals could be identified. From the selected area diffraction pattern and FFT simulations, the following orientation relationship between the oxides was determined: [01-10] Al₂O₃ || [01-10] Cr₂O₃ || [001] CrO₂.

In conclusion, the CVD films develop with a different interfacial structure depending on deposition temperature which might be used to build different types of devices.

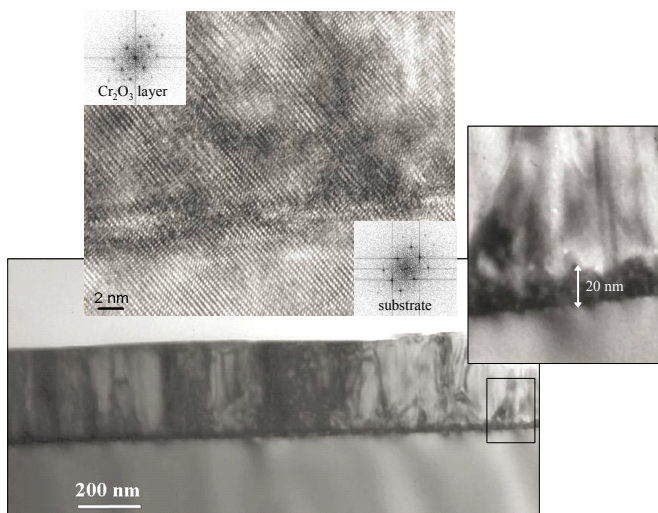


Fig. 1. Bright field and high resolution electron microscopy images and FFT simulations of a film grown at 360 °C with an oxygen flow rate of 100 sccm.

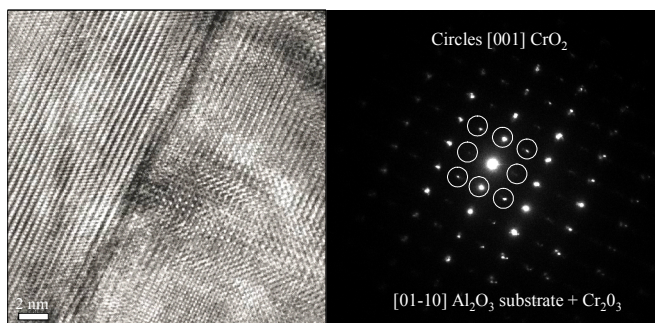


Fig. 2. High resolution electron microscopy image and selected area diffraction pattern of a film grown at 340 °C with an oxygen flow rate of 100 sccm.

References

- [1] K. Schwartz, *J. Phys. F: Met. Phys.* 16 (1986) L211.
- [2] K.P. Kämper et al., *Phys. Rev. Lett.* 59 (1987) 2788.
- [3] R.J. Soulen, et al, *Science* 282 (1998) 85.
- [4] H. Imamura, S. Takahashi, S. Maekawa, *Concepts in Spin Electronics*, Oxford University Press, Oxford, UK, 2006.
- [5] J.M.D. Coey, and M. Venkatesan, *J. Appl. Phys.*, 91 (2002) 8345.
- [6] P. M. Sousa et al., *Chem. Vapor Deposition*, 13 (2007) 537-545.
- [7] The authors gratefully acknowledge the financial support of Fundação para a Ciência e Tecnologia (FCT) under contract POCTI/CTM/41413/2001, CRUP/CSIC bilateral contract E-19/06, and CRUP/British council bilateral contract B-7/07. P.M. Sousa also acknowledges FCT for a PhD grant (BD16567/2004).