CVD of CrO$_2$: towards a lower temperature deposition process

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The ability to manipulate and amplify currents of different spin-type is the basis of an important and rapidly developing field of fundamental and applied research known as spintronics. Among the magnetic materials being actively investigated for their potential use in spintronic devices, chromium dioxide (CrO$_2$) is one of the most attractive because it is a half-metal fully spin polarized at the Fermi level with a Curie temperature above room temperature ($T_c=393$ K) and a calculated magnetic moment of $2 \mu_B$/f.u.$^{[1-4]}$. Therefore, much effort has been put into developing efficient and controlled methods for preparing CrO$_2$ films. Nevertheless, the synthesis of CrO$_2$ films has been a difficult task because it lacks a thermodynamic stable plateau at atmospheric pressure and, if heated, easily decomposes into the insulating antiferromagnetic Cr$_2$O$_3$ phase which is the most stable chromium oxide at ambient conditions.

Although efforts to grow CrO$_2$ thin films have involved several techniques,$^{[5-11]}$ until now
chemical vapour deposition (CVD) seems to be the most successful one to produce these films. Highly oriented thin films of CrO$_2$ are currently grown on TiO$_2$ rutile phase and Al$_2$O$_3$(0001) by thermal CVD using CrO$_3$ as chromium precursor.$^{[12-15]}$ CrO$_3$ is vaporised at 260 °C, carried into the reaction zone by an oxygen/argon flux and thermally decomposed onto a heated substrate. Besides CrO$_3$, other precursors such as Cr$_3$O$_{21}$ and CrO$_2$Cl$_2$ have also been used for the CVD of CrO$_2$ layers with similar properties to those grown with CrO$_3$. The quality of the CrO$_2$ films has been claimed to depend critically on the substrate temperature, no matter the precursor used, the best results having been obtained at substrate temperatures between 390 and 400 °C.$^{[12,14]}$ Up to now, films produced outside this temperature range have always been reported as containing also the Cr$_2$O$_3$ or Cr$_2$O$_5$ phases.

In this work we report on the synthesis of highly oriented a-axis CrO$_2$ films onto Al$_2$O$_3$(0001) by atmospheric pressure CVD at temperatures as low as 330 °C. Our experiments were based on the method described by Ishibashi et al.$^{[12]}$ and already modified by S.M. Watts.$^{[16,19]}$ Therefore, a quartz tube placed inside a single-zone furnace and an independent control of the substrate temperature were used. However, the reactor was designed with a configuration that attempts to minimize the turbulence along the tube, guaranteeing processing conditions close to the ideal for laminar flux over the substrate surface and increasing the reactor efficiency (see experimental section). CrO$_3$ powder was used as precursor and O$_2$ as carrier gas. The powder was loaded into a stainless steel boat aligned with the substrate holder, 15 cm apart from it. Films were grown for deposition times ($t_{dep}$) of 4 and 8 hours, by using an oxygen flow rate ($\phi_{O2}$) of 50 sccm, a precursor temperature ($T_p$) of 260 °C and substrate temperatures ($T_s$) ranging from 330 to 410 °C.

All the films were produced on 10×10 mm$^2$ substrates, are homogeneous and exhibit a good adherence and a black shiny metallic colour characteristic of chromium dioxide. Surface morphology and roughness (rms) depend mainly on film thickness, the lowest value for the
rms having been measured ~7 nm over an area of 20×20 μm² by AFM of 200 nm thick films. Film thickness strongly depends on substrate temperature, values of 1424±49 nm and 57±13 nm having been measured for films deposited during 4 hours at $T_s=410$ °C and $T_s=330$ °C, respectively. Therefore, CrO₂ deposition rates ($r_{CrO_2}$) varying between 59.3 and 2.4 Å min⁻¹ were calculated, the highest values being much larger than those reported in literature [16,17].

The Arrhenius diagram shown in figure 1 allows to determine an apparent activation energy of 121.0±4.3 kJ mol⁻¹, indicating that surface chemical reaction kinetics is the rate-limiting step for film growth.

Figure 2 displays the X-ray diffraction (XRD) patterns of films grown at different substrate temperatures, between 330 and 390 °C. Only two regions of interest are shown, i.e. 39°– 43° and 86°–94°, corresponding to the 2θ ranges where diffraction peaks are observed in the full 25°–95° analysed range. As can be seen, only the (200) and (400) diffraction lines of CrO₂ can be clearly identified, besides those from the sapphire substrate indicated by “S”, revealing a highly a-axis oriented film growth. Furthermore, the diffraction lines originating from the (006) and (0012) planes of Cr₂O₃, at 2θ = 39.7° and 85.7°, which were clearly visible in a previous work [20] carried out in a less efficient CVD reactor, are now absent or at least their intensity is negligible, even for the sample grown at the lowest temperature of 330°C. In order to assess the degree of orientation of the crystallites, rocking curves (RC) for the (200) reflection were measured and their full-width at half-maximum (FWHM) values plotted as a function of deposition temperature (Fig. 3). As expected, crystal quality improves as growth temperature increases revealed by the narrower of the RC at higher $T_s$; however, for the lowest $T_s=330$°C the RC-FWHM value is ~0.68° showing that this sample is still strongly textured although it exists some degree of misorientation between the crystallites.

Low temperature grown samples keep the same room temperature magnetic behaviour as those films grown at higher temperatures. Figure 4 shows the room temperature out-of-
plane magnetization vs. field loops for samples deposited at 380°C, (674±40 nm), 340°C (113±22 nm) and 330°C (62±17 nm), which have respective room temperature saturation magnetizations of 1.30±0.07 μB/f.u., 1.5±0.3 μB/f.u., 1.5±0.4 μB/f.u. The uncertainty is in the magnetic volume. The measured magnetic properties of the films are consistent, within error, with both bulk[5] and high quality film[21] saturation magnetization of 2.0 μB/f.u. at 5K and a Curie temperature of 393K, resulting in a room temperature saturation magnetization of ~1.5 μB/f.u. for both bulk[5] and films[21]. The inset to figure 4 shows a simple fit to a point contact Andreev reflection spectrum of a junction between a lead tip and the 340°C film, using the Blonder-Tinkham-Klapwijk (BTK)[22] model modified by Mazin et al.[23] in the diffusive regime, showing that the best fit gives a transport spin polarization of 85%±3%.

In conclusion, we succeeded in lowering the growth temperature of CrO₂ films by 70 °C in relation to published data, which should be looked as a promising result in view of the use of these films with thermally sensitive materials such as those envisaged in spintronic devices (e.g. narrow band gap semiconductors). It was shown that highly oriented a-axis CrO₂ films can be synthesised onto Al₂O₃(0001) by atmospheric pressure CVD at temperatures as low as 330 °C. Deposition rates strongly depend on the substrate temperature whereas for film surface microstructures the dependence is mainly on film thickness. For the experimental conditions used in this work, CrO₂ growth kinetics is dominated by a surface reaction mechanism with an apparent activation energy of 121.0±4.3 kJ mol⁻¹. The magnitude and temperature dependence of the saturation magnetization up to room temperature is consistent with bulk measurements.

**Experimental**

**Reactor characteristics:** As previously described, our system is similar to that described in ref. 16 and 19, although implementing two significant modifications: i) the quartz tube length
was shortened to 55 cm reducing the reactor cold zones outside the furnace and, consequently, minimising convective phenomena along the reactor, and ii) the distance between the precursor boat and the substrate heather block was increased in order to homogenise the gas mixture, at the substrate surface, that results from the intersection of the oxygen longitudinal flux with the upstream flux of the CrO$_3$ precursor at the boat level. In principle, the process may be scaled up if both phenomena described above are taken into account.

**CVD procedures:** CrO$_3$ powder (purity 99.9%) was used as precursor and loaded into a stainless steel boat aligned with the substrate holder, 15 cm apart from it. Prior to their insertion into the reactor, the substrates were ultrasonically cleaned in organic solvents, rinsed in distilled water and dried with a N$_2$ flux. Oxygen (purity 99.999%) was used as carrier gas. Films were grown for deposition times of 4 and 8 hours, by using an oxygen flow rate of 50 sccm, a precursor temperature of 260 ºC and substrate temperatures ranging from 330 ºC to 410 ºC. In order to avoid the deposition of any kind of impurities during the initial stages of the deposition process, the substrate was always heated up to the deposition temperature before the melting of the CrO$_3$ precursor occurs (196 ºC).

**Film analysis:** The morphology and microstructure of the films were analysed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Film thicknesses were evaluated by image digital processing of SEM cross-section micrographs. Their crystallographic structure was studied by Bragg-Brentano X-ray diffraction (XRD) with Cu Kα radiation. Magnetization measurements were performed on an Oxford Instruments vibrating sample magnetometer, with the applied field perpendicular to the surface of the film. Point contact Andreev reflection spectra (which is a measure of the differential conductance $G = dI/dV$ as a function of bias voltage $V$) were measured on the film grown at 340ºC using a mechanically sharpened lead tip at 4.2 K. We present the simple analysis of this data using the modified BTK model of Mazin$^{[23]}$ in the diffusive regime. The parameters extracted from
that model are defined in ref 22. A more thorough analysis comparing ballistic and diffusive limit fitting to a complete set of Andreev reflection spectra as a function of temperature using both lead and niobium tips will be presented in a future publication. Nevertheless the values for the spin polarisation of the transport current are similar to values reported in the literature for films grown at higher temperatures. We can say that the lower growth temperature has not compromised this important parameter in any obvious respect.

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FIGURE CAPTIONS

**Figure 1** - Logarithm of the apparent deposition rate as a function of the substrate reciprocal temperature. ■, measured values; ——, Arrhenius line fitting.

**Figure 2** - XRD diffractograms of CrO$_2$ films deposited at different substrate temperatures. All the films were grown for $t_{dep}=4$ hours except for the film deposited at $T_s=330$ °C where $t_{dep}=8$ hours. Film thicknesses are 57, 113, 169, 272, 326, 657 and 846 nm, from 330 °C up to 390 °C.

**Figure 3** - Full-Width Half-Maximum (FWHM) of the rocking curves measured for the (200) diffraction peak vs substrate temperature. The inset shows the rocking curve of the film grown at $T_s=330$ °C for 8 hours.

**Figure 4** - Out-of-plane magnetization vs. applied field at room temperature, for samples grown at 380, 340, and 330 °C. Inset: Point Contact Andreev reflection spectrum (open circles) for 340°C film with junction resistance of 79Ω where G is the differential conductance (dI/dV). The fit to the modified BTK model$^{[22]}$ in the diffusive regime is shown. The parameters from the fit are the polarisation P, the interface parameter Z, the superconducting energy gap Δ and the spreading parameter $\omega$. 
Figure 1

$E_{\text{act}} = 121.0 \pm 4.3 \text{ kJ mol}^{-1}$
Figure 2
Figure 3
Figure 4