KrF Laser CVD of Chromium Oxide by Photodissociation of Cr(CO)₆

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Abstract. This work reports on the synthesis of chromium oxide thin films prepared by photodissociation of Cr(CO)₆ in an oxidizing atmosphere, using a pulsed UV laser (KrF, λ = 248 nm). The experimental conditions which should enable the synthesis of CrO₂ are discussed and results on the deposition of CrₓOᵧ films on Al₂O₃ (0001) substrates are presented.

Introduction

The prospect of building spintronic devices, in which electron spins are used to store and transport information, has attracted considerable attention in recent years [1-3]. Many of these proposed devices demand carefully-controlled growth of ferromagnetic/insulator or ferromagnetic/semiconductor interfaces, the development of these interfaces being one of the main technological challenges to be overcome before realistic devices can be fabricated. Chromium dioxide (CrO₂) is an attractive compound to be used in these heterostructures since it is strongly ferromagnetic at room temperature and has a half-metallic band structure fully spin-polarised at the Fermi level [4-7], making it attractive, for instance, for use in tunnel junctions with enhanced low field magnetoresistance [8] or in the fabrication of spin polarised field effect transistors [1-3]. Despite thermal CVD achievements [9-16], much effort has gone into developing efficient and controlled methods for preparing CrO₂ films at sufficiently low temperatures, which are of crucial importance to ensure interface quality and the ability to coat thermal-sensitive substrates such as those envisaged for building spintronic devices (e.g. narrow gap semiconductors). Nevertheless, the synthesis of CrO₂ films at low temperatures has been a difficult task due to the metastable nature of this oxide – CrO₂ is metastable at atmospheric pressure and, if heated, easily decomposes into the insulating antiferromagnetic Cr₂O₃ compound, which is the most stable Cr oxide at ambient conditions.

Laser-assisted CVD is a selective area deposition technique which has the potential to meet the requirements stated above. In previous studies conducted in static conditions, photolytic decomposition of Cr(CO)₆ by ultra-violet radiation at λ = 337 nm (nitrogen laser) has already led to the synthesis of films containing both Cr₂O₃ and CrO₂ phases, the relative amount of these phases depending on the oxygen partial pressure used [17-20]. However, and looking for a better efficiency of the Cr(CO)₆ photodissociation, it should be advantageous to explore dynamic atmospheres, which also allow for easy automation and continuous high-rate coating, and, on the other hand, to use other UV wavelengths, e.g. 248 nm, for which Cr(CO)₆ absorption cross section is much higher than for the nitrogen laser radiation [21].

It is the purpose of this paper to report on the synthesis of chromium oxide thin films on sapphire substrates, prepared by photodissociation of Cr(CO)₆ in an oxidizing dynamic atmosphere, using a KrF excimer laser (λ = 248 nm).

Experimental approach

Experimental set-up. The equipment used for the LCVD experiments consists of a KrF excimer laser, a stainless steel HV chamber, a pumping system based on a cryogenic pump and a gas sys-

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tem, which delivers the reactants into the reactor. The experimental set-up allows for dynamic and static deposition experiments.

The KrF laser ($\lambda = 248$ nm, pulse width = 30 ns) has a beam dimension of $24 \times 12$ mm$^2$. The laser beam impinges on the substrate at perpendicular incidence and by using an adequate optical system (lenses and masks) it is possible to control the beam spot size at the substrate level and thus the fluence reaching the substrate surface. Prior to any deposition experiment, the reactor was always evacuated to a base pressure lower than $5 \times 10^{-6}$ mbar. Chromium hexacarbonyl powder, whose vapour pressure is given by [17]

$$\log_{10} P[\text{Torr}] = 10.63 - 3285/T[\text{K}],$$

was used as Cr precursor; the Cr(CO)$_6$ powder was sublimated in a controlled temperature stainless steel cell connected to the LCVD reactor. The partial pressure of Cr(CO)$_6$ inside the reactor is settled by the cell temperature, the flux of the carrier gas (oxygen) and the total working pressure.

**Cr(CO)$_6$ photodissociation at 248 nm.** When absorbing two photons at 248 nm, an isolated Cr(CO)$_6$ molecule should decompose to Cr with a quantum yield given in literature as $\sim 1$ [22]. By reacting with O$_2$, the photodissociated Cr would give rise to CrO$_2$. However, the mechanism by which the photodissociation of Cr(CO)$_6$ may lead to chromium dioxide is a much more complex one. The major single photoproduct formed at 248 nm upon dissociation of Cr(CO)$_6$ is Cr(CO)$_4$. At laser fluence higher than $5$ mJ.cm$^{-2}$ secondary photodissociation of Cr(CO)$_4$ to Cr becomes considerable [21,22]. But these features are only true for a very low pressure of Cr(CO)$_6$, for which collisions are absent. In systems where collisions play an important role, the statistical fragmentation processes that follow the initial photodissociation event may be inhibited by collision vibrational relaxation of the photoproducts. Yet the degree of this effect is not completely known, low pressure of Cr(CO)$_6$ is still considered the ideal working condition for CrO$_2$ deposition.

To achieve the required laser fluence on the substrate it is important to quantify not only the beam energy loss on the optical components but also the energy loss due to absorption by the reactant gas mixture. Molecular oxygen absorbs UV radiation only bellow 242 nm. This fact makes Cr(CO)$_6$ vapour the major contributor to the beam absorption in the gas mixture. Chromium hexacarbonyl presents an absorption cross section $\sigma = 5.3 \times 10^{-17}$ cm$^2$ at $\lambda = 248$ nm [21]. By using the Beer-Lambert relation

$$I/I_0 = e^{-\sigma cl}$$

where $I/I_0$ represents the fraction of radiation transmitted in an absorption path length $l$ (cm) for a given concentration $c$ (cm$^{-3}$), it is possible to calculate the fluence at the substrate surface. Fig. 1 shows the I/Io values as a function of the partial pressure of Cr(CO)$_6$ for different path lengths (distance between the inner face of the chamber window used for transmission of the laser beam and the substrate surface). Based on the transmittance values it is also possible to compute the number of photons per Cr(CO)$_6$ molecule, $n_\nu$, at the substrate level. Fig. 2 shows the dependence of this parameter on the partial pressure of hexacarbonyl for a laser beam with a transverse section of 5.4 mm$^2$ and energy of 31.5 mJ/pulse, and an absorption path length of 12 cm. The horizontal dashed line in fig. 2 represents the threshold of two photons per Cr(CO)$_6$ molecule needed to photodecompose completely the hexacarbonyl.

From figures 1 and 2 it can be concluded that ideal working conditions are those for which low partial pressures of Cr(CO)$_6$ and/or small beam path lengths are selected, resulting in higher transmittance and higher number of photons per Cr(CO)$_6$ molecule.
Experimental parameters and film characterization. The Cr_2O_3 films were grown at room temperature on Al_2O_3 (0001) substrates during 2 hours at a laser pulse repetition rate of 5 Hz. Due to the geometry of our LCVD reactor it is only possible to work in gas flow mode with path lengths between 12 and 15 cm. The overall experimental parameters used are presented in table 1.

Characterisation of the films was carried out by optical microscopy (OM), atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), micro-Raman spectrometry and optical profilometry.

Results and discussion

Surface morphology and microstructure. The use of Al_2O_3 (0001) substrates for the growth of chromium oxide thin films should allow for a quasi-pure photolytic process since the sapphire substrates are transparent to KrF laser radiation. Therefore, no intense thermal contributions are expected during the synthesis of the chromium oxide. Furthermore, it is known that the use of Al_2O_3 (0001) substrates favours the growth of epitaxial CrO_2 thin films [13]. OM observation revealed that the deposited films are homogeneous and exhibit a dark colour. SEM and AFM analyses of different films have shown that their morphology consists of a uniform and fine grain structure with a mean grain size of few tens of nanometers all over the deposits, as can be seen in the AFM image of fig. 3. The deposits present good adherence and are approximately rectangular in shape with thicknesses of about 100 nm and deposition rates ~8.4 Å.min^{-1}.

<table>
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<tr>
<th>Table 1 – LCVD experimental conditions used to deposit the Cr_2O_3 thin films</th>
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<td><strong>Experimental parameters</strong></td>
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<tr>
<td>Beam energy, E [mJ]</td>
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<td>Spot area, S [mm^2]</td>
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<tr>
<td>Cr(CO)<em>6 cell temperature, T</em>{cell} [°C]</td>
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<tr>
<td>O_2 carrier flux, \phi_{carrier} [sccm]</td>
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<td>Total pressure, P_t [mbar]</td>
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Fig. 1 – Transmittance vs. Cr(CO)_6 partial pressure for several absorption path lengths.

Fig. 2 – Number of photons per hexacarbonyl molecule as a function of Cr(CO)_6 partial pressure for the given experimental conditions.

Fig. 3 – AFM image of a Cr_2O_3 film deposited with E = 31.5 mJ/pulse, P_t = 0.21 mbar, \phi_{carrier} = 10 sccm and T_{cell} = 10 °C. Estimated parameters: F = 65 mJ.cm^{-2}, p_{Cr} = 0.14 mbar, p_{O2} = 0.07 mbar.
**Chemical and structural analysis.** EDS microanalysis was performed to monitor the existence of any degree of Cr(CO)$_6$ photodecomposition. The presence of chromium oxide phases was analysed by micro-Raman spectroscopy.

Fig. 4 shows these results for a film deposited with $F = 65$ mJ/cm$^2$, $p_{cr} = 0.14$ mbar, $p_{O2} = 0.07$ mbar and $n_v = 2$. The EDS spectrum in fig. 4a shows the two K$_\alpha$ (5.4 keV) and K$_\beta$ (5.9 keV) lines of Cr, besides the K$_\alpha$ (1.48 keV) line of Al, which confirms that decomposition of Cr(CO)$_6$ was attained during the deposition process. The Raman spectrum (fig. 4b) reveals peaks that match the Raman shifts assigned to both Cr$_2$O$_3$ and CrO$_2$ oxides [23, 24]. It should be noted that, since most of CrO$_2$ Raman peaks overlap those of Al$_2$O$_3$ (substrate material), only the B$_{2g}$ (682 cm$^{-1}$) peak of CrO$_2$ may be used to clearly identify the presence of this oxide phase. The synthesised chromium oxides are probably amorphous or have a low crystallinity, as suggested by the broadening of the Raman peaks.

By keeping constant the partial pressure of Cr(CO)$_6$ and decreasing the laser fluence at the substrate surface, which implies $n_v < 2$, the photolytic decomposition of Cr(CO)$_6$ still occurs but no chromium oxide phases were obtained, even when the partial pressure of oxygen was increased, as can be seen from the two spectra of fig. 5, recorded over a film deposited with $F = 47$ mJ/cm$^2$, $p_{cr} = 0.14$ mbar, $p_{O2} = 0.11$ mbar and $n_v = 0.7$. As for the film of fig. 4, the EDS spectrum of this film (fig. 5a) also shows the two lines of Cr; however the Raman spectrum (fig. 5b) reveals no other peaks than those matched by the Raman shifts assigned to Al$_2$O$_3$. Therefore, chromium oxide formation did not occur showing that $n_v = 0.7$ is clearly lower than the value needed to photodecom-
pose completely the hexacarbonyl. Consequently, the chromium present in the deposited material (fig. 5a) can only be due to the adsorbed Cr(CO)$_x$ photofragments resulting from the incomplete Cr(CO)$_6$ decomposition during the deposition process.

Dowben and co-workers [17-20] have pointed out that the partial pressure of oxygen is the prominent parameter to be controlled in order to achieve CrO$_2$ growth by UV laser photodissocia-
tion of Cr(CO)$_6$, for a given partial pressure of this precursor (10$^{-5}$ Torr). Our results, which were obtained for higher Cr(CO)$_6$ partial pressure although in the same range of p$_{Cr}/p_{O2}$ as in ref. [17-20], show that the number of photons available per Cr precursor molecule is the crucial parameter to achieve CrO$_2$ deposition. In fact, $n_v$ summarises the effect of both Cr(CO)$_6$ partial pressure and laser fluence.

Conclusions

In this paper, it was shown that Cr(CO)$_6$ can be a suitable precursor for the KrF laser-assisted CVD of chromium oxide. Thin films with good adherence, fine grain structure and containing both Cr$_2$O$_3$ and CrO$_2$ oxide phases were obtained. It was also shown that the number of photons per hexacarbonyl molecule is a crucial experimental parameter in the KrF laser photodissociation of Cr(CO)$_6$ towards synthesis of chromium dioxide. Further experimental work is currently being done in order to tune the experimental conditions that will lead to pure chromium dioxide deposition.

Acknowledgements

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References