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Preparation and characterization of CrO_2 films by Low Pressure Chemical Vapor Deposition from CrO_3

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ABSTRACT

Highly oriented CrO_2 thin films have been heteroepitaxially grown on TiO_2 rutile (110), (100) and (001) single crystalline substrates, by Low Pressure Chemical Vapor Deposition from CrO_3 as precursor and flowing oxygen as carrier gas, under a pressure of 67 Pa. The experimental conditions were fine tuned by depositing on polycrystalline Ti foils, to improve the purity of the films and the deposition rate. A maximum deposition rate of 175 nm h^{-1} was obtained.

The composition and texture of films, up to 2 μm thick, have been determined by X-ray diffraction (XRD) and Micro Raman, while their microstructure has been examined by Scanning Electron Microcopy and Atomic Force Microscopy, and their magnetic behavior has been tested by superconducting quantum interference device magnetometry. These techniques reveal that the phase purity, texture, microstructure and thickness of these films are dependent on the crystalline face of the rutile substrate and the deposition temperature. Thus, microscopy techniques, XRD and Raman spectroscopy confirm that highly textured CrO_2 films were always obtained on the three rutile substrate faces when deposition temperature ranges between 616 K and 636 K. But these techniques also show that CrO_2 films are unpurified with inclusions or patches of Cr_2O_3, for the most of the substrates and especially at high deposition temperatures. Magnetic measurements conclusively demonstrate that pure CrO_2 films are only obtained when TiO_2 (110) is used as a substrate.

1. Introduction

The present paper deals with the preparation and characterization of CrO_2 films by Low Pressure Chemical Vapor Deposition (LPCVD) from CrO_3 in oxygen as a carrier gas. Chromium dioxide CrO_2 is a half-metallic ferromagnetic material [1–3]. By virtue of this property, it has been proposed as a source of spin-polarized electrons for the fabrication of spintronic devices, such as magnetic tunnel junctions and spin valves [4,5].

CrO_2 is thermodynamically metastable, and its temperature stability range strongly depends on the oxygen partial pressure [6]. Thus, it irreversibly decomposes to Cr_2O_3 at about 700 K at partial pressures of oxygen lower than 10^5 Pa, but only at about 473 K at 10^2 Pa [7]. This pressure dependence offers a way to synthesize CrO_2 by thermal decomposition of CrO_3, according to the reaction: $CrO_3 \rightarrow CrO_2 + ½ O_2$. This process can be carried out by heating this chemical in a closed vessel, so that the required oxygen pressure is provided by the decomposition reaction itself. Powders, small single crystals and even thin films of CrO_2 have been obtained by this method, under very high oxygen partial pressures (up to 10^8 Pa) and temperatures around 673 K [7]. At industrial scale, this method has been applied to synthesize acicular powder films of CrO_2 used as magnetic recording media [8].

The crystalline structure of bulk CrO_2, tetragonal space group $P4_2/mnm$, is isomorphic to TiO_2 rutile [9], with a lattice mismatch between the two phases of 1.37% along the [001] direction and of 3.84% along the [100] and [010] directions. These differences are small enough to permit the heteroepitaxial growth of CrO_2 on TiO_2 single crystals, although the films would be under tension in the plane. Indeed, high quality thin films of CrO_2 have been grown on TiO_2 substrates during the last years [10–14].

Atmospheric Pressure Chemical Vapor Deposition (APCVD) seems to be the most widespread technique for depositing CrO_2 thin films at present. The method was reported by Isibashi et al. [15,16], and subsequently utilized with minor modifications by several authors [10,17–20]. Volatile CrO_3 [10–12,17–20], Cr_8O_{21} [17,21,22], and CrO_2Cl_2 [23] have been used as precursors under an oxygen pressure of 1 atm. TiO_2 rutile (100), (110) and (001) single crystals [10–14,23,24], Al_2O_3 (0001) single crystals [13,19] and polycrystalline TiO_2 films have been used as substrates [17,25]. The deposition or substrate temperature, T_S, has been varied between 593 K and 723 K. At low T_S, reactions do not proceed or their rates are too slow, while at $T_S > 673$ K CrO_2 decomposes to Cr_2O_3 and thus mixture of phases are obtained. The best quality films are those deposited at around 663 K. High O_2 flow rates, between 50

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and 500 ml min^{-1}, have been always required to carry the precursor vapors from the evaporation source to the substrates surface and to prevent the thermal decomposition of the deposited CrO_2.

Other works have also dealt with the mechanism of the Chemical Vapor Deposition (CVD) process itself. In particular, when CrO_3 is used as a precursor, the APCVD process has been usually explained as a simple thermal decomposition of CrO_3 molecules previously adsorbed on the surface of the hot substrates. However, it was reported recently by Ivanov et al. [21] that under the experimental conditions used for sublimation of the precursor (1 atm of O_2 and temperature in the range 533 K to 553 K), most of CrO_3 load does not evaporate, but decomposes inside the crucible to Cr_8O_{21}. Actually, this compound is the first intermediate suboxide in the thermal decomposition of CrO_3 to Cr_2O_3, and it is stable between 523 and 573 K [26–28].

Although the growth of CrO_2 based on the decomposition of the CrO_3 precursor by APCVD is so far the most popular technique and it has proven to yield high quality epitaxial films, deposition methods at atmospheric pressure are hardly compatible with the microelectronic industry. In other words, if spintronic devices based on CrO_2 are to be fabricated, this material should be deposited by a low pressure methodology. Therefore, other techniques working at low O_2 pressures (10 Pa < P < 450 Pa), like laser photolysis [29–31], plasma assisted deposition [29] and thermal decomposition [32] have been explored. In these alternative processes, $Cr(CO)_6$ or CrO_2Cl_2 have been used as precursors. Although each of these low pressure techniques has its relative merits, unfortunately, a significant amount of Cr_2O_3, a phase which degrades the electrical and magnetic properties of the films, has been always obtained.

In our work, we have produced CrO_2 films by LPCVD from CrO_3 as a precursor, in the presence of O_2 at $P = 67$ Pa. Films with thicknesses up to several micrometers have been deposited on different substrates: polycrystalline Ti foils and (100), (001) and (110) rutile single crystals of TiO_2. Our aim is to determine the best temperature conditions for obtaining pure CrO_2 films under low O_2 pressure.

2. Experimental procedures

2.1. Description of the LPCVD reactor and sublimation conditions

The LPCVD hot wall reactor, made at home, consisted of a fused silica tube (1 m long and an inner diameter of 46 mm) placed inside a 70 cm long cylindrical oven, which was resistively heated. The furnace was place vertically and had two thermal zones independently heated: the bottom one, or source zone, where the precursor is evaporated; and the upper one, or reaction zone, where the CrO_2 deposition takes places. CrO_3 powder (Alfa-Aesar, 99.99% purity, ~200 mg) was loaded into a cylindrical fused silica boat (1 cm^3 volume) located in the centre of the source zone, while the substrates were placed on a stainless steel holder located in the centre of the reaction zone, 20 cm apart from the source zone. Both ends of the silica tube, kept at room temperature, were attached to stainless steel tubes by compression-fit piping adapters. The top end of the reactor was connected to a vacuum line pumped by a rotary vane pump and a liquid nitrogen trap. A base pressure of 0.1 Pa was routinely achieved with this experimental set up. The bottom end of the silica tube was connected to an O_2 gas pipe line, and a flow of O_2 25 ml min^{-1} was used to carry the vaporized CrO_3 from the evaporation zone to the reaction one. The oxygen flux was introduced below the ceramic boat level to improve the transport of the precursor vapors. A capacitance diaphragm transmitter and a throttle valve located in the vacuum line enabled an accurate measurement and control of the pressure during deposition. By partially closing this valve, a constant pressure of O_2 was kept throughout the deposition process.

After the deposition zone of the reactor had reached an isothermal state in the range of 616–656 K, the evaporation zone was slowly heated from room temperature up to the sublimation temperature. It is must be noted that CrO_3 sublimation at high temperature competes with its thermal decomposition to Cr_8O_{21} in the boat [8,26–28]. It is also relevant that for a given sublimation temperature, the pressure in the reactor determines the mean free path of the precursor gas molecules and affects the possibilities of the vapor molecules to escape from the crucible [33]. In other words, the lower the pressure, the lower the temperature required for sublimation of the CrO_3 precursor, and the higher the amount of sublimated material. By trial and error, we found that CrO_3 can be fully sublimated, without leaving any traces of Cr_8O_{21} in the boat, when pressure, P, is lower than 67 Pa and sublimation temperature, T_V, is risen up to 442 K. A low heating ramp (0.5 K min^{-1}) was used to reach the sublimation temperature by ensuring a proper drying of the precursor which is a highly hygroscopic material. Under these conditions, $P = 67$ Pa and $T_V = 442$ K, it took nearly a day to fully sublimate 200 mg of CrO_3. Substrate temperature was varied between 616 K and 656 K. At $T_S = 656$ K, a maximum deposition rate of about 175 nm h^{-1} was found.

CrO_2 thin films have been grown simultaneously on four different substrates: polycrystalline Ti foils (Goodfellow, 99.99% purity), and rutile single crystals of TiO_2 (100), (001) and (110) (provided by CrysTec GmbH, research grade). Prior to deposition, the surface of Ti polycrystalline foils were scraped with a stainless steel blade, while the surface of the other substrates were etched by dipping in concentrated HCl solution (1M) for 3 min and then rinsed in distilled water. Dimensions of the substrates were ~ $0.5 \times 0.5 \times 0.05$ cm^3 for single crystals and $1 \times 1 \times 0.05$ cm^3 for polycrystalline Ti substrates. The edges of single crystalline substrates are roughly aligned along the in plane crystalline axis, within an error of $\pm 2°$. The four substrates were placed perpendicularly to the axis of the silica tube, at four geometrically equivalent positions.

2.2. Description of characterization techniques

The thicknesses of the CrO_x films were determined by X-ray fluorescence analysis. For that purpose, the fluorescence $TiK\alpha_1$ line ($h\nu =$ 4.51 keV) was recorded for each sample, and its intensity compared with that of a clean substrate. $Rh_{k\alpha}$ (20.21 keV) radiation was used as excitation source and a LiF(200) single crystal as monochromator. To estimate the film thickness, it was assumed that CrO_2, with a density of 4.93 g cm^{-3}, was the only chromium phase attenuating the intensity of the Ti line emitted by the substrates. These thicknesses have been confirmed by measuring a selected group of samples by Rutherford Backscattering Spectrometry with a 3 MV tandem accelerator. The primary energy of the $^4He^{+2}$ impinging ions was 2 MeV and the detector was set at 165°.The spot size of the ion beam on the surface of the film was 1 mm^2.

Phase composition and crystallographic structure of the films were examined with a PANALYTICAL diffractometer, model X'PERT PRO, equipped with CuKα (1.5419 Å) radiation and operating at 45 kV, 40 mA. From $\theta - 2\theta$ scans, average crystalline sizes of the CrO_2 grains were determined by the Scherrer equation [34], after correcting the widths of the diffraction peaks by a proper instrumental factor. In addition, for films deposited on single crystalline TiO_2 substrates, rocking curves (ω scans) for the CrO_2 (200), (002) or (110) reflections were taken. For $\theta - 2\theta$ and ω scans, the full widths at half maximum of the diffracted peaks, β_T, were obtained by fitting them with a Gaussian–Lorenztian Sum function. Then they were corrected for the instrumental broadening by means of the equation $\beta = SQRT(\beta_T^2 - \beta_0^2)$, where β_0 values were obtained from TiO_2 (200), (002) or (110) reflections from the bare substrates.

Unpolarized Raman spectra were acquired with a LabRam spectrophotometer (Horiba Jobin Yvon) attached to an Olympus RX41 microscope. A non polarized light from an Ar laser ($\lambda = 514.5$ nm) was normal incidence pointed to the front face of the samples, and the backscattered light was collected. All measurements were carried out at room temperature. Band shifts or shape changes of the spectra were never observed during acquisition. The size of the laser spot on the surface was 1 μm diameter. No dependence of spectra was observed