Microstructural characterization of chromium oxide thin films grown by remote plasma assisted pulsed laser deposition

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Abstract
In this work, we investigate the use of Remote Plasma Assisted PLD for the growth of chromium oxide thin films. In an attempt to enhance oxygen incorporation in the growing layers, laser ablation takes place in an activated oxygen background that contains atomic oxygen as well as excited oxygen molecules, thereby creating growth conditions that are inaccessible by reactive PLD. All films were grown on Si (100) substrates by ablating a pure Cr\textsubscript{2}O\textsubscript{3} target using a KrF excimer laser. The micro-structural analysis of the grown layers was achieved using Infra-Red Spectroscopy, X-Ray Diffraction, Atomic Force Microscopy and Rutherford Back-Scattering. It is found that films deposited under remote plasma conditions show a predominance of the higher oxidation states of chromium while the antiferromagnetic Cr\textsubscript{2}O\textsubscript{3} phase is mostly present in films grown in an O\textsubscript{2} ambient. The effect of substrate temperature on the microstructure of the films was also studied. At low substrate temperatures (<350 \degree C), the films have an amorphous microstructure with elongated rod-like features that could indicate the formation of the CrO\textsubscript{2} phase. With increasing temperature up to 450 \degree C, the structure of the films reverts to a crystalline Cr\textsubscript{2}O\textsubscript{3} phase as inferred from the appearance of the corresponding peaks in the XRD spectra and from the narrowing of the infra-red absorption bands.

1. Introduction
Magnetic transition metal oxides are very important materials for applications in magnetic and magnetoelectronic devices. Of particular interest nowadays is chromium dioxide (CrO\textsubscript{2}), a ferromagnet with a Curie temperature of ~ 390 K, for which a “half-metallic” behavior with almost complete spin polarization of the 3d electrons at the Fermi level has been predicted theoretically \cite{1} and recently confirmed experimentally \cite{2}. However, CrO\textsubscript{2} is one phase among many other more stable phases of chromium oxide, such as Cr\textsubscript{2}O\textsubscript{3}. Therefore, careful tuning and understanding of synthesis conditions are needed to grow the pure chromium dioxide phase. In recent years, CrO\textsubscript{2} film growth was achieved using atmospheric pressure chemical vapor deposition (CVD) \cite{3}, but the low pressure techniques, such as Molecular Beam Epitaxy (MBE) and Pulsed Laser Deposition (PLD), where film synthesis takes place far from thermal equilibrium conditions, have not been thoroughly exploited to that end \cite{4-5}. In this work, we investigate the growth of CrO\textsubscript{2} thin films on silicon using Remote Plasma Assisted Pulsed Laser Deposition (RPA-PLD). The main advantage of RPA-PLD is the capability of controlling the chemical composition and the oxidation state of the grown layers through the interaction of the laser ablated species with activated O atoms generated by a remote plasma source as opposed to ground state O\textsubscript{2} molecules, as is the case in reactive PLD.

In what follows, we emphasize the effect of process parameters such as oxygen remote plasma and substrate temperature on the bonding and structural properties of the deposited chromium oxide layers.
2. Experimental details

All deposition runs were performed using the SURFACE Laser Workstation system based on a KrF excimer laser (λ = 248 nm with 20 ns pulse duration) operated at 10 Hz with laser energies of 250 to 500 mJ/pulse. The laser beam is guided into the chamber through a beam line consisting of two mirrors and a converging lens with a focal distance of 45 cm. The focused laser beam is incident at an angle of 45° on a toggling and rotating polycrystalline Cr₂O₃ target to ensure uniform erosion and reduce target drilling by the laser. The laser spot size on the target was estimated at about 9 mm². Ablation was performed in pure O₂ and in an oxygen remote plasma consisting of excited O₂ molecules and dissociated O atoms, generated by a microwave (2.45 GHz) plasma source attached to the deposition chamber. The plasma power was fixed at 400 W. The chromium oxides films were grown on conventionally cleaned Si (100) wafers placed on a heatable holder at a distance of 50 mm from the target. Substrate temperature ranged between 25 and 450 °C, as measured by a thermocouple placed on the backside of the substrate. In this study, the laser energy and oxygen pressure were fixed at 300 mJ (leading to a laser fluence of 3.3 J/cm²) and 30 mTorr, respectively. The crystalline phases present in the deposited films were examined by Grazing Incidence X-Ray Diffraction (GIXRD) using a Discover 8 diffractometer from Bruker AXS Systems. A MultiMode™ Scanning Probe Microscope (NanoScope III) from Digital Instruments was used for imaging the surface morphology of the films and was operated in the Contact Mode. Chemical bonding in the layers was studied by Fourier Transform Infra Red spectroscopy (FTIR), using an Avatar 360 spectrometer (Nicolet Instrument Corporation) working in the mid-infrared range from 400 to 4000 cm⁻¹. All spectra were acquired in absorption mode with a resolution of 1 cm⁻² and a minimum of 200 scans for each sample. RBS measurements on the films were performed with a Van de Graaff tandem accelerator generating a beam of ²He⁺ at 2 MeV. The beam spot size at the surface of the sample was set to 1 mm². The backscattered ions were detected at a scattering angle of 165°. Data collection and analysis were carried out using the SIMNRA software. All information about stoichiometry and film thickness was decoded by curve fitting of the acquired spectrum.

3. Results

Figure 1 shows the FTIR spectra of chromium oxide thin films deposited at room temperature in (a) ambient O₂ with no plasma activation and (b) under remote plasma conditions. For the film deposited in an O₂ ambient (curve a), the spectrum is dominated by a broad band peaked at about 600 cm⁻¹. This band can be fitted with two Gaussians curves centered at about 545 and 750 cm⁻¹, that are attributed to Cr₂O₃ [6-7]. The occurrence of such broad bands indicates that the films are predominantly amorphous. At higher wavenumbers, two smaller but distinguishable peaks appear at about 880 and 995 cm⁻¹ and could correspond to the presence of the CrO₂ phase [8-10]. For the films deposited under remote plasma conditions, the three above mentioned absorption bands are still detected but with a notable increase in the intensity of those corresponding to CrO₂ as compared to the films deposited in O₂. This is a clear indication that the use of a remote plasma source promotes higher oxidation states of Cr such as CrO₂, an effect that is attributed to the interaction of the ablated species with atomic oxygen in the remote plasma.

Figure 2 presents the evolution of the FTIR spectra for films deposited under remote plasma conditions as function of substrate temperature (Tₛ). Clearly, as temperature is increased from 25 to 250 °C, the intensity of the CrO₂ absorption bands occurring at 995 (antisymmetric stretching) and 880 cm⁻¹ (symmetric stretching) decreased significantly. At deposition temperature of 350 °C, the corresponding CrO₂ peaks disappear completely and the FTIR spectra consist of a sharp peak at 545 and a much weaker one at 610 cm⁻¹, both of which are vibrational modes of Cr₃O₇ and their intensity increases rapidly for the film deposited at 450 °C. The strong narrowing of the Cr₂O₃ bands (from 750 to 500 cm⁻¹) with increasing temperature is an indication of temperature induced ordering that could translate into the onset of a crystallization process in the layers.
Figure 1. FTIR spectra of CrO\textsubscript{x} thin films deposited at room temperature in (a) O\textsubscript{2} ambient (plasma Off) and (b) under remote plasma conditions (plasma On).

Figure 2. FTIR spectra of CrO\textsubscript{x} thin films deposited at 30 mTorr under remote plasma conditions at laser energy of 300 mJ, microwave power of 400 W, and at different substrate temperatures.

These results are confirmed by GIXRD analysis as presented in figure 3 for films grown at 350°C. The spectrum exhibits diffraction peaks corresponding to the (012) and (110) orientations of the corundum structured Cr\textsubscript{2}O\textsubscript{3} phase. For T\textsubscript{S} = 250 °C, no x-ray peaks are detected thereby supporting the dominance of an amorphous phase.

Figure 3. GIXRD of CrO\textsubscript{x} thin film deposited at 350 °C under remote plasma conditions.

Atomic force microscopy analysis for the chromium oxide film deposited at T\textsubscript{S} = 25°C reveals the growth of rod-shaped particles as shown in Figure 4 (a). Such features have a typical grain size ranging from 0.1 to 0.7 μm, and are oriented with their axes parallel to the plane of the substrate. The formation of such rod-like elongated particles with high aspect ratio could be attributed to the growth of CrO\textsubscript{2} crystallites that have been reported to grow with such a characteristic shape [11-12]. Figure 4 (b) depicts the AFM image of the CrO\textsubscript{x} film grown at T\textsubscript{S} = 250°C, which shows the appearance of craters with lateral grain size of the order of 1.5 μm. As deposition temperature is further increased to 350°C, the morphology of the films and the growth mode change significantly as shown in Fig.4 (c). Indeed, for T\textsubscript{S} = 350°C, the surface becomes smoother with a roughness of the order of 40 Å with a noticeable absence of the craters and rod-like features that appear at lower T\textsubscript{S} values. Instead, regular
crystallites with a typical lateral size of ~ 0.4 µm are observed, thereby indicating the occurrence of an oriented crystalline growth of Cr₂O₃ on the silicon substrate. These modifications in the bonding, crystalline quality and surface morphology of the films are consistent with the variation of the stoichiometry with temperature, as deduced by RBS. Indeed, preliminary RBS measurements indicate that films deposited at Tₛ = 25°C have a Cr/O atomic ratio close to 0.4, a value that is lower than that of CrO₂. This observation supports the FTIR data which indicate that the films could consist of a mixture of several phases with different stoichiometries, such as CrO₂ and Cr₂O₃, with the higher oxidized states being the more dominant. However, as the substrate temperature is further increased, the Cr/O value increases above 0.5 and edges towards the 0.67 value expected for Cr₂O₃.

Figure 4. AFM pictures of CrOₓ films deposited at (a) 25 °C, (b) 250 °C, and (c) 350 °C. Note that the x-y scale of picture (c) is 1 × 1 µm while that of pictures (a) and (b) is 10 × 10 µm. The z-scale for pictures (a), (b) and, (c) are 300, 350 and 20 nm/division, respectively.

4. Discussion and conclusion
The microstructural analysis of our deposited chromium oxide layers leads us to the following conclusions. The combination of Pulsed Laser Deposition with an oxygen remote plasma promotes the formation of CrOₓ thin films with a high oxygen content, greater than that of CrO₂, thereby underlining the effectiveness of our technique to attain the higher oxidation states of Cr. At low deposition temperatures, namely below 350 °C, the films consists of a mixture of several oxide phases with the occurrence of elongated CrO₂ particles embedded in a pre-dominantly amorphous matrix. As deposition temperature is increased 350°C and above, the microstructure of the films reverts to a highly oriented crystalline Cr₂O₃ phase. These results are in agreement with those of Ingle et al. [4], who synthesized CrOₓ thin films consisting of a mixture of phases, using atomic oxygen assisted
MBE. They reported the existence of a temperature domain (25-250 °C) within which the films show the presence of small amounts of CrO₂. Above 250 °C, the structure of their films is dominated by the antiferromagnetic Cr₂O₃ phase. The presence of a relatively small amount of CrO₂ (about 5 %), in the films deposited at low temperatures, was attributed to the low pressure used in the MBE process. In our case, the oxygen deposition pressure used is several orders of magnitude larger than that employed in MBE, thereby promoting the formation of the CrO₂ phase. Further experiments at high remote plasma pressure are currently under way in an effort to investigate the formation of single phase crystalline CrO₂ films.

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