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Crystalline phase control and growth selectivity of β-MnO_2 thin films by remote plasma assisted pulsed laser deposition

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ABSTRACT

In this paper, we exploit the effect of coupling an oxygen remote plasma source to Pulsed Laser Deposition (PLD) for the growth of pure and well crystallized β-MnO_2 films. Films were grown on Si substrates by laser ablation of a MnO target in oxygen ambient and remote plasma. X-Ray Diffraction, Fourier Transform Infra-Red spectroscopy and Raman scattering were used to determine the crystalline structure and bonding in the grown layers, whereas Atomic Force Microscopy was used to study their morphology and surface roughness. Deposition at 500 °C and high oxygen pressure (33.3–66.6 Pa) resulted in the formation of films with roughness of 12 nm consisting of nsutite γ-MnO_2, a structure characterized by the intergrowth of the pyrolusite β-MnO_2 in a ramsdellite R-MnO_2 matrix. Deposition at the same temperature but low pressure (1.33–3.33 Pa) in oxygen ambient lead to the formation of Mn_2O_3 whereas plasma activation within the same pressure range induced the growth of single phase highly crystalline β-MnO_2 having smooth surfaces with a roughness value of 0.6 nm. Such results underline the capability of remote plasma assisted PLD in selecting and controlling the crystalline phase of manganese oxide layers.

1. Introduction

Manganese cations can exist in several oxidation states crystallizing in different phases of which MnO, Mn_3O_4, Mn_2O_3, and MnO_2 are the most commonly known. MnO_2 is particularly attractive due to its use in a variety of domains such as energy-storage devices [1], biosensors [2], catalysis in oxidation reactions [3], supercapacitors [4], and as electrode material in batteries [5]. Several deposition techniques, such as Chemical Vapor Deposition (CVD) [6], sol-gel and electro-deposition [7], Atomic Layer Deposition (ALD) [8] as well as Plasma Enhanced ALD [9] have been employed to grow thin films of MnO_2 with a variable degree of success in terms of synthesis a pure MnO_2 phase. One technique that is renowned for growing high quality oxide materials is Pulsed Laser Deposition (PLD). PLD has several advantages compared to other materials deposition techniques that include, among others, the non-equilibrium nature of the growth process and the range of pressure that can be used during deposition. PLD has actually been used to synthesize manganese oxide materials [10–15]. Specifically, Yang [10] performed a parametric study on the PLD of manganese oxide using Mn and Mn_3O_4 targets and showed that PLD can lead to pure or mixed phases of Mn_2O_3 or Mn_3O_4, depending on deposition pressure and substrate temperature. Isber et al. [11] reported a transition from Mn_2O_3 to Mn_3O_4 when deposition temperature is increased beyond 700 °C at a deposition pressure of 1.33 Pa. Xia and co-workers [12] also successfully prepared MnO, Mn_3O_4 and Mn_2O_3 films by PLD, with the phase dictated by deposition pressure whereas Neubeck et al. [13] reported the epitaxial growth of the MnO phase on sapphire and MgO. In terms of synthesizing the MnO_2 phase, our group reported that the laser ablation of a MnO target could induce MnO_2 growth over a narrow process window, namely a substrate temperature of 500 °C, and oxygen ambient of 33.3 Pa up to 66.6 Pa [14]. These findings were supported by the results of Espinal and co-workers [15] who synthesized cryptomelane-type manganese oxide (OMS-2) at 26.6 Pa. However, operating at such relatively high pressure could result in having the laser ablated species lose their kinetic energy due to increased collisions with the background gas, leading to a deterioration of the crystalline quality of the growing layers and a roughening of the surface morphology [16].

Therefore, in an attempt to operate at lower pressure while preserving the oxygen content in the films, we coupled our PLD system to a remote oxygen plasma source so that film growth can take place in an ambient containing reactive oxygen species (such as ions or neutral oxygen atoms). Plasma assisted PLD can positively influence the growth of the oxide films [17–22] in terms of stoichiometry, surface roughness, crystalline orientation and elimination of the macroscopic particulates in the layers. In this work, we explore the potential of Remote Plasma Assisted-PLD (RPA-PLD) as a technique for the growth of manganese

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oxide thin films with particular focus on the stabilization of the MnO_2 phase. The effects of plasma activation, deposition pressure and temperature on the properties of the grown layers are emphasized, in order to identify the optimal remote plasma conditions for MnO_2 phase formation. X-Ray Diffraction (XRD) was used to assess the crystalline quality and structure of the layers whereas chemical bonding and short-range order were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Raman Scattering (RS), respectively. Atomic Force Microscopy (AFM) was used to determine the surface morphology and roughness of the layers.

2. Experimental

The PLD system used in this work is a "SURFACE" workstation consisting mainly of a turbo-pumped high vacuum chamber (base pressure of 10^{-5} Pa) that houses the substrate and target manipulators. A KrF excimer laser (Lambda Physik Compex 201) operating at 248 nm wavelength, with a 20 ns pulse duration, adjustable repetition rate (1–10 Hz), and laser energy up to 600 mJ, is focused to a spot size of about 3×4 mm^2 on the surface of the target at an angle of incidence of 45°. In order to ensure homogeneous consumption of the target, the latter is mounted on rotary drives that allow rotation and toggling. Further technical details on the PLD system can be found elsewhere [23].

Ablation was performed in pure O_2 flown into the chamber through stainless steel tubes or under oxygen remote plasma conditions. In the latter case, a microwave plasma source operated at 2.45 GHz is attached to the deposition chamber, on a flange situated 0.2 m from the substrate [22]. The microwave launcher consists of an annular wave guide (ring resonator) with axial slot antennas positioned azimuthally at regular intervals around a quartz tube (diameter 5 cm) where the plasma is generated in flowing oxygen. Power is supplied to the launcher by a Sairem microwave generator (2.45 GHz, operated up to 500 W) through a WR-340 waveguide. A plunger and three knobs can be adjusted to ensure the best coupling condition of the microwave to the plasma, with reflected power no more than 5% of the power injected in the plasma. The flow of the O_2 gas into the quartz tube ensures the transport of the plasma excited species to the region where the deposition process occurs to form what is commonly referred to as remote plasma [24].

Films were grown on Si (100) single crystal substrates on the heatable manipulator placed at a distance of 5 cm from a 2″ diameter MnO target (Kurt J. Lesker, purity 99.9%). Deposition runs were performed at substrate temperatures between 350 and 600 °C and gas/remote plasma pressures between 1.33 and 66.6 Pa. Laser power was set at 200 mJ for films grown in the pressure range from 1.33 to 6.66 Pa, whereas a laser power of 500 mJ was used for pressures of 13.3 Pa and higher. This ensured a growth rate ranging between 0.3 and 0.6 μm/h for a laser repetition rate of 10 Hz. For remote plasma assisted deposition, all runs were performed at a microwave power of 400 W.

Grazing Incidence X-Ray Diffraction (GIXRD) measurements were performed using a Discover 8 diffractometer from Bruker AXS systems. The X-ray source consists of a ceramic Siemens tube operating at 40 kV with a current of 40 mA and emitting CuKα radiation of wavelength $\lambda = 1.5418$ Å. The incidence angle was set at 2° while the detector was scanned from $2\theta = 15°$ to 80°. For the FTIR measurements, an Avatar 360 spectrometer (Nicolet Instrument Corporation), working in the mid-infrared range from 400 to 4000 cm^{-1}, was used. All spectra were acquired in absorption mode with a resolution of 1 cm^{-1} and a minimum of 200 scans for each sample. A background spectrum was collected prior to each measurement and subtracted from the spectrum of the sample to remove the contribution of the instrument and environment to the infrared spectrum. Raman spectroscopy on the films was performed using a Jobin Yvon Lab Raman HR 800 UV spectrometer with a triple monochromator. The laser source was 325 nm unpolarized radiation from He-Cd laser. Each Raman spectrum recorded is the average of two successive scans obtained at a spectral resolution of ~1 cm^{-1} and each scan corresponds to an irradiation time of 3 h. The excitation power used was 50 mW and the spot size on the sample was ~1 μm. A Multimode™ Scanning Probe Microscope (Nanoscope III) from Digital Instruments operating in tapping mode was used for imaging the surface topography of the films.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of manganese oxide films grown at a temperature of 500 °C and a pressure of 1.33 Pa (a) in oxygen gas ambient and (b) under remote plasma conditions. For the film deposited in O_2 ambient, the XRD pattern exhibits diffraction peaks that are all matching those of Mn_2O_3 as inferred from the peak assignment in the figure and in agreement with results published elsewhere [10,11]. For the film deposited under remote plasma conditions, the pattern is significantly different with no Mn_2O_3 peaks detected, but we observe instead peaks that are strictly attributed to the MnO_2 phase. This is an indication that low pressure plasma activation of the oxygen gas has enhanced the oxidation state of manganese from Mn_2O_3 to MnO_2 phase. Additional investigation of this finding was performed using FTIR in order to determine the bonding and structural arrangement of the MnO_2 layers, since MnO_2 can crystallize in different polymorphs that may be difficult to distinguish by XRD alone.

Fig. 2 shows the FTIR spectra of manganese oxide films grown at a temperature of 500 °C and pressure of 1.33 Pa (a) in an oxygen gas ambient and (b) under remote plasma conditions. For the film deposited in O_2 ambient, the spectrum display several bands covering a wide range from 400 to 700 cm^{-1} identified as the vibrational bands of Mn_2O_3 [11,14]. Such complex IR features are typical of Mn_2O_3 phases such as the α-Mn_2O_3 bixbyite C-type structure or the tetragonal γ-Mn_2O_3 resulting from the structural arrangement of the Mn-O bonds [25]. For the film deposited under remote plasma conditions, the IR band is very different from the previous case, as two well resolved bands centered at around 500 and 600 cm^{-1} and a tail around 650 cm^{-1} are detected. This particular FTIR signal is very similar to the one obtained by Nilsen and co-workers [8] who reported that ALD grown β-MnO_2 films exhibit an IR signature very close to that of a β-MnO_2 powdered reference sample, but shifted to lower wavenumbers. The IR bands observed from the film grown under remote plasma conditions result from the stretching vibrations of the MnO_6 octahedral units that make up manganese dioxide materials. The MnO_6 octahedron consists of six oxygen atoms surrounding a central manganese cation (Mn^{4+}). The octahedra share opposite octahedral edges to form endless chains, and these latter

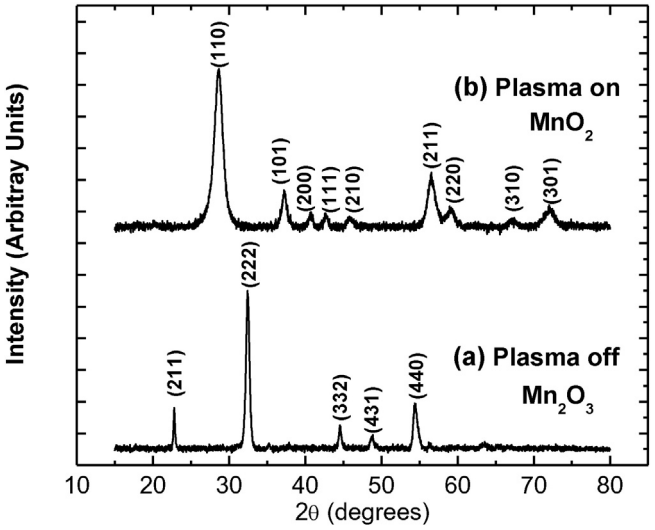

Fig. 1. X-ray diffraction patterns of manganese oxide films grown at grown at 1.33 Pa (a) in oxygen gas ambient and (b) under remote plasma conditions. Deposition temperature was set at 500 °C.