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One-step synthesis of crystalline Mn_2O_3 thin film by ultrasonic spray pyrolysis

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ABSTRACT

Recently, metal oxides have been gaining large interest in the field of renewable energy. This fact is mostly related to their properties which make them suitable for long lasting, cost efficient and environmentally friendly devices. Dimanganese trioxide (Mn_2O_3) was investigated in the past in different fields, yet, the fabrication of the film in most cases is not straightforward and requires several steps, consequently there is insufficient data provided in literature regarding this material. This paper presents a single step deposition of dimanganese trioxide (Mn_2O_3) thin films by spray pyrolysis on glass substrates at temperatures lower than 450 °C. The process was conducted under atmospheric conditions, making it an ideal and cost effective fabrication technique for large scale manufacture. The obtained Mn_2O_3 film was characterized chemically and physically. The film X-ray diffraction analysis reveals a crystalline phase of α-Mn_2O_3 in a bixbyite-like structure. Physical characterization included optical absorptance, band gap analysis, energy band diagram, and four-point probe resistivity measurement. The film exhibits a band gap of 1.4 eV making it a good candidate for applications such as solar cells.

1. Introduction

Over the past decade, transition metal-oxides have been gaining large interest in various fields of research such as electrodes for Li-ion batteries, gas sensors, photovoltaics and catalysts [1–4]. The incorporation of metal-oxides in these fields is ideal thanks to the development of metal oxide nanoscale structures. These structures enhance the material properties due to large surface area and well defined morphologies [5–7]. In addition, metal-oxides are inherently low cost, and simple to fabricate in the nanoscale level with large range of techniques such as pulse laser deposition, RF sputtering, spray pyrolysis and electrochemical deposition [8–11].

Dimanganese trioxide (Mn_2O_3) is one metal-oxide out of several stable oxidation states of metallic manganese including MnO, Mn_2O_3, Mn_3O_4 and MnO_2. These oxidation states differ by their properties such as band gap, resistivity and Seebeck coefficients [12,13]. While attaining significant interest in many fields of research, dimanganese trioxide has primarily been investigated as a water splitting catalyst, electrodes for lithium ion batteries, and supercapacitors [14–17]. Based on literature, Mn_2O_3 has relatively high conductivity, thermodynamic stability and a reported band gap of 1.2 eV, which makes it a suitable material for optoelectronics and photovoltaic applications [18].

So far, several deposition techniques of Mn_2O_3 were reported in literature such as hydrothermal, facile solvothermal, calcination and reduction of MnO_2 [18–20]. The limitation of these methods is the complexity of preparation. These routes require the use of polymers and include several steps, which in some cases can be time consuming and suffer from contamination of organic materials. In addition, in most reported deposition technique the product is a powder, while there are hardly any reports on Mn_2O_3 crystalline films deposition.

Spray pyrolysis is a versatile technique for fabricating a wide range of materials [21]. This technique is exceptionally low cost and highly scalable. In most cases, the system consists of an atomizer nozzle, an organometallic precursor, a hot plate, and a carrier gas. The pyrolysis step is initiated when contact is formed between the organometallic solution and the hot plate. In this process, the organic ligands attached to the metal ion, either evaporate or disassemble and oxygen enters as a substitute, resulting in the formation of a metal-oxide layer [22].

This paper presents, for the first time, the deposition of α-Mn2O3 crystalline phase at temperatures lower than 450 °C. The deposition is done in a single step on glass substrate and does not require postannealing, thus, making it time efficient. The obtained film has a

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high surface area thanks to the mesoporous structure, which may be beneficial for various of applications.

2. Methods

Mn_2O_3 films were deposited via spray pyrolysis technique [21]. The spray pyrolysis set-up is custom-made. It consists of a 3-axis CNC robot (EAS GmbH), a Ceran hot plate (Harry Gestigkeit GmbH, BORAX glass) with temperatures ranging from 50 to 500 °C, syringe pump (New Era Pump Systems Inc.) and a Sono-tek 120 KHz ultrasonic nozzle.

Precursor solution was freshly prepared by dissolving manganese acetate tetrahydrate (Acros Organics, 99%) in double distilled water to achieve a 0.1 M concentration. Two different Hartford Glass Co. Inc. glass substrates ($71 \times 71 \times 2.2$ mm^3) were used; pure glass and fluorine doped tin oxide (FTO) TEC-15 coated glass. The substrates were cleaned using an ultrasonic bath followed by ethanol rinse. The spray pyrolysis program was set to form a material gradient by spraying a smaller substrate area spraying cycle. The hot plate was set to 450 °C for 30 min to allow heat to spread equally over the substrates. The precursor flow rate was set to 60 mL/h and the carrier gas, which consisted of dry clean air, was purged at 2 bars. Substrate-nozzle distance was kept at 7 cm and x-y axis speed was 30 mm/s. Spray duration was 35 min, resulting in a linear gradient over the substrates with thicknesses varying between 320 and 1100 nm of the Mn_2O_3 layer.

Mn_2O_3 structural characterizations were carried out for the pure material on a glass substrate. X-ray diffraction measurements were performed with a Rigaku Smartlab work station with a θ–2θ scan range from 10° to 90° at a scan rate of 1°/min. Raman spectra were measured in a dual laser Raman system (LabRam HR Raman spectrometer) with the aid of an automated switching filter that allowed for stable and accurate mapping measurements. In each measurement, an excitation laser beam was first transmitted through an objective of 100× to a certain spot on the surface, then the scattered light was collected by that same objective into a CCD camera. For the Raman characterization we used an excitation wavelength of 532 nm in the range of 50–1700 cm-^{1}.

Transmission and reflectance spectra were measured by a homebuilt system, consisting of a computer controlled x-y scanning table, a specular reflectance probe, and two integrating spheres, connected by optical fibers to a CCD array spectrometer (HR4000, Ocean Optics Inc.) [23].

The work function and the ionization energy of the sample were measured under ambient conditions using a scanning Kelvin Probe combined with air photo emission system (ASKP150200, KP Technology Ltd.) with a 2 mm diameter stainless-steel tip. The tip was calibrated against a gold reference sample with a work function of 5.1 eV.

Thickness measurements were carried out using Energy Dispersive X-ray Spectroscopy (EDS) 80 mm^2 X-max detector (Oxford Instruments), which was mounted on a field emission, FEI, Magellan 400 L high-resolution scanning electron microscope (HRSEM), allowing for precise thickness modeling of metal-oxides thin films.

Four-point probe resistivity measurements were carried out using a custom-made system described elsewhere [24].

3. Results and discussion

Atmospheric deposition in combination with high temperature allows, in most cases, for the synthesis of thermodynamically stable products during the pyrolysis process. Given the different varieties of manganese oxidation states, a phase analysis confirmation is needed. While most reports of manganese spray pyrolysis results in MnO_2, our phase identification (Fig. 1) points to a pure polycrystalline Mn_2O_3, single phase material throughout the substrate [25,26]. An X-ray diffraction pattern shows diffraction lines at 2-theta angles of 23.20°, 33.03°, 38.24°, 45.22°, 49.38°, 55.30°, 64.43°, and 65.95°, all in full agreement with the International center for diffraction's data (ICDD, 01-071-0636) [27]. It is noticeable that although a polycrystalline thin film is grown, there is a preferred growth along the [222] axis. To eliminate

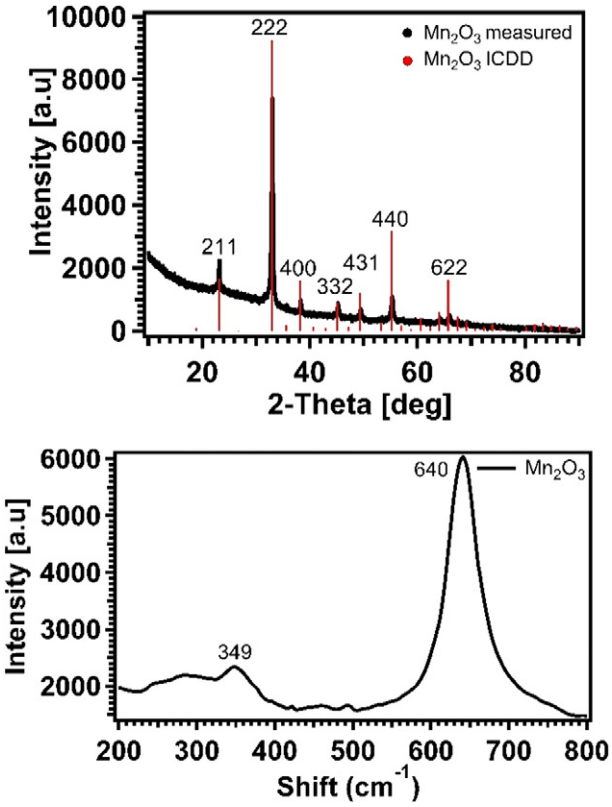

Fig. 1. Mn_2O_3 phase identification: (a) XRD diffraction pattern for deposited Mn_2O_3; diffraction lines fully match the ICDD data; (b) Raman spectrum showing two peaks which are in agreement with Mn_2O_3 literature values. Additional amorphous phase cannot be observed.

the possibility of the presence of any amorphous phases, Raman measurements were carried out. Peaks can be observed at 349 cm^{-1}, and 640 cm^{-1}; The major peak at 640 cm^{-1} corresponds to the symmetric stretching of the Mn–O bond of trivalent Manganese ions in occupied octahedral sites. The weaker peak at 349 cm^{-1} corresponds to the asymmetric stretching of bridge oxygen species (Mn–O–Mn) [28,29]. In order to estimate grain size, calculations were made (Table 1), using the Scherrer equation.[30] Grain size was found to be in the range of 30 nm.

Mn_2O_3 was deposited on an FTO coated glass so that less charging would appear during the scanning electron microscopy (SEM) process. Morphology and layer properties were investigated after cutting the sample, so a cross-section view (Fig. 2) could be taken with no ionic beam contact, which in most cases smoothens the surface and distorts the image. The cross-section shows a mesoporous layer which consists of nanoparticles with a diameter of about 30 nm, which correlates with the calculations done on uncoated glass using the Scherrer equation. These results indicate that grain size does not change between the different substrates; plain glass and FTO coated glass and permits a comparison between the films grown on either substrate.

The Shockley-Queisser limit determines the ideal band gap of an absorber in a photovoltaic cell to be 1.34 eV under AM1.5G sun light radiation [31]. In order to determine the Mn_2O_3 band gap, optical and

Table 1
Summary of X-ray diffraction results on Mn_2O_3 films relevant for employing the Scherrer equation calculations for grain size.

Peak location [2θ]	Miller index [hkl]	X-ray Wavelength [λ]	FWHM [deg]	Calculated grain size [nm]
23.13°	(211)	1.5418 Å	0.262°	32.36
32.95°	(222)	1.5418 Å	0.306°	28.31