Materials Science in Semiconductor Processing 24 (2014) 57–61

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Electrospray deposition and characterization of cobalt oxide thin films

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ARTICLE INFO

Available online 25 March 2014

Keywords:
Thin films
Electrospray deposition
Temperature effect

ABSTRACT

Cobalt oxide thin films were fabricated by means of electrospray deposition. The obtained films were characterized by Raman spectroscopy, X-ray diffraction and Scanning electron microscopy. The solution that was used gave the Co_3O_4 phase at different growth temperatures. The best granular surfaces were obtained at 250 °C as verified by all characterization techniques, while flaky surfaces were obtained at higher temperatures. The surface morphology is mostly granular except for high temperatures where the cobalt oxide is formed as flakes instead of grains.

1. Introduction

Cobalt oxide is a very interesting material due to its numerous applications and uses in the domain of materials science. For instance, cobalt oxide is used to fabricate sensors [1], electrochemical supercapacitors [2], catalyzers [3], and many other thin film based devices. Cobalt oxide could be found in several forms (CoO or Co_3O_4), and has been highly studied because of its exceptional properties. Such board potential applications led many researchers to develop a number of synthesis procedures that include a lot of low cost methods. As an example, cobalt oxides have been obtained by sol–gel preparation [4], spin-coating preparation [5], and electrospray deposition [6]. Every deposition technique was developed in such a way to meet with the specifications of certain applications. Electrospray is a deposition method where a solution is sprayed by the means of electrical force, and in which the flow and droplet size are controlled through a capillary nozzle. In fact the droplets are charged, which facilitates control over their motion by the means of an electric field. In an electrospray deposition, the size distribution of droplets is approximately monodisperse [6]; therefore it would be perfect for thin film deposition because a good dispersion of droplets will eventually prevent coagulation and clusters on the surface. This important feature makes electrospraying a very efficient technique in thin film production, in particular when moving from laboratory scale to industrial scale. Electrospray has previously been used to deposit thin films for solar cells, fuel cells, batteries, and biological membranes [7]; all of these previous efforts have been successful by combining a low cost production technique with relatively good films properties.

With all the above mentioned advantages of the electrospray technique, it was our best choice for depositing cobalt oxide films, knowing that only very few researchers have tried to grow cobalt oxide by this method.

In this work, cobalt oxide thin films were grown by electrospray at different substrate temperatures with the

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http://dx.doi.org/10.1016/j.mssp.2014.03.008
1369-8001/

aim of studying the effects of heat on the quality of films obtained by this low cost deposition method. The main application for cobalt oxide is its usage as a catalyst [8–10]. The goal behind mastering a low cost deposition process of cobalt oxide is to be able to produce it in large quantities for catalytic applications.

2. Experiment

Cobalt oxide samples were deposited by a electrospray technique which is, as previously mentioned, a relatively low cost method. The solution was injected through a syringe pump which regulated the flow into a metallic capillary nozzle plugged to a high voltage source [6]. The liquid was forced to be dispersed into fine droplets that traveled a certain distance in ambient air before hitting a glass substrate underneath. The substrates were cut into 1 cm^2 pieces and were rinsed in deionized water and cleaned in an ultrasonic cleaner. The solution was prepared by dissolving a hexahydrated cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) in ethanol and water (3/1 ratio) solution, under 10 min of agitation, in order to obtain a concentration of 0.25 mol/l. The solution was then introduced into the syringe pump of the electrosprayer. All variable parameters of the electrosprayer were fixed, with the exception of the substrate temperature which could be varied from 200 to 400 °C. The substrates were placed on a heating plate which controlled the temperature, the deposition time was 1 h, the distance of nozzle-substrate was 5 cm, and the syringe flow was 5 ml/h.

3. Results and discussion

3.1. Raman spectroscopy characterization

After deposition, the samples were thermally annealed for 3 h at 400 °C while characterizations were performed both before and after the annealing. First we begin with the Raman spectroscopy measurements shown in Fig. 1 for

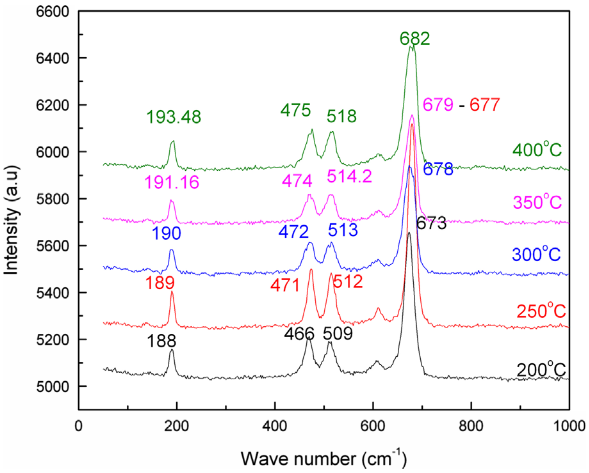

Fig. 1. Raman intensity as a function of wave number before annealing for cobalt oxide samples grown at different temperatures.

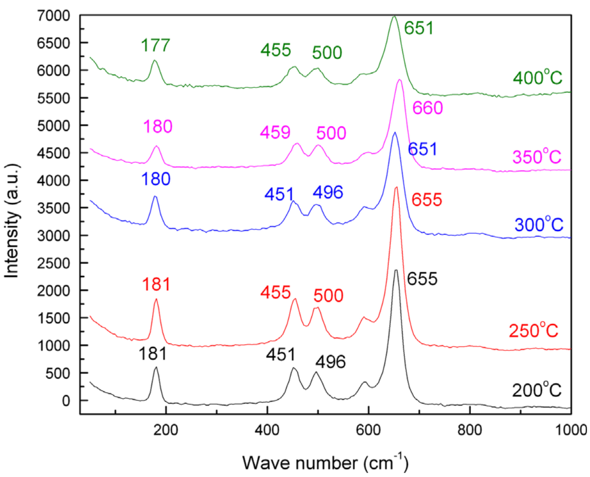

Fig. 2. Raman intensity as a function of wave number after annealing for cobalt oxide samples grown at different temperatures.

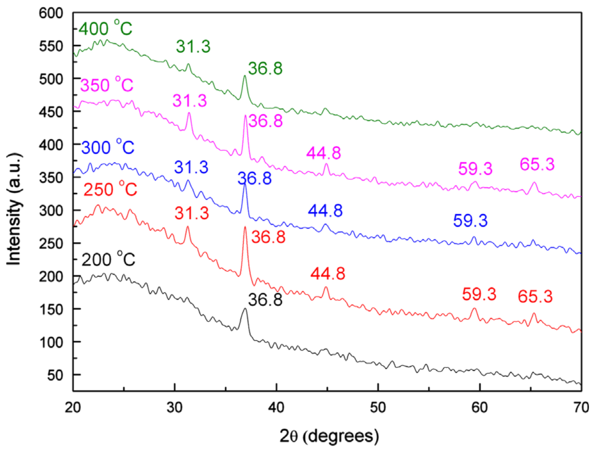

Fig. 3. Peak area (around 678 cm^{-1}) as a function of the growth temperature, before and after annealing.

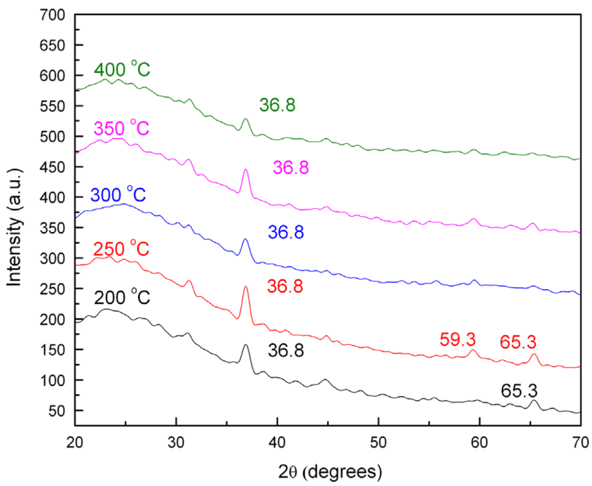

Fig. 4. X-ray diffraction peaks as function of 2θ before annealing for cobalt oxide samples grown at different temperatures.