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Technical note

Effects of deposition variables on spray-deposited MnO_2 thin films prepared from $Mn(C_2H_3O_2)_2 \cdot 4H_2O$

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Abstract

Undoped MnO_2 thin films have been prepared by a modified spray pyrolysis technique under various deposition conditions and the effects of different variables on electrical and optical properties have been studied in detail. It is found that substrate temperature, spray rate, solution concentration, carrier air pressure and post-deposition heat-treatment, spray outlet to substrate distance play important role in obtaining optimum films.

Electrical conductivity study shows an anomaly in conductivity at a temperature 323 K and its thickness dependent resistivity follows Fuchs–Sondheimer theory. The Hall effect and thermoelectric studies indicate that the deposited sample is an n-type semiconductor. Optical study in the entire wavelength 0.3–2.5 μm range exhibits a high transmittance in the visible as well as in the near infrared. Calculation from optical data, the sample exhibits a band gap at 0.28 eV, which also supports the value obtained from the Hall effect study. These studies may be of importance for the applications of this material in energy efficient surface coating devices.

Keywords: Preparation technique; Spray pyrolysis; MnO_2 films; Deposition variables; Anomaly in conductivity; Selective surface

1. Introduction

Research and development on thin films has led to the conclusion that different classes of materials are of particular interest for different applications. Manganese dioxide is of

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particular interest because the material has in recent a variety of applications in electrochemical [1,2], electrochromic [2], and fuel cell [3,4] devices. Manganese dioxide is a low band gap, high optical constant semiconductor that exhibits ferroelectric properties [5,6].

Literature reports indicate that thin films of manganese dioxide have been produced by a number of techniques by many researchers. These include the reactive deposition [7], electrochemical and thermal deposition [2,8,9], plasma assisted molecular beam epitaxy [10], r.f. sputtering [11], thermal decomposition [12], and sol–gel [13,14] derived techniques. Most of the reports address themselves to the electrochromic, electrochemical and spectroscopic performance of the films, emphasizing the inter-relation between the substrate materials, film structure and their performance in catalytic and rechargeable battery oriented applications. Although there have been a number of investigation on the electrical, optical and electrochromic properties of the films [14–16], no systematic study appears to have been done on electrical and optical properties at varying deposition conditions. Moreover, there is a considerable lack of understanding [7,9,17], concerning the surface properties of the oxides in different applications oriented measuring techniques. Different microstructures caused by different deposition conditions could be the probable reasons for the lacks in understanding. Hence there is a need to study how varying deposition conditions affect the physical properties of manganese dioxide films to assess its usefulness in the energy efficient devices applications. In this paper, we present and discuss the effect of deposition variables in the production of manganese dioxide films by a simple spray pyrolysis technique and to study the physical properties of the films.

2. Experimental

Undoped MnO_2 thin films were prepared from a solution of $Mn_2(C_2H_3O_2)_2 \cdot 4H_2O$ onto glass substrates at various thicknesses by modified spray pyrolysis techniques, a technique which is similar to the production of tin oxide films in our laboratory [18]. It is a very simple, indigenous, low-cost technique, which has not been used before for the deposition of thin manganese dioxide films.

A mixture of manganese acetate $[Mn_2(C_2H_3O_2)_2 \cdot 4H_2O]$ compound and deionized H_2O in the form of solution is taken in the pyrolysis flask as working solution for the formation of MnO_2. The basic reaction involved in the process is:

$$Mn(C_2H_3O_2)_2 \cdot 4H_2O + H_2O \leftrightarrow MnO_2 + 2CH_3COOH + 3H_2O + H_2 \quad (1)$$

2.1. Description of apparatus

Fig. 1 shows a schematic diagram of the experimental setup in our laboratory for the production of MnO_2 films. The left part of the above setup is designated as pyrolysis system and the right one is the reactor zone. Some of the special aspects of the aerosol production unit are: A, aerosol production nozzle in a flask; F, pyrex flask; P, compressed air inlet; C, conduit tube; E, stainless steel enclosure; S, substrate; H, heater; G, graphite block and Tc, the thermocouple to measure the substrate temperature.