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Synthesis, characterization and optical properties of selective Co_3O_4 films 1-D interlinked nanowires prepared by spray pyrolysis technique

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HIGHLIGHTS

- Spray pyrolysis is simple and versatile method for the deposition of thin films.
- Spray pyrolysis method gives phase and material pure Co_3O_4 films of controlled morphology.
- Optical properties of Co_3O_4 films depend on the thickness of film.
- The Co_3O_4 films gave better optical properties: $\alpha = 0.94$, $\varepsilon = 0.17$ and selectivity = 5.529.
- Better optical properties of Co_3O_4 films are due to 1-D interlinked nanowired morphology.

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ABSTRACT

The preparation of cobalt oxide (Co_3O_4) films containing 1-D interlinked nanowires by spray pyrolysis technique using cobaltous acetate $(CH_3COO)_2Co{\cdot}4H_2O$ solutions in 1:1 water–methanol mixture and study of their optical properties are reported in this paper. The films are characterized by using different physical techniques- X-ray diffraction (XRD), UV–Visible and Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The characterization studies showed that the resultant films are impurity free, phase pure with cubic spinel Co_3O_4 and contain 1-D interlinked nanowires having diameter and length in the ranges of 250–350 nm and 2–10 μm respectively. The resultant films also showed the better values of absorptance (α) = 0.94, emittance (ε) = 0.17 as compared to the data reported in literature. The selectivity of resultant films is found to be 5.529. These films are found to have good prospects for selective solar absorption coatings because their optical properties indicate the red shift of absorption peaks, exhibiting thereby quantum-confined effect and behavior of semiconductor.

1. Introduction

The increased interest in solar energy applications in recent decade has led to the development of spectrally selective surfaces with the maximum possible absorptance across the solar spectrum and the minimum possible emittance for the longer wavelengths relevant to thermal eradication [1]. Other essential properties of a practical solar selective coating are low cost, ease of mass production, stability at operating temperatures and good resistance to thermal shocks, oxidation, UV radiation, humidity and handling. For such application cobalt oxide Co_3O_4 is one of the promising transition metal oxide materials [2]. Co_3O_4 is a p-type antiferromagnetic oxide semiconductor with a Neel temperature T_N, of 290 K [3]. The cobalt oxide is emerged as a good candidate for high-temperature solar selective absorbers and many industrial applications such as solar selective absorber [4,5], catalyst in the hydrocracking process of crude fuels, pigment for glasses and ceramics [6], and catalyst for oxygen evolution and oxygen reduction reaction [7]. It is also widely used as an electrochromic material [6,8].

Different methods viz. electron beam evaporation [6], electrochemical deposition [8], chemical vapor deposition [9], dip coating process [10], sol–gel [11] and spray pyrolysis technique [12] are

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reported in literature for the preparation of Co_3O_4 films. The spray pyrolysis technique is a very simple, cheap, versatile method for the deposition of thin films because of having number of parameters for optimization of properties and surface morphology of thin films as compared to the other methods [13]. The much detailed information about pneumatic spray pyrolysis technique (PSPT) is reported in literature [14]. The deposition of cobalt oxide films containing nanowires on amorphous glass substrates by using spray pyrolysis technique is also reported in literature [13]. The optimization of preparative parameters to obtain good quality of cobalt oxide films containing 1-D interlinked nanowires [15,16] and their characterization are also reported in literature [3,17]. The highest values of absorptance (α) for Co_3O_4 films reported in literature are found to be in the range of $\alpha = 0.92–0.93$ [18–20].

It is well known that the properties of films are susceptible to both the deposition technique and preparative parameters. The film thickness is one of the important parameter in deciding properties of films. Further, the thickness of film can be controlled to obtain desired properties suitable for the given application. Consequently, the material of film can be tailored in terms of the structure, grain size, resistivity and band gap energy [13].

In view of this, the main objective of the present work was to use the novel pneumatic spray pyrolysis technique (PSPT) for the deposition of the Co_3O_4 films with better optical properties as compared to the literature [18–20]. Further, the another objectives of the this work was (i) to deposit the Co_3O_4 films comprising 1-D interlinked wires in nanometric range with better optical properties not reported earlier [3,17] and (ii) to see the effect of change of thickness of Co_3O_4 film on the its optical properties. The work related to above-mentioned objectives is presented in this communication.

2. Experimental

2.1. Cleaning of substrates

Initially, the stainless steel (SS) substrates (area of each substrate = 4 cm^2) were cleaned thoroughly. The SS substrates were cleaned by dipping them in a solution containing 50% HNO_3 and 10% chromium at room temperature (RT) for 30 min. Then SS substrates were cleaned by dipping them in a solution containing 10% H_2SO_4 at RT for 10 min. to remove the effects of HNO_3 and chromium arised during the passivation treatment. These SS substrates were then rinsed with acetone to remove the effects of H_2SO_4. The SS substrates were then subjected for cleaning with soap solution in double distilled water to remove the fingerprints if any. These substrates were again rinsed with acetone by dip method for 15 min. An additional cleaning of ultrasonic rinsing for 10 min. is also applied for SS substrate. Finally, the SS substrates were cleaned with dilute detergent and warm water. After these treatments, the substrates were kept in acetone prior to the deposition process.

2.2. Preparation of films

The thin films were deposited on thoroughly cleaned stainless steel (SS) substrates by using a typical home-built spray pyrolysis system as shown in Fig. 1. A 0.08 M solution of cobaltous acetate $(CH_3COO)_2Co\cdot4H_2O$ was prepared in a 1:1 mixture of water and methanol. The films were prepared by spraying 20, 30, 40, 50 and 60 ml of above-mentioned solution on SS substrates through a spray nozzle having diameter = 0.2 mm. All the films were prepared by using the following constant deposition parameters: (i) spray nozzle to substrate distance = 29 cm, (ii) flow rate for solution = 0.9 ml/min, (iii) flow rate for carrier gas = 75 ml/min and (iv) substrate temperature = 350 °C. The films were cooled naturally and removed from deposition chamber at room temperature. The films deposited by using 20, 30, 40, 50 and 60 ml of deposition solutions were identified as SS20, SS30, SS40, SS50 and SS60 respectively.

2.3. Characterization of films

The as-prepared films were characterized by using different physical techniques. The X-ray diffractometer (Bruker AXS, D8 Advance) was used for phase analysis of films. The impurity and phase analysis of films were done by using X-ray photoelectron spectroscopy (XPS). In XPS studies, a non-monochromatic MgKα

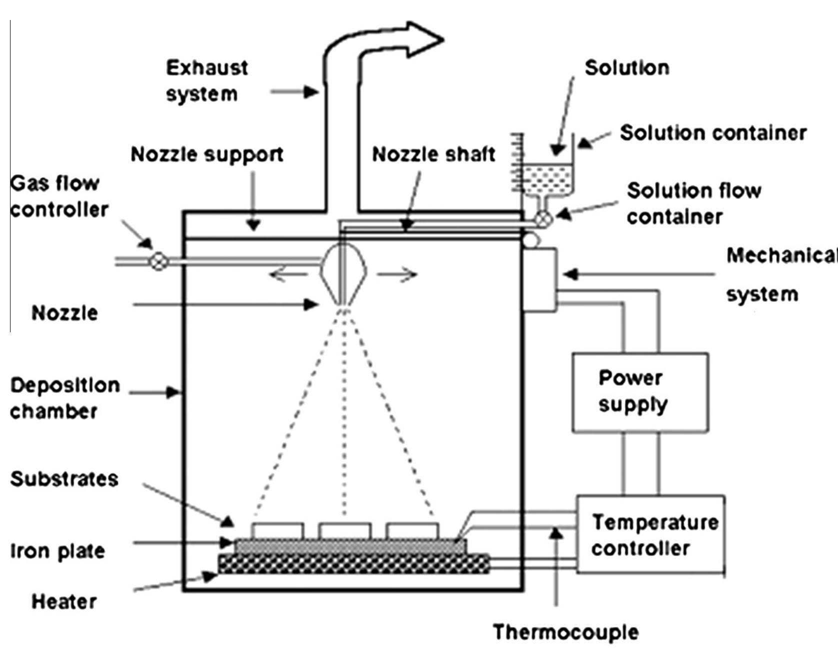

Fig. 1. Schematic diagram of spray pyrolysis system.