Studies on nanocomposites nanoplates and pervoskite nanorod thin films

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Abstract:

Nano crystalline nickel oxide thin films of different film thickness were deposited onto glass substrate at 350 oC by varying volume of precursor solution using spray pyrolysis technique. This structural, morphological and microstructure properties were investigated using XRD, FE-SEM and TEM. The element composition was studied using EDAX. It is found that increase in the volume of sprayed solution leads to the increment in film thickness and amelioration of crystallinity of the film. The results are discussed and interpreted.

Keywords: *Spray Pyrolysis, Nano crystalline nickel oxide, thin films, Electrical conductivity.*

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1. Introduction

Semiconductor metal oxide, nanocomposites, perovskite thin films sensor is extensively used across several domains that involve gas analysis, including air quality monitoring, environmental pollution detection, and identification of harmful gases [1-3].

Recently, a lot of investigators have focused their attention towards studying gas sensing potential of NiO owing to its high thermal stability and unique nanostructure [4]. The gas sensing performance of conventional NiO sensors, however, are limited, including low sensitivity, weak reliability, and high operating temperature, which restricts the production of sensors with a high performance [5]. Additional challenges are posed by the hazardous effects of prolonged NO₂ exposure [6].

Owing to the chemical stability, SnO₂, an *n*-type oxygen-deficient metal oxide, is most widely used for the fabrication of gas sensing sensors [7, 8]. Furthermore, the small size effect of SnO₂ makes it viable for the formation of n-n or p-n heterojunctions in conjunction with other nanomaterials [9].

Previous studies have shown that sensors made from NiO–SnO₂ nanocomposite combine the properties of both components and exhibit much better gas-sensing performances, lower optimum working temperature, rapid response-recovery, and better gas response than conventional SnO₂-based sensors [10].

Several studies have been conducted to overcome the limitations of the conventional nanomaterials, such as alterations in morphology, doping with metals, nanocomposites, etc. [10-13]. However, of all the approaches, fabrication of nanocomposite has been shown to enhance the gas sensing performance substantially [14]. In addition, nanostructures provide a high surface area for interaction with the gas molecules [15].

To improve the electrochemical performance and conductivity of the SnO₂ and NiO nanoparticles, the semiconducting materials are composed of NiSnO₃/GNS and NiSnO₃ as electrodes. For instance, NiSnO₃ has been used in lithium-ion batteries as anode [16].

Previously, there has been some debate around the basic material properties of NiSnO₃, like fundamental band gap [17]. Species with the general formula ABO₃, where A is monovalent or divalent metal and B is a tetra- or pentavalent atom are mixed with perovskite to enhance their electrical characteristics [18-21].

Several methods have been used to produce NiSnO₃ thin films, such as hydrothermal process [22], green synthesis method [23], and chemical oxidation method. [24]. For large thin films, the spray pyrolysis (SP) method seems to be the most optimum technique owing to its low cost, simplicity and applicability with metal doping. This technique can be used to synthesize smooth, pinhole-free, and homogenous thin films [25].

In this study, we used the spray pyrolysis technique for the synthesis of perovskite-based thin films and nanocomposites with the aim to enhance the gas response. We used several analytical techniques to assess the performance of these films.

2. Experimental details

2.1 Preparation of NiO-SnO₂ nanocomposites and perovskite NiSnO₃ thin films

For the preparation of NiO-SnO₂ nanocomposites and perovskite NiSnO₃ thin films were nickel chloride hexahydrate (NiCl₂.6H₂O) and tin (II) chloride dehydrate (SnCl₂.2H₂O Merck extra pure). Nickel chloride hexahydrate and tin (II) chloride dehydrate were mixed at different ratios like 25:75, 50:50, and 75:25 (1:3, 1:1, and 3:1) (Table 1).

Table 1: Varying amount of reactants and spraying solutions

Sample No.	NiCl ₂ .6H ₂ O (cm ³)	SnCl ₂ .2H ₂ O (cm ³)	Volume Ratio	Reactants
S1	25	75	1:3	NiO-SnO ₂
S2	50	50	1:1	NiO-SnO ₂
S3	75	25	3:1	NiSnO ₃

Based on the composition, the prepared films were named as S1 and S2 (both NiO-SnO₂ nanocomposites), and S3 (perovskite-based NiSnO₃ thin films).

The formation of the film is critically dependent upon landing of the droplets, reaction, and evaporation of the solvent, all of which are dependent on the size of the droplets. We optimized the process parameters as listed in Table 2. The carrier gas pressure, to and fro nozzle movement and substrate temperature were kept constant during the process.

It is noteworthy that the ideal condition for film synthesis is the point where the droplet reaches close enough to the substrate for the solvent to evaporate entirely.

2.2 Optimized parameter

Table 2: Optimum parameter to obtain NiO-SnO₂ nanocomposites and pervoskite NiSnO₃ thin films.

Deposition parameter	Optimum value / item
Spray deposition time	10 min.
Nozzle-to-substrate distance	30 cm
Concentration of precursor	0.05 M
Solvent	Deionized water
Deposition temperature	400 °C
Flow rate of solution	8 mlmin ⁻¹
Annealing temperature	500 °C
Annealing time	1 hr

2.3 Film annealing

The NiO-SnO₂ nanocomposites and pervoskite NiSnO₃ thin films samples were annealed at 500 °C for 1 h in the presence of air to increase its micro-structural properties and gas sensing performance.

3. Materials characterization

3.1 Determination of film thickness

Measurement of thickness was conducted using surface profiler (AMBIOS Tech. (USA) XP.I). The thickness of the films were found to S1=789, S2 =890 and S3= 678 respectively. Thickness of the thin films were random it may be due to different volume proportion of the Ni and Sn (Different at% of Ni and Sn during the formation of the NiO-SnO₂ nanocomposites and pervoskite NiSnO₃ thin films).

3.2 XRD of NiO-SnO₂ nanocomposite thin films

Figure 1: X-ray diffractogram of nanocomposites thin films samples: S1 and S2

The XRD was used to assess the structural properties of the thin films. The 2θ values were in the range of 20° to 80° . The XRD patterns of pure NiO indicate cubic structure (Chapter 3) and pure SnO₂ shows tetragonal structure (Chapter 4). The S1-S2 sample shows a mixture of phases of NiO (+) and SnO₂ (*) (Fig. 1).

The XRD findings did not reveal presence of any impurities in the sample. The sharp diffraction peaks additionally indicated high sample purity. XRD pattern revealed the (from sample S1-S2) the formation of NiO-SnO₂ nanocomposites thin film. The NiO and SnO₂ diffraction peaks matched with standard value for NiO and SnO₂ [JCPDS data card no. 4-0835 (NiO) and JCPDS data Card no.21-1250 (SnO₂)].

There is no shift of the diffraction line position for the nanocomposites thin film samples. The broad diffraction peaks indicates the nanocrystalline nature of the component crystal in nanoplates. Strong diffraction peaks confirm the presence of mixed phases of NiO and SnO₂ formations. The average crystallite size of NiO-SnO₂ nanocomposite-based thin film samples ranged between 12 nm and 14 nm as assessed using the Scherrer formula [20].

3.3 XRD of pervoskite NiSnO_3 thin film

Figure 2: X-ray diffractogram of pervoskite NiSnO_3 thin film sample S3.

The crystalline and phase structure of sample S3 was also examined using XRD (Fig. 2). The peaks (103), (104), and (302) corresponds to NiSnO_3 (JCPDS file no. 28-0711). No impurity phases were identified in the film sample. These XRD patterns confirm the formation and composition of pervoskite NiSnO_3 thin film. Of all the peaks, the (103) peak is the predominant peak, which indicates preferential growth and that the surface of the substrate is perpendicular to the c -axis of the grains. This means that the grains have perpendicular to the substrate surface. It should be noted that low intensity of the peaks was observed indicating the formation of pervoskite phase.

The average thickness of the films as calculated using the Debye-Scherrer formula [26] was 10 nm.

3.4 Surface morphology using FESEM

- FESEM images of nanocomposites NiO-SnO_2**

Figure 3: FE-SEM images of NiO-SnO_2 nanocomposites thin films: S1 (a), S2 (b)

We also examine the surface morphology of the films using FESEM. As shown in Fig. 3, irrespective of the volume ratios of Sn and Ni, the nanoplates were clearly defined across the whole substrate; however the vertical alignment of the nanoplate's orientation changed from horizontal alignment with respect to the volume ratio (1:3 and 1:1). The nanocomposite thin films (Fig. 3 (a)) exhibit vertically oriented nanoplates [27].

For volume ratio of 1:1, there was a slight distortion in the nanoplates, changing their alignment from vertical to horizontal (Fig. 3((b) (S2))).

The lengths of S1 and S2 nanoplates were 227 nm and 367 nm, respectively. The nanoplate structure will enhance the performance of these films.

3.5 FESEM image of pervoskite NiSnO_3 thin film

Figure 4 (a) and (b): FESEM images of NiSnO_3 perovskite thin film: S3 (Different magnification power)

FESEM image of nanorod NiSnO_3 pervoskite thin film (Sample=S3) is represented in Fig. 4. It appeared to be uniform distribution over the substrate and the corresponding low and high magnification image is shown in Fig. 4 (a) and (b). Nanorods are grown from vertically and horizontally aligned exhibits high-density nanorod. No other morphologies, such as nanopowders, nanoplates were formed. Fig. 4 (a) and (b) show the presence of several interconnected grains composed of nanorod with diameter 123-150 nm and lengths of 230-300 nm, indicating that these nanorod were produced on a large scale with uniform size and morphology. Fig 4 (b) at higher magnification, clearly reveals that the surface of the nanorod consists of many small nanoparticles.

3.6 Quantitative elemental analysis using EDAX

• EDAX spectra of NiO-SnO₂ nanocomposites

(a)

(b)

Figure 5: EDAX spectra of NiO-SnO₂ nanocomposites thin film samples S1 (a) and S2 (b).

We performed EDAX analysis to further elucidate the elemental composition of films (Fig. 5 (a) and (b)). Stoichiometrically expected at % of Ni, Sn and O for NiO-SnO₂ nanocomposite thin films are: 20.00, 20.00 and 60.00 respectively. Observed at % for NiO-SnO₂ nanocomposites thin films were inset in the EDAX spectra Fig 5 (a) and (b). Our findings showed that the conventional samples comprised Ni and O, while the comprised Ni, Sn, and O.

As volume ratio of Ni and Sn changes during the formation of nanocomposites thin films at % of Ni in Sn also changes. From the table inset in Fig. (5) shows that the prepared NiO-SnO₂ nanocomposites thin film were nonstoichiometric in nature.

- EDAX spectra of NiSnO_3

Figure 6: EDAX spectra of NiSnO_3 pervoskite.

The constituent of elements in the thin film sample was conducted using EDAX spectra. Stoichiometrically expected at % of Ni, Sn and O for NiSnO_3 nanocomposites thin films is: 20.00, 20.00 and 60.00, respectively.

Observed at % for NiSnO_3 pervoskite thin films were inset in the Fig 6 and it was observed to be nonstoichiometric in nature.

4. Electrical properties

- TEP measurement

Figure 7: TEP measurements of S1, S2, and S3

From the TEP measurement (From Fig.7) it was found that as prepared nanocomposites and pervoskite thin films was *n* type conductivity.

- I–V characteristics**

Figure 8: I–V characteristics of S1, S2, and S3

The I-V characteristics of the samples were studied to examine the nature of contact (Fig. 8). The linearity observed in Fig. 8 shows that pressure contact has an ohmic nature [28].

- Electrical conductivity**

Figure 9: Log (σ) versus inverse of operating temperature (°K).

For a given semiconductor, the thermal energy that is needed to transfer the electrons from the valence and to the conduction band is known as activation energy. We assessed the variation in conductivity (σ) as a function of inverse of temperature (range: 323–423 K; Fig. 9). We observed a linear correlation between temperature and electrical conductivity (σ). The Arrhenius law [29] was used to evaluate the activation energy of the film samples:

$$\sigma = \sigma_0 \exp (- \Delta E/kT) \text{ ----- (1)}$$

Where, σ = conductivity

σ_0 = conductivity constant

k = Boltzmann constant

T = Temperature

The thermal activation energies of S1, S2, and S3 were 0.10 meV, 0.28 meV, and 0.12 meV, respectively.

5. Conclusions

The spray pyrolysis method was used to build nanocomposites and pervoskite thin films. XRD pattern indicates the formation of nanocomposites and pervoskite thin films. Surface morphology studies confirm the formation of nanocrystalline nature of the prepared thin films. Elemental analysis revealed that the thin films were nonstoichiometric. Analysis of the microstructures revealed that the nanocomposites and pervoskite thin films were nanostructure in nature. TEP profile indicates n type conductivity. I-V characteristics confirm ohmic contact of the thin films. Analysis of electrical conductivity revealed that the films were semiconducting. Furthermore, its other features, make them a promising material for the nanoscale gas sensors.

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