Fabrication and Characterization of Nickel Cobaltite Nanostructures for Gas Sensing Applications

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Abstract
In this work, nickel cobaltite nanostructures were prepared by dc reactive sputtering technique. The characterization measurements performed on the prepared films showed that the transmittance increases with the incident wavelengths, the polycrystalline structure contains of 5 crystallographic planes, the average particle size is about 25nm, the electrical conductivity is increasing linearly with increasing temperature, the activation energy is about 0.41 eV, and finally they showed high sensitivity to ethanol. This attempt is encouraging to fabricate nickel cobaltite nanostructures for some important applications.

Keywords: Nickel cobaltite; Magnetron sputtering; Reactive sputtering; Gas sensing
Received: 19 January 2024; **Revised:** 14 March 2024r; **Accepted:** 21 March 2024; **Published:** 1 April 2024

1. Introduction

Amongst too many metal oxides with spinel structures, nickel cobaltite ($NiCo_2O_4$) has its featured applications in electrochemistry and sensing devices [1-3]. It is utilized efficiently as electrode material in sodium-ion cells as well as electro-catalyst in alkaline water electrolyzer because of the low-cost production, environmental friendliness, high electrical conductivity and optical properties in the infrared region of electromagnetic spectrum [4-6]. One reasonably important application such as energy storage is based on the employment of nickel cobaltite as super-capacitors, also known as “electrochemical capacitors” [7]. These devices are characterized by their ultra-high power density, long cycling stability, wide operation temperature range and improved safety [8-10].

Due to the high flexibility, reliability and low-cost of magnetron sputtering technique, atoms from one or more different targets can be sputtered and oxidized before deposited as thin films or nanostructures on different substrates [11,12]. These films and structures can be produced at high purity and homogeneity since the operation parameters and preparation conditions can be controlled well [13].

In this work, thin films of nickel cobaltite are deposited on transparent substrates. Two targets of nickel and cobalt are co-sputtered in presence of oxygen as a reactive gas. The optical and structural characteristics of the deposited films are introduced.

2. Experimental Part

A dc reactive plasma sputtering system was used to prepare the nickel cobaltite films. The chamber was first evacuated to 0.01 mbar in order to remove any reactive contaminants or residual particles. Plasma was produced by discharge of argon as a process gas in presence of oxygen as a reactive gas with a $Ar:O_2$ mixing ratio of 5:1 at total pressure of 0.5 mbar, flow rate of 100 sccm, discharge current of 40 mA, and discharge voltage of 1.5 kV. Both electrodes were cooled to 20°C in order to avoid the effects of rising temperatures on the quality of the prepared structures. Pure nickel (99.9%) and cobalt (96%) hemispherical sheets of 8cm diameter was mounted by Teflon mount on the cathode as the sputtering targets to be sputtered while the glass substrates were placed on the anode electrode. These substrates were cleaned by ethanol to remove any residuals on their surfaces and then rinsed in distilled water to remove the ethanol before dried by hot air and kept in closed vessel. As the substrate was placed upon the anode, its temperature was expected to be the same as the temperature of the anode (20°C). More details can be found in published works [14-17].

The prepared samples were tested by the UV-Visible-NIR spectrometry in the spectral range 166-962nm using SpectraAcademy C110905 spectrophotometer with resolution of 0.2nm, X-ray diffraction using Cu-Kα Phillips-PW1710 x-ray tube (λ=1.54Å), and field-emission scanning electron microscopy (TESCAN VEGA FE-SEM). Four-point probe (F.P.P.) apparatus was used for the measurements of magnetization with magnetic field. A Keithley 616 picoammeter was used for the measurements of the electrical conductivity, which were equipped with a K-type thermocouple to measure the temperature of the sample. The gas sensitivity of the prepared samples was measured in a glass enclosure with adjustable gas concentration. The value of sensitivity (S) was determined by $S=|R_g-R_a|/R_a$, where R_g and R_a are the electrical resistance of the thin film in the gas to be sensed and in the air, respectively.

3. Results and Discussion

The prepared films were visibly grayish-brown in color and figure (1) shows the average transmittance and absorbance of $NiCo_2O_4$ films with thickness of 100nm. It is clear that these films have low transmittance (high absorbance) in the UV region of electromagnetic spectrum. This transmittance is increasing with increasing incident wavelength to reach about 70% at 900nm (NIR).

To introduce the crystalline structure of the prepared samples, the XRD pattern was recorded, as shown in Fig. (2). Five distinct peaks were identified according to the JCPDS 20-0781 at 2θ of 31.7, 36.8, 38.6, 65 and 69.2 degrees. These angles correspond to crystallographic planes of (220), (311), (222), (511) and (440), respectively. The polycrystalline structure assign high purity of the prepared samples as no peaks belonging to pure Ni or Co were observed on the XRD pattern. Using Scherrer's equation, the average grain size (G.S.) was determined to be 2.33nm. However, the $NiCo_2O_4$ particle size was determined from the FE-SEM image, shown in Fig. (3), to be about 25nm, which is approximately the average value for all tested samples.

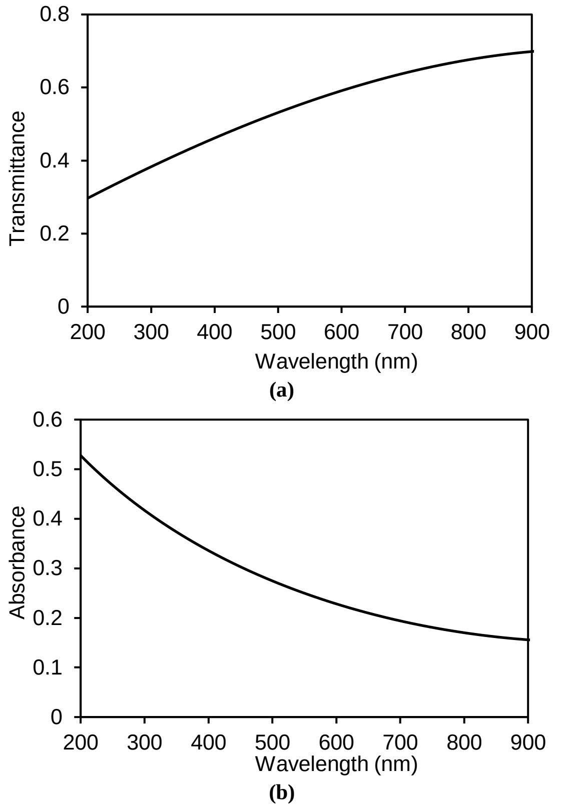

Fig. (1) Average transmittance (a) and absorbance (b) of 100nm $NiCo_2O_4$ films in the range of wavelengths 200-900nm

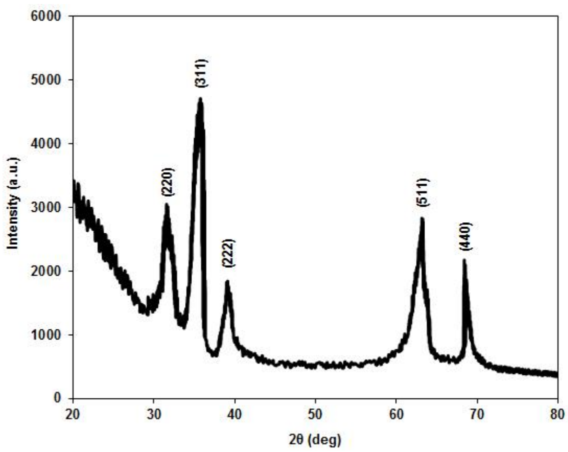

Fig. (2) XRD pattern of the prepared sample of 100nm thickness

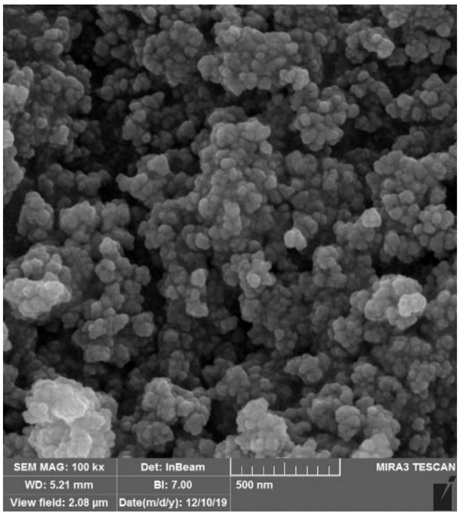

Fig. (3) SEM image of the prepared sample. The particle size is about 25nm

The electrical conductivity (σ) of the prepared $NiCo_2O_4$ films was found to increase with increasing temperature and this behavior is expected due to the changes in oxygen binding energy. As well, the role of nickel ions in the electrical conduction of this compound is of reasonable importance. In order to determine the thermal activation energy (E_a) of this compound ($NiCo_2O_4$), the variation of Ln(σ) with 1000/T in case of heating 100nm film sample is plotted, as shown in Fig. (4). From the slope of produced line, the thermal activation energy was determined to be 0.41eV, which is little higher than that of degenerate semiconductors.

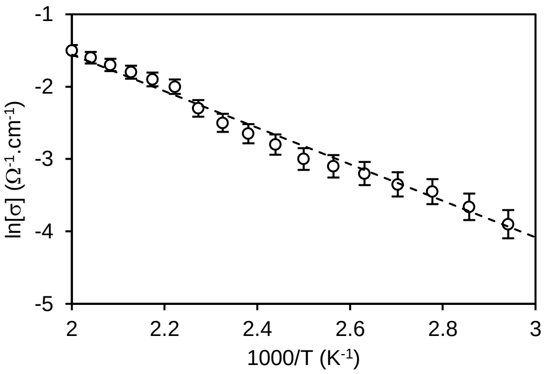

Fig. (4) Plot of Ln(σ) against 1000/T for $NiCo_2O_4$ thin film during sample heating (thickness is 100nm). The activation energy (E_a) is determined from the slope to be about 0.41 eV

One of the most promising applications of $NiCo_2O_4$ thin films is their ability to detect gases and vapors. Therefore, the sensitivity of the prepared films to ethanol vapor was measured at room temperature (300K), as shown in Fig. (5), and the maximum value was observed at 7.5 at ethanol concentration of 1000 ppm of ethanol. This value of sensitivity can be considered as high.

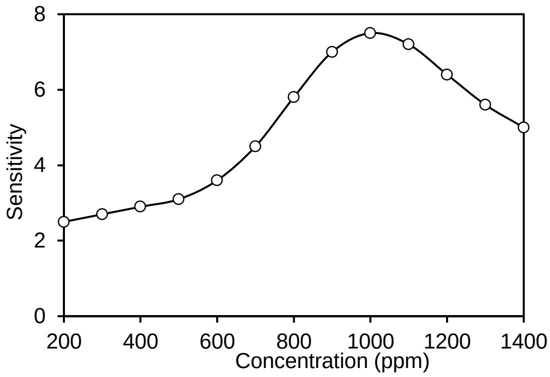

Fig. (5) The measured sensitivity of $NiCo_2O_4$ thin films to the ethanol

4. Conclusions

In concluding remarks, homogeneous, nanostructured nickel cobaltite thin films were prepared and deposited on transparent substrates by magnetron sputtering technique. Thin films of 100nm thickness were partially transparent. These films were polycrystalline with high structural purity and a minimum particle size of 25nm was observed. Thermal activation energy of the prepared sample was 0.41eV. High sensitivity of the prepared films to ethanol was measured at room temperature. Magnetron sputtering technique is a low-cost, flexible and reliable technique to prepare $NiCo_2O_4$ nanostructures.

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