

Hydrogen Gas Sensors Based on Electrostatically Spray Deposited Nickel Oxide Thin Film Structures

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Abstract: A simple, low-cost, and home-built electrostatic spray deposition (ESD) system with the stable cone-jet mode was used to deposit nickel oxide (NiO) thin films on glass substrates kept at temperature of 400 °C as the primary precursor solution of 0.1 M concentration hydrated nickel chloride was dissolved in isopropyl alcohol. Electrical measurements showed that these films were of n-type conductivity while their resistance response to hydrogen flow in air ambient was varied by 2.81% with the rise and recovery time of 48 s and 40 s, respectively.

Keywords: Gas sensors, electrostatic spray deposition, nickel oxide, thin films

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1. Introduction

Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide. It is a NaCl-structure like antiferromagnetic oxide semiconductor. It offers a promising candidature for many applications such as the solar thermal absorber [1], catalyst for O₂ evolution [2], photoelectrolysis [3] and electrochromic device [4]. NiO is also a well-studied material as the positive electrode in batteries [5]. Pure stoichiometric NiO crystals are perfect insulators. Several efforts have been made to explain the insulating behavior of NiO. Appreciable conductivity can be achieved in NiO by creating Ni vacancies or substituting Li for Ni at Ni sites [6]. Electrostatic spray deposition (ESD) is of particular interest because of its simplicity, low cost, and minimal waste production. The ESD technique involves the generation of an aerosol from a precursor solution when a strong electric field is

applied between a metallic nozzle and a substrate. The precursor solution comprises an organic solvent in which an inorganic salt is dissolved. For a particularly applied voltage difference and liquid flow rate, certain spaying modes are obtained of which the cone-jet mode (Taylor cone-jet mode) is the most encountered one [7, 8]. The highly charged aerosol droplets made by the applied high electric field shrink by solvent evaporation. When the droplet reaches the maximum amount of charge limit, it can carry "Rayleigh limit", and it would throw out fine jets of a huge number of liquid droplets of the nanometer size (10⁸ droplets/s – 10¹⁰ droplets/s). These droplets are then attracted by the grounded and heated substrate where they impinge and lose their charge. Hydrogen sensing is important for many industrial applications because hydrogen becomes explosive in air with the lowest explosion limit of 4% (40000 ppm). Hydrogen used as fuel is a major concern for fire detectors:

traditionally, fire alarms use a smoke detector or a heat detector. Recent studies have shown that NiO thin films can be used successfully as sensing materials in gas and humidity detection devices [9]. NiO, one of the very few known p-type metaloxide semiconductors [10], is an antiferromagnetic [11], electrochromic [12], and catalytic [13] material with the excellent chemical stability [14] and good gas sensing properties [15, 16].

This work focused on using the aqueous solution of nickel chloride to deposit NiO thin films on glass substrates by the ESD technique. The resistance response of the NiO thin film towards H₂ flow was examined.

2. Experiment

Electrostatic spraying, one of the chemical techniques applied to form a variety of thin films, results in the good productivity from a simple apparatus. In the current research, nickel oxide thin films were deposited on glass substrates employing a locally-made ESD system [17]. It was essentially made up of a precursor solution, an electrostatic HV-DC power supply, a precursor atomization nozzle assembly, and a temperature-controlled hot plate heater. The atomizer had an adjustable steel capillary tube of 0.25 mm inner diameter nozzle clamped to a holder and supported by a metal tripod. The prepared precursor solution to be sprayed was flowing through the nozzle due to gravity with a flow rate ranging from 0.2 mL/min to 1 mL/min. For the direct current (DC) high voltage power supply used in the measurement, a simple high frequency (14 kHz – 42 kHz) and variable duty cycle circuit was built. The NE 555 timer drove the flyback transformer in the “flyback mode”. Due to the high voltage applied at the metal needle, a Taylor cone-jet was created at the tip of the nozzle, and the solution disrupted upon the droplets charge density reaching Rayleigh limit after which the spray started [18].

A 0.1 M concentration aqueous precursor solution of hydrated nickel chloride NiCl₂·6H₂O

(molecular weight 237.7048 g/mole) has been prepared by dissolving a solute quantity of 1.2 g of NiCl₂·6H₂O in 100 ml 0.999 pure isopropyl alcohol C₃H₉O (the solvent). A magnetic stirrer was incorporated for this purpose for about 10 minutes – 15 minutes together with addition of 0.1 mL hydrochloric acid to facilitate the complete dissolution of the solute in the solvent. Prior to depositing the films, the commercial glass substrates were thoroughly cleaned in distilled water and dried in air for 5 minutes. After that, they were soaked in alcohol to remove any stains and contaminants. The electrostatic spray was conducted at substrate temperature within 400 °C during the deposition. The film thickness was controlled by both the precursor concentration and the number of sprays, or alternatively, spraying time. Thus, a 4-second spray time was maintained during the experiment. The normalized distance between the spray nozzle and substrate was fixed at 2 cm. The spray rate of the solution was maintained at 0.2 mL/min throughout the experiment. The nickel chloride solution was sprayed onto the preheated glass substrate, which underwent evaporation, solute precipitation, and pyrolytic decomposition, thereby resulting in the formation of NiO thin films according to the following reaction:



The surface topography of the prepared samples was introduced by the atomic force microscopy (AFM) as shown in Fig. 1, in which the values

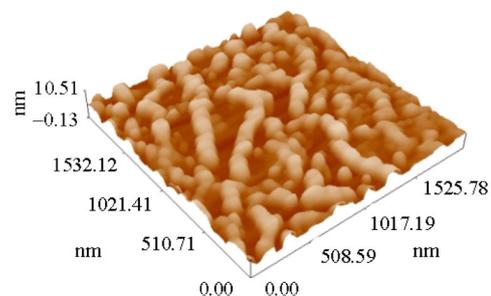


Fig. 1 3D AFM image of the prepared NiO film.

of average, root mean, square, and peak-peak roughness were 1.2 nm, 1.37 nm, and 5.57 nm, respectively, while the average diameter of NiO grains was 91.11 nm.

The experimental setup of gas sensing consisted of a vacuum-tight stainless steel cylindrical test chamber of 163 mm in diameter and 200 mm in height with a removable bottom base sealed with O-ring. The chamber had an inlet for the test gas to flow in and an air admittance valve to enter air after evacuation. The effective volume of the chamber was 4173.49 cm³. Another third port was provided for vacuum gauge connection. A multi-pin feedthrough at the base of the chamber allowed for the electrical connections to be established to the heater assembly as well as to the sensor electrodes via spring loaded pins [19–21].

The heater assembly consisted of a hot plate and a k-type thermocouple inside the chamber in order to control the operating temperature of the sensor. The thermocouple sensed the temperature at the surface of the film exposed to pre-determined air-hydrogen gas mixing ratio. The chamber can be evacuated using a rotary pump to a rough vacuum of 10⁻³ bar. A gas mixing manifold was incorporated to control the mixing ratios of the test and carrier gases prior to being injected into the test chamber. The mixing gas manifold was fed by zero air and test gas through a flow meter and needle valve arrangement. This arrangement of mixing scheme was done to ensure that the gas mixture entering the test chamber was premixed, thereby giving the real sensitivity.

The response time of a gas sensor is defined as the time it takes to reach 90% of the maximum/minimum value of conductance upon the introduction of the reducing/oxidizing gas. Similarly, the recovery time is defined as the time required to recover it within 10% of the original baseline when the flow of reducing or oxidizing gas is removed. Figure 2 shows how the time is determined from the time-dependent conductance of the sensor.

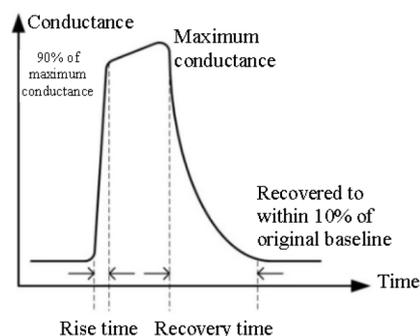


Fig. 2 Determination of rise and recovery time from the time-dependent conductance plot of the sensor.

3. Results and discussion

The conductivity type of the NiO thin film is determined by Hall coefficient (R_H) measurement at room temperature. The carrier concentration (n_H or p_H) and the Hall mobility (μ_H) are obtained from the combined Hall coefficient and electrical resistivity (ρ) measurement using the equations:

$$n_H = \frac{1}{eR_H} \tag{2}$$

$$\mu_H = \frac{R_H}{\rho}$$

The carrier concentration is given by the relation $n = r \cdot n_H$ where r (scatter factor) is usually assumed to be 1. Electrical resistivity of NiO thin films was studied by many researchers [22–26], and reported resistivity was in the range of 10 Ω-cm – 10⁶ Ω-cm. Table 1 shows the Hall effect measurement data of NiO films at 400 °C temperature. The value of resistivity, Hall coefficient, and carrier concentration variation are dependent on substrate temperature.

Table 1 Hall effect measurement data.

| | |
|--------------------------------|--|
| Mobility μ_H | 1.032 cm ² /V·s |
| Resistivity ρ | 5.157 Ω-cm |
| p_H or n_H | 2.06 × 10 ⁻¹⁷ m ⁻³ |
| Conductivity σ | 1.939 1/Ω |
| Average Hall coefficient R_H | -5.322 m ³ /C |

Figure 3 shows the current-voltage (I - V) characteristics of NiO films, from which we conclude that the curves are identical and it is due to

the resistance on the outskirts of equal polarity as a result of the homogeneity of the thin film.

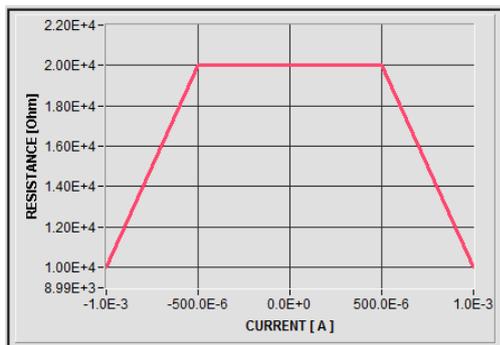


Fig. 3 I-V curves of the NiO thin film.

Figure 4 shows the variation of electrical conductivity (σ) with reciprocal temperature ($1000/T$) for NiO thin films. It was observed that σ increased rapidly with a slight increase in temperature to reach 0.01 at 100 °C, beyond which a gradual increase in σ was observed. The thermal activation energy (E_a) calculated by the Arrhenius equation was equal to 2.7 eV. The estimated activation energy was found to depend on the structure of the prepared material (single or poly crystalline) as well as on the range of temperatures [24–25].

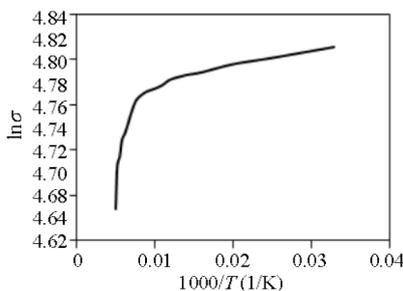


Fig. 4 Variation of logarithmic conductivity ($\ln\sigma$) vs. $1000/T$ for NiO thin films.

Dynamic response measurement of the prepared film was performed against H_2 in air flow at working temperature of 350 °C, 375 °C, and 400 °C inside a stainless steel chamber. The relative response (sensitivity) against gas flow is determined by

$$S = \frac{R_0 - R_g}{R_g} \tag{3}$$

where R_0 and R_g are the film resistances in air and in the presence of the H_2 gas, respectively.

Gas sensitivity is strongly related to the adsorption/desorption processes occurring at the gas-surface interface. The dynamic response of the NiO thin film deposited at 400 °C against H_2 in air ambience at different operating temperatures is shown in Fig. 5 and Table 2, where the resistance of these films decreases when exposed to a reduction gas.

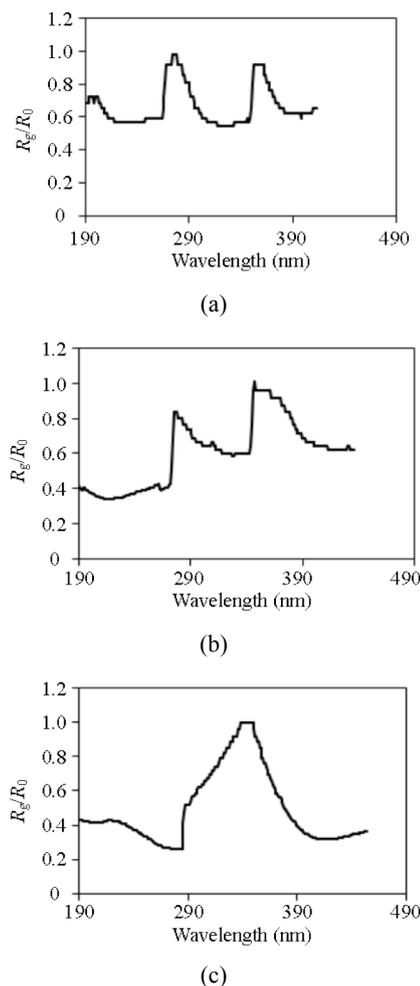


Fig. 5 H_2 gas sensing behavior of the NiO thin films at different working chamber temperatures: (a) 350 °C, (b) 375 °C, and (c) 400 °C.

Moreover, the H_2 sensing properties of the NiO thin films strongly depend on the working temperature. In particular, both rise and recovery time increases when the working temperature increases as this may accelerate the adsorption/

desorption process on the surface of the NiO thin film. For this reason, the maximum sensitivity of the NiO films was increased from 0.64 to 2.81 with an increase in working temperature.

Table 2 Gas sensor measurement data.

| Temperature (°C) | Sensitivity (%) | Rise time (s) | Recovery time (s) |
|------------------|-----------------|---------------|-------------------|
| 350 | 0.64 | 2 | 20 |
| 375 | 0.67 | 5 | 26 |
| 400 | 2.81 | 48 | 40 |

4. Conclusions

NiO thin films were deposited by spraying the solution on the glass substrates using a simple and inexpensive ESD technique at 400 °C. The room-temperature electrical resistivity of the thin film was about 5 Ω·cm. Finally, the H₂ sensing properties of the NiO thin film strongly depended on the working temperature, where the sensitivity increased with an increase in the working temperature.

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