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# Sol–Gel Derived Spin-Coated NiO Thin Films for LPG Detection

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**Abstract:**
Nickel oxide (NiO) thin films were successfully synthesized using a simple sol–gel spin coating technique. Nickel nitrate hexahydrate and citric acid were used as precursor and complexing agent respectively, with double distilled water as solvent. The spin coating was performed on glass substrates at 2000 rpm for 60 seconds. The prepared NiO thin films showed thickness of 38 nm, resistivity of 271.2 Ω·m, temperature coefficient of resistance (TCR) of -0.0022 $°C^{-1}$, and activation energy of 0.11355 eV. The fabricated NiO thin films were characterized for their gas sensing performance towards liquefied petroleum gas (LPG). The films exhibited a sensitivity of 78.95% at an optimum operating temperature of 100°C for 500 ppm of LPG. The response and recovery times were found to be 18 s and 61 s respectively, indicating good semiconducting behavior and suitability for gas sensing applications.

**Keywords:** Nickel oxide, spin coating, gas sensing, resistivity, semiconducting behavior.

## 1. Introduction:

Semiconducting metal oxides (SMOs) have been extensively investigated in recent decades for their potential applications in gas sensing due to their tunable electrical, optical, and structural characteristics [1, 2]. These materials exhibit changes in their electrical conductivity when exposed to various gaseous environments, which can be correlated with the concentration of specific gases. This property makes them ideal candidates for chemiresistive gas sensors, where sensitivity, selectivity, and stability are key performance parameters. The unique advantages of SMOs such as low fabrication cost, ease of miniaturization, and high chemical stability have made them indispensable materials in developing sensors for monitoring toxic, combustible, and hazardous gases in environmental, industrial, and domestic settings [2-4]. Among various metal oxides, nickel oxide (NiO) has emerged as one of the most promising p-type semiconducting materials for gas sensing applications due to its wide band gap energy (3.6–4.0 eV), superior thermal stability, excellent chemical robustness, and high sensitivity towards reducing gases such as liquefied petroleum gas (LPG), hydrogen ($H_2$), and carbon monoxide [4, 5].

Nickel oxide is a transition metal oxide that crystallizes in a rock-salt cubic structure (NaCl-type), in which each nickel ion is octahedrally coordinated by six oxygen ions. The non-stoichiometric nature of NiO, represented as $Ni_{1-x}O$, arises from the presence of nickel vacancies, which are responsible for its p-type electrical conductivity. These intrinsic defects act as acceptor states that generate holes as majority charge carriers [6]. The conduction mechanism in NiO is predominantly based on small-polaron hopping between $Ni^{2+}$ and $Ni^{3+}$ ions. The defect chemistry and electronic structure of NiO strongly influence its gas sensing properties. When exposed to air, oxygen molecules adsorb on the surface of NiO and capture electrons from the valence band to form negatively charged oxygen species ($O^-$, $O_2^-$, or $O^{2-}$) [6-8]. This process increases hole concentration near the surface, forming a hole accumulation layer (HAL). When a reducing gas such as LPG is introduced, it reacts with these adsorbed oxygen ions, releasing electrons that recombine with holes, thereby reducing the hole concentration and increasing the electrical resistance of the film. This reversible change in resistance forms the basis of NiO's gas sensing mechanism [8, 9]. The high reactivity of surface-adsorbed oxygen species, along with NiO's stability and controllable defect chemistry, make it a superior candidate for detecting reducing gases at relatively low operating temperatures [9, 10].

The demand for efficient gas sensors is continuously increasing due to growing concerns about safety and environmental monitoring. Liquefied petroleum gas (LPG), a common domestic and industrial fuel, is a highly flammable hydrocarbon mixture mainly consisting of propane and butane [11]. While LPG is valued for its clean combustion and high energy content, its accidental leakage poses severe safety hazards including fire, explosion, and suffocation risks [11, 12]. The detection of LPG leakage at low concentrations and with rapid response time is therefore of paramount importance for preventing catastrophic incidents. Conventional metal oxide sensors based on $SnO_2$, ZnO, or $TiO_2$ have shown high sensitivity towards LPG and other gases; however, they often require high operating temperatures (200–400°C), which lead to increased power consumption and reduced sensor lifespan. In contrast, NiO sensors exhibit good sensitivity even at lower operating temperatures (around 100°C), making them energy-efficient and suitable for compact sensor designs. The p-type nature of NiO also provides complementary selectivity to n-type oxides, making it ideal for use in heterojunction-based or composite sensing devices [11-14].

The fabrication method plays a crucial role in determining the morphology, crystallinity, porosity, and defect structure of NiO thin films, which directly influence their sensing behavior. Various physical and chemical deposition techniques have been developed to synthesize NiO thin films [15, 16], including sputtering, chemical vapor deposition (CVD), spray pyrolysis, pulsed laser deposition (PLD), chemical bath deposition, and sol–gel spin coating. Among these methods, the sol–gel spin coating technique has gained considerable attention due to its simplicity, low processing cost, excellent reproducibility, and precise control over film thickness and uniformity. In this method, a precursor solution or sol containing metal salts and complexing agents undergoes hydrolysis and condensation to form a gel-like network [16]. The sol is then deposited onto a substrate by spinning at high speed, allowing uniform film formation through centrifugal spreading. The resulting film is subsequently annealed to remove organic components and crystallize the NiO phase. The sol–gel spin coating process offers several advantages such as low-temperature synthesis, compositional homogeneity, and flexibility to incorporate dopants or composite materials, making it highly suitable for large-area thin film fabrication. The sol–gel spin coating technique offers several advantages over other film fabrication methods [17, 18]. It enables excellent stoichiometric control through solution chemistry, allows deposition over large substrate areas, and provides flexibility in tuning film thickness by adjusting the sol viscosity or spin speed. The technique also facilitates the incorporation of dopants or composite materials to modify film properties, such as conductivity and gas sensing behavior. In gas sensing applications, the electrical properties such as resistivity, temperature coefficient of resistance (TCR), and activation energy are also critical parameters that influence the sensor's operating efficiency and response time. A lower activation energy indicates facile charge carrier movement, resulting in improved gas sensing at lower temperatures [19-21].

The continuous research in this area has shown that the sensing performance of NiO thin films can be further improved through nanostructuring, surface modification, and doping with other metal cations such as cobalt, copper, or zinc. These modifications can alter the electronic structure, create additional active sites, and enhance catalytic activity, thus improving gas adsorption and charge transfer efficiency [15, 22]. Furthermore, the formation of heterojunctions between NiO and n-type oxides such as $SnO_2$, ZnO, or $In_2O_3$ can enhance the modulation of the depletion and accumulation layers, leading to improved sensitivity and selectivity [6, 13]. However, despite numerous advances, there is still a need to develop fabrication methods that are both simple and cost-effective while maintaining control over film uniformity and nanostructure. The present study focuses on the synthesis of NiO thin films using the sol–gel spin coating technique and their evaluation for LPG gas sensing applications. The research aim is to investigate the influence of electrical parameters on the gas sensing characteristics, including sensitivity, response time, and recovery time.

## 2. Experimental wok

### 2.1 Materials

All the chemicals used were of analytical grade. Nickel nitrate hexahydrate [Ni $(NO_3)_2.6H_2O$] served as the nickel source, and citric acid acted as the chelating agent. Double distilled water was used as solvent. Glass slides were used as substrates after thorough cleaning.

### 2.2 Synthesis and preparation of NiO thin films

The sol was prepared by dissolving nickel nitrate in double distilled water under continuous stirring, followed by the addition of citric acid in a stoichiometric ratio (1:1 molar ratio of metal to ligand). The obtained homogeneous green solution was stirred for 2 hours at 60°C to form a stable sol suitable for coating. The prepared sol was spin-coated on pre-cleaned glass substrates at 2000 rpm for 60 seconds. The coated films were pre-heated at 150°C for 10 minutes to remove organic residues and then annealed in air to obtain crystalline NiO films. The prepared films were used for further electrical and gas sensing characterizations [23-25].

## 3. Results and discussion

The electrical characterizations was carried out using half bridge method while the gas sensing study was conducted using static gas sensing system. The electrical characterizations were carried out on the basis of resistivity, TCR and activation energy. The resistivity, TCR and activation energy were estimated using Eqs. 1, 2 and 3 respectively [26, 27]. The thickness of films was estimated using mass difference method. The thickness of film was found to be 38 nm.

$$\rho = \left( \frac{R \times b \times t}{l} \right) \Omega - m \qquad (1)$$

Where,

ρ - Resistivity of prepared film, R- Resistance at normal temperature, b - Breadth of film,
t - Thickness of the film, L - Length of the film.

$$TCR = \frac{1}{R_o} \left( \frac{\Delta R}{\Delta T} \right) \; /^{o} C \qquad (2)$$

Where,

$\Delta R$ - Change in resistance, $\Delta T$ - Temperature difference, and $R_o$ - Initial resistance of the film.

$$\Delta E = \frac{log\, R}{log\ Ro} \times KT \qquad (3)$$

Where,

ΔE - Activation energy, R- Resistance at raised temperature, $R_0$ - Resistance at room temperature.

The variation of electrical resistance of NiO thin films with temperature, as shown in Fig. 1, reveals a typical semiconducting behavior where resistance decreases progressively with an increase in temperature. At lower temperatures, the NiO thin film exhibits high resistance in the order of $10^{10}$ Ω, which gradually decreases to approximately $10^9$ Ω as the temperature rises from 300°C to 600°C. This negative temperature coefficient of resistance (TCR) of –0.0022 $°C^{-1}$ confirms the p-type semiconducting nature of the NiO thin films [27, 28]. The observed decrease in resistance with increasing temperature is primarily attributed to the thermally activated transport of charge carriers. As temperature increases, more holes are thermally excited into the valence band, thereby enhancing conductivity and resulting in reduced resistance [25, 27].

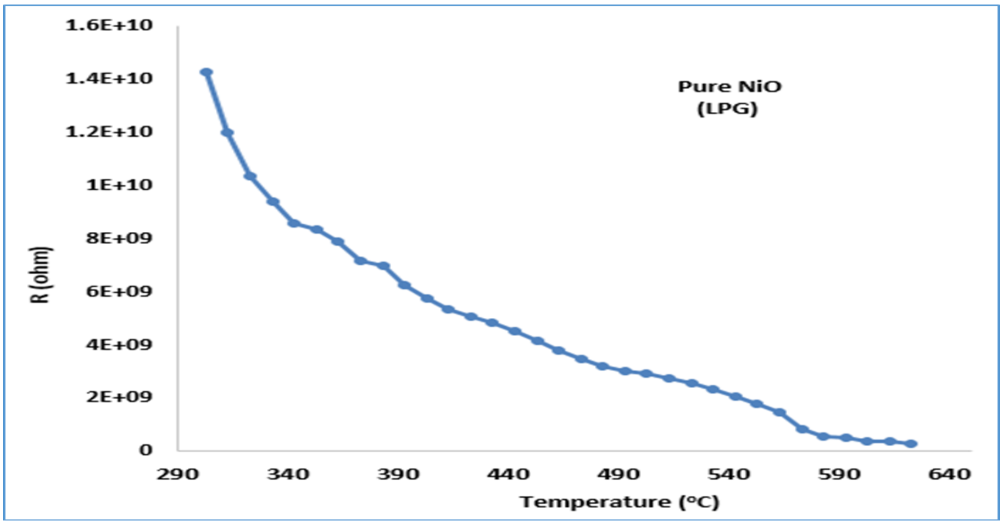

**Fig. 1.** Resistance versus temperature plot of NiO thin films

| Thin Film | Thickness (nm) | Resistivity (Ω.m) | TCR (/°C) | Activation Energy (eV) |
|---|---|---|---|---|
| NiO | 38 | 271.2 | -0.0022 | 0.11355 |

The main focus of this work is to study the sensitivity versus operating temperature of NiO thin films at selected concentrations of LPG such as 100, 200, 500 and 1000 ppm. Sensitivity (S) was calculated using Eq. 4.

$$S = (Ra - Rg) / Rg \times 100 \qquad (4)$$

Where, Ra and Rg are the resistances in air and in LPG respectively.

The response time is defined as the time required to reach 90% of the total resistance change after gas exposure, and the recovery time as the time taken to return to 90% of the baseline resistance after gas removal [28, 29]. The variation of gas sensitivity of the NiO thin films with operating temperature as shown in Fig. 2, demonstrates the influence of temperature and gas concentration on the LPG sensing performance. The sensitivity initially increases with temperature, reaches a maximum value, and then gradually decreases with further temperature rise, forming a characteristic bell-shaped response curve. Among the different concentrations of LPG tested (100, 200, 500, and 1000 ppm), the film exhibits the highest sensitivity of approximately 78.95% at 100°C for 500 ppm of LPG, indicating this as the optimum operating temperature [29, 30]. At lower temperatures (<50°C), the sensitivity remains low because the surface adsorption of oxygen species is limited and insufficient thermal energy is available to activate surface reactions between the adsorbed oxygen ions ($O^-$, $O_2^-$) and the reducing LPG molecules [25, 29].

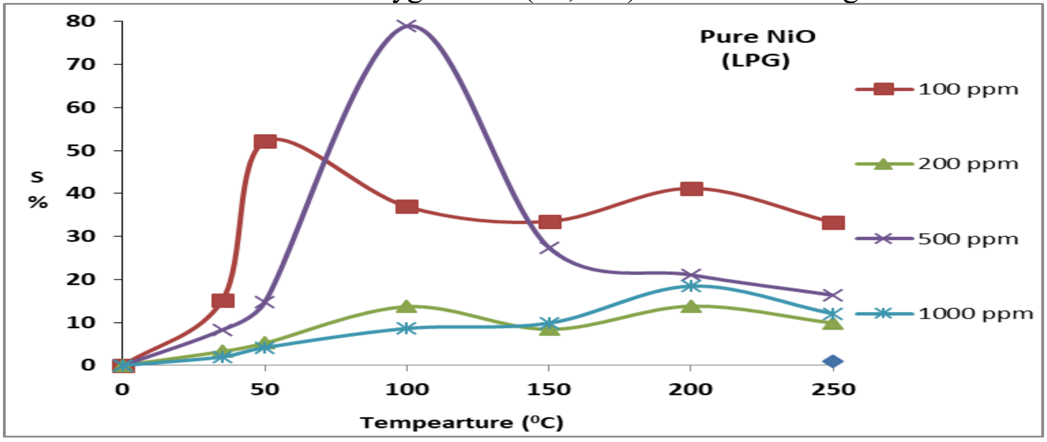

**Fig. 2.** Sensitivity versus operating temperature plot of NiO thin films

As the temperature increases, more oxygen molecules are ionized on the film surface, and the reaction rate between LPG molecules and these adsorbed oxygen species accelerates, leading to a pronounced change in film resistance and hence a rise in sensitivity. This enhanced response at moderate temperatures (around 100°C) could be attributed due to the effective interaction between gas molecules and chemisorbed oxygen species, which facilitates rapid electron exchange at the surface [3, 26]. Beyond this optimum temperature, sensitivity starts to decline because excessive thermal energy leads to desorption of oxygen species from the film surface, thereby reducing the number of active sites available for reaction. At higher temperatures (>150°C), the residence time of gas molecules on the sensor surface decreases, limiting the gas–solid interaction and consequently lowering the sensitivity [22, 25].

The dynamic behavior of the NiO thin film sensor toward LPG exposure is illustrated in Fig. 3, which shows the response and recovery characteristics of the film as a function of time. The plot demonstrates the temporal variation in sensor sensitivity (S%) when the gas is alternately introduced (ON time) and removed (OFF time) from the sensing chamber. Upon exposure to LPG, the sensor resistance changes rapidly due to chemical interactions between the gas molecules and the surface-adsorbed oxygen species, leading to a sharp rise in sensitivity [28, 29]. The response time, defined as the duration required to reach 90% of the total change in resistance after gas exposure, was measured to be approximately 18 seconds, indicating a fast response behavior of the NiO thin film sensor. This quick response could be attributed due to the high surface area and nanostructured morphology of the film, which provide abundant active sites for gas adsorption and facilitate rapid electron exchange during surface reactions.

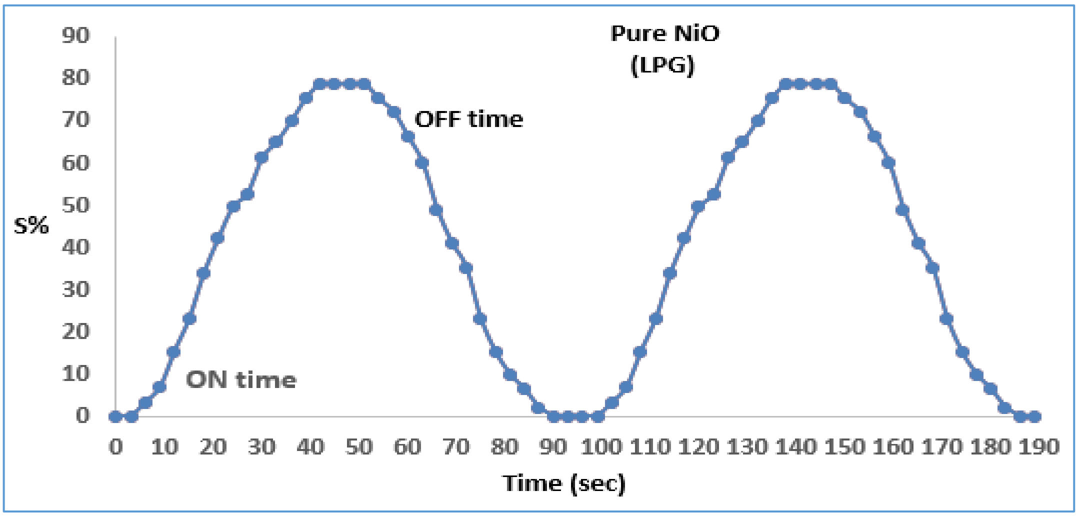

**Fig. 3.** Response and recovery plot of NiO thin films to LPG

When the gas supply is stopped, the sensor begins to recover its initial resistance as the adsorbed gas molecules desorb from the surface and oxygen species reoccupy the vacant sites. The recovery time, corresponding to the period required for the sensor to regain 90% of its baseline resistance, was found to be around 61 seconds. This relatively short recovery time signifies efficient desorption kinetics and stable surface reactivity of the NiO film. The reversible nature of the response and recovery cycles confirms the sensor's repeatability and stability during multiple gas exposure cycles [29, 30]. The nearly identical amplitude of the two response peaks in the plot further validates the reproducibility and durability of the sensing layer. The response and recovery behavior of the NiO thin film sensor reveals excellent dynamic sensing performance characterized by fast response (18 s), quick recovery (61 s), and stable cyclic behavior. These results demonstrate that the sol–gel spin-coated NiO thin films are highly effective for real-time LPG detection, combining fast operation with reliable reproducibility and stability attributes that are critical for practical gas sensing device applications [30, 31].

## Conclusions

The NiO thin films were successfully synthesized using the sol–gel spin coating technique. The fabricated films shows good semiconducting properties, including a resistivity of 271.2 Ω·m, a negative TCR of –0.0022 °C$^{-1}$, and a low activation energy of 0.11355 eV. The films exhibited typical p-type behavior, with resistance decreasing as temperature increased. Gas sensing studies demonstrated excellent LPG sensitivity, achieving a maximum response of 78.95% at 100°C for 500 ppm LPG. The sensor showed fast and reversible operation, with response and recovery times of 18 s and 61 s, respectively. The sensing mechanism was governed by surface redox interactions between adsorbed oxygen species and LPG molecules. The results confirm that sol–gel spin-coated NiO thin films are highly suitable for low-temperature, energy-efficient LPG sensing applications. Future improvements may be achieved through doping or forming composite/heterojunction structures to enhance selectivity and long-term stability.

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