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STUDY OF ELECTRICAL AND GAS SENSING PROPERTIES OF THERMALLY EVAPORATED NICKEL OXIDE THIN FILMS

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Abstract:

Thin films currently play an important role in the field of gas sensors. Thin films are changing the physical, electrical, structural, and gas sensing properties of the functional material. The current study explicates on the fabrication of NiO thin films by using thermal evaporation method and investigates their electrical and gas sensing properties. The films were fabricated on glass substrate. After fabrication, in a muffle furnace the films were annealed for 3 hours at 400°C. Resistivity, temperature coefficient ratio (TCR), and activation energy were used to investigate the electrical properties of fabricated NiO thin films. Gas sensing studies were carried out in the presence of NH_3, LPG, NO_2, and methanol in the surroundings of NiO thin films at various surrounding temperatures. The characteristics of sensitivity, selectivity, and response and recovery time were investigated. The maximum sensitivity was found to be NO_2 gas. The sensitivity was 82.65% at 100 ºC to NO_2 gas of concentration 200 PPM. The response and recovery time were found to be ~ 05 sec and ~ 13 sec respectively.

Keywords- *NiO, Thin films,*NO_2*, selectivity and reproducibility.*

I. INTRODUCTION:

Nano materials have been used in gas sensors for decades. The potential for employing nano materials with dimensions of less than 100 nm in a variety of applications is now being studied in a variety of fields [1]. The synthesis of the material is the first criterion in any new nanoparticle investigation. Many researchers used various approaches of synthesis like physical and chemical routes. These routes also contain different methods of synthesis [2]. Films are divided into two categories based on the thickness of the deposited material layer on the substrate: thick film and thin film. Thin films have a diameter of 50 nm to 300 nm; whereas thick films have a diameter of 15 µm to 80 µm [3, 4]. Thin films can be prepared using the physical vapor deposition process. It covers a number of vacuum deposition techniques. When using the physical vapor deposition process, the phase of the material changes from solid to vapor, then back to solid during the formation of the thin film, this is vapor condensation on the substrate. Glass or alumina can be utilized as a substrate. One of the most significant advantages of the physical deposition method is that no chemical process is required for the fabrication of thin films. The PVD process is quite convenient, and it may be used to make thin films out of a variety of materials. The nano structure of several metal oxide semiconductors can also be fabricated using this technology. Ion sputtering, thermal evaporation and arc discharge are the three types of PVD methods. PVD is used in a variety of fields, including mechanical item manufacture, optical, electrical, chemical coating, textile, firearms, and solar panels, medical, industrial, jewellery purposes, battery and fabrication of microelectronic devices [5-7].

Nickel oxide (NiO) is a prevalent p-type semiconductor with a 3.6–3.8 eV band gap. At ambient temperature, the p-type conductivity ranges from 10^{-4}–10^{-2} S cm^{-1}. Electrical conductivity is dependent on the concentration of Ni(III) centers that act as holes carriers, resulting in a wide spectrum of conductivities [8, 9]. Some of the observers also find out the band gap of NiO as 3.6 to 4 eV. NiO is a renowned semiconductor because of its many applications in photo catalysis, batteries, electro chromic displays, and gas sensing. NiO is also useful as a catalyst and ferromagnetic layers in aircraft low weight engineering structures, and alkaline battery cathode materials.CVD, CBD, RF sputtering; pulsed laser deposition, plasma deposition; electrochemical deposition, spray pyrolysis and the sol–gel method have all been used to make NiO thin films [10].

Nitrogen dioxide (NO_2) is oxidizing gas. It's a potential oxidizing agent that decomposes into nitrogen and oxygen when heated. The identification of NO_2 has sparked widespread worry because NO_2 is toxic to plants and living things' respiratory systems. Acid rain is one of the most serious environmental issues; nitrous dioxide and other types of nitrous oxide are the primary sources of acid rain in the atmosphere. Prompt industrialization results in the discharge of highly poisonous and flammable gases. The discharge of various polluting gases from industry is the primary source of air pollution. So, the building of an extremely effective NO_2 gas sensor is very essential [11, 12, 23].

The current research work focus on the fabrication of NiO thin films by using thermal evaporation method and studied electrical and gas sensing properties of fabricated NiO thin films.

II. EXPERIMENTAL WORK:

Fabrication of NiO thin films by thermal evaporated method:

Commercial nanocrystalline NiO nano powder (99.9% purity) was utilized as the functional material for fabrication of NiO thin films in this study. The thermal evaporated method was used to fabricate NiO thin films. A typical vacuum system was used, which was evacuated to 10-6 mbar using a rotary and diffusion pump setup. The chamber was vacuumed, and glass substrates were employed for deposition. The substrates were cleaned with acetone and an IR lamp before being placed into the deposition chamber. The substrates were exposed to an IR lamp for 30-35 minutes. After that, NiO powder was placed in tungsten filament using a suitable arrangement and a high voltage power source, which served as the evaporation target. The obtained thin films of NiO were annealed in a muffle furnace at 400°C and used for future research work.

Characterizations of fabricated NiO thin films:

Electrical characterizations of NiO thin films:

The following parameters were used in the electrical study:

- Resistivity
- TCR (thermal coefficient of resistance) and
- Activation energy at high and low temperatures

Equations 1, 2 and 3 were used to derive resistivity, temperature coefficient of resistance (TCR), and activation energy, respectively [13].

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

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.

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

Where,

ΔR = change in resistance between temperature T_1 and T_2,

ΔT = temperature difference between T_1 and T_2 and R_o = Initial resistance of the film sample

$$\Delta E = \frac{\log R}{\log Ro} \times KT \quad \text{---------------------------------(3)}$$

Where,

ΔE = Activation energy, R = Resistance at elevated temperature, R_0 = Resistance at 0°C.

Gas sensing study of NiO thin films:

With the use of a static gas sensing device, the properties of gas sensing were investigated. The sensing component was made of NiO thin films. The thin film's resistance was determined at different operating temperatures in an air atmosphere as well as in the presence of a gas of interest (at various ppm quantities). Ra denotes film resistance in air, while Rg denotes film resistance in a gaseous environment. Half-bridge method was used to determine the resistance of thin film. Figure 1 depicts a schematic design of the electrical and gas sensing static system that was employed in this study.

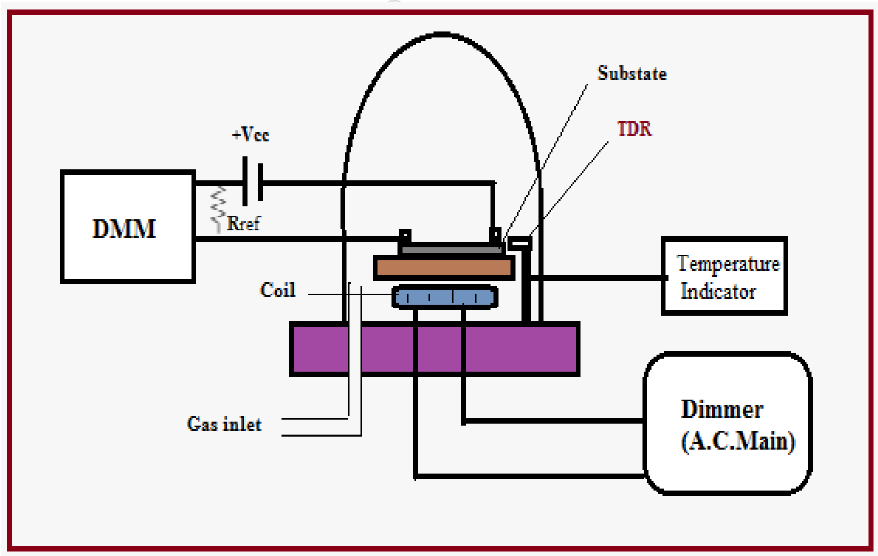

Figure 1 : Schematic diagram of electrical and gas sensing system.

Gas sensing experiments were conducted in a static gas system under standard controlledenvironments conditions. To determine the gas response (Sensitivity), the electrical resistance of thin films was measured in air (Ra) and in the presence of NO_2 gas (Rg) by using the equation 4 [15, 25].

$$S\% = \left| \frac{R_{air} - R_{gas}}{R_{air}} \right| \times 100 \text{ ----------------------------- } (4)$$

III. RESULT AND DISCUSSION:

Electrical Characterization:

Resistivity:

Different factors influence the film's resistivity, including the fabrication technique, system parameters, doping material, annealing temperature, and even monitoring conditions [16]. Equation 1 was used to compute the resistivity of the fabricated NiO thin films.

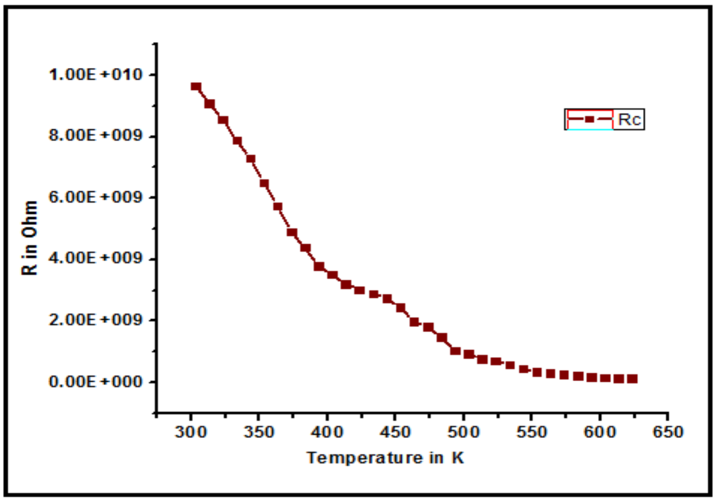

Figure 2 : Resistance v/s temperature of fabricated NiO thin films

Half bridge method was used to determine the DC resistance of NiO thin films as a function of temperature. The resistance of the film falls with temperature, and the drop in resistance with rising surrounding temperature indicates semiconductor behavior, as seen in the Figure 2. Semiconductor behavior of fabricated NiO thin films may possible due to the electrons receiving enough energy to penetrate the grain boundary barrier, lowering the thin film's effective resistance to a consistent level at high temperatures [14, 15]. The resistivity of NiO thin film was calculated 1.16009 Ω-m.

Activation energy:

From Figure, it has been observed that as temperature raises, the resistivity drops, which is the natural property of semiconductor materials with a negative thermal coefficient of resistance, whereas the densities of carriers increase [17]. In both heating and cooling cycles, the plot is reversible according to the Arrhenius equation the activation energy value of fabricated NiO thin films is found to be 0.172012 eV at lower temperature region (LTR) and 0.396223eV at higher temperature region (HTR).

Temperature coefficient of resistance (TCR):

The temperature coefficient of resistance (TCR) of NiO thin films was calculated using a DC electrical resistivity graph using equation 2. The temperature coefficient of resistance for NiO thin films is found to be -0.022016/ ^{0}C. TCR of NiO thin film was found to be negative shows semiconducting nature of the material [18].

Table-1: Electrical outcomes of fabricated NiO thin films

Resistivity (Ω-m)	TCR (/°C)	Activation energy (eV)	
		LTR	HTR
1.16009	-0.022016	0.172012	0.396223

Gas sensing study of fabricated NiO thin films:

Sensitivity:

The NH_3, NO_2, LPG, and methanol gases were exposed on the fabricated thin films of NiO with the use of a static system in order to evaluate the effects of thermally evaporated parameters on the gas sensing properties of NiO-based sensors, as seen in Figure 1. Among NH_3, NO_2, LPG, and methanol gases NO_2 shows more response to the fabricated NiO thin films. The different NO_2 gas-sensing tests were performed where gas was taken. The sensors were exposed to various NO_2 concentrations (100, 200, 300 and 400 ppm) and at various working temperatures (50, 100, 150, 200, and 250 ° C). While the working at constant temperature, followed by a recovery exposure period in dry air. Through the inlet, nitrogen dioxide was inserted into the gas sensor characterization system's testing chamber. The sensitivity of the sensors was determined by comparing the sample's resistance in the NO_2 gas atmosphere to its resistance in air. The sensitivity (S) values were determined using the equation 4.

Figure 4 depicts the NO_2 gas sensitivity as a function of operation temperature. Figure 3 illustrates that the gas response to NO_2 reaches its maximum response at a temperature at about 100 °C and the gas concentration was 200 ppm for thin films. Furthermore, the NiO-based sensors were fabricated under various thermally evaporated conditions using the thermal evaporation method.

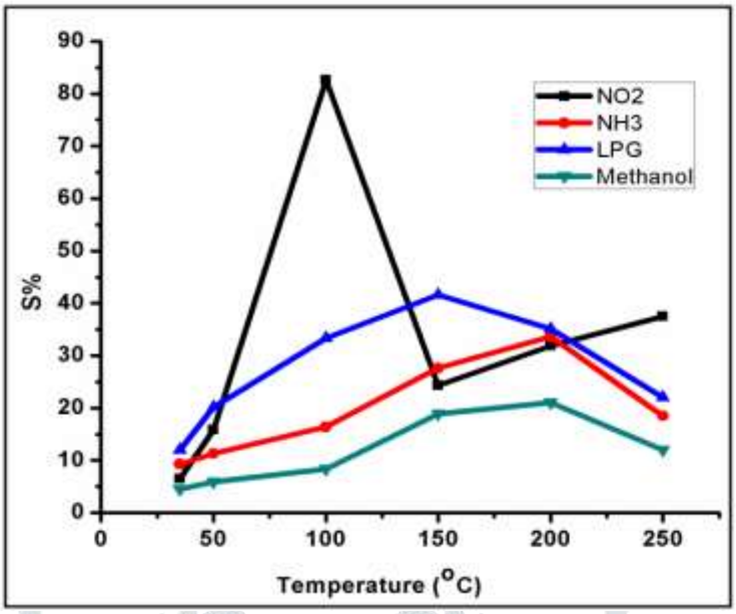

Figure 3 : Gas response vs. operating temperature of fabricated NiO thin films

Response and recovery time of fabricated NiO thin films:

The other two important qualities for a gas sensor are response time and recovery time, which are defined as the time required to reach 90% of the maximum response when gas is in and 10% when gas is out, respectively. Figure 4 depicts the fabricated NiO thin films sensor's response-recovery characteristic at its optimum operating temperature. The gas reaction grows significantly with gas in and returns to its previous state with gas out, as seen in the diagram [19, 24]. According to the definition above, the reaction and recovery time for NO_2 is approximately 05 and 13 seconds, as illustrated in Figure 4.

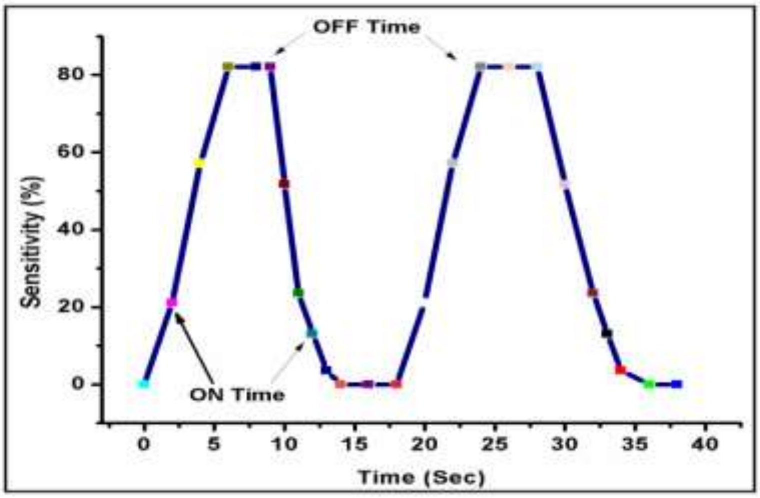

Figure 4 : Response and recovery time of fabricated NiO thin films for NO_2 gas.

Selectivity:

Selectivity refers to a sensor's ability to respond selectively to a group of analytes /gases, or even to a single analyte /gas. The Figure 5 shows the maximum selectivity to NO_2 gas. The selectivity of a sensor in respect to a certain gas is closely related to the temperature at which it operates. The selectivity of a target gas to some other gas is described as $K = Sx/Sy$, where Sx and Sy are the sensor's responses to a target gas X and an intrusion gas Y respectively.

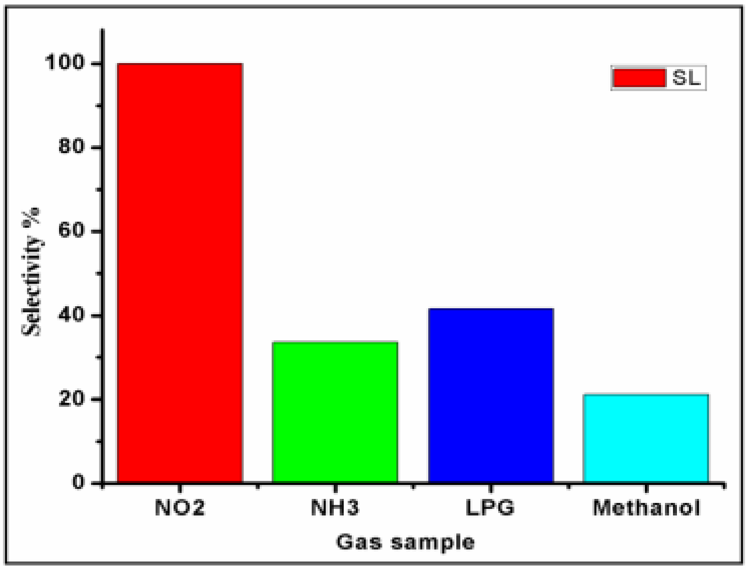

Figure 5: Selectivity of fabricated NiO thin films

NO_2 gas sensing mechanism of fabricated NiO thin films:

The NO_2 gas exhibits oxidizing properties, while NiO exhibits p type semiconducting behavior, with the bulk of carriers being holes. The electrons injected into the valence band recombine with holes, decreasing the amount of charge carriers and raising resistance. This research is taking place. When oxidizing gases are adsorbed on the surfaces of p-type semiconductors, however, their electrical conductivity increases. Adsorbed oxygen acts as a surface acceptor state in a p-type semiconducting oxide, trapping electrons from the valence band and raising the holes concentration [15, 25].The operating mechanism of NiO material is based on changes in electrical resistance generated by changes in unbound electron density as a result of analytic interactions between the analyte gas and the material's surface. The reaction of thin film surface to various gases is a surface-related phenomenon, and increasing the specific surface area of the functional oxide might improve the gas sensing effect [21, 22].The interaction between the sensor surface and the target gas molecules affects the sensitivity of MOS based sensors. Because of the larger surface area, there is greater interaction between the sensor surface and the adsorbed gases, resulting in increased gas sensitivity [26].

CONCLUSIONS:

NiO thin film could be prepared by physical vapor deposition technique on glass substrate.The fabricated NiO thin film was maximum sensitivity to NO_2gas at operating temperature 100^0C and gas concentration was at 200 ppm. Response and recovery time is also found very fast in seconds. The selectivity study showed that films were most selective to NO_2 against NH_3, LPG and Methanol. Nano form of NiO use as a NO_2 gas sensor fabrication as a sensing material.

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