Investigation of electrical and gas sensing properties of cobalt oxide thick films prepared by screen printing technique

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Abstract:
The current research work focused on the investigation of electrical and gas sensing properties of cobalt oxide thick films. Thick films were prepared on glass substrate by using conventional screen printing technique. The electrical properties were investigated by using resistivity, temperature coefficient resistance, and activation energy. The gas sensing properties were investigated using sensitivity, selectivity, ppm variation and reusability. The pure cobalt oxide (Co_3O_4) thick films exposed to ammonia (NH_3), LPG, Methanol and ethanol gases to find sensitivity and selectivity. The Co_3O_4 thick films show a maximum sensitivity to NH_3 gas as compared to other selected gases. The maximum sensitivity was found to be 68.13% to NH_3 gas at a concentration of 500 ppm and operating temperature was 200 °C. The Co_3O_4 thick films also show quick response (~9) and recovery time (~22) seconds.
Keywords- Cobalt oxide, thick films temperature coefficient resistance, sensitivity, ammonia.

1. INTRODUCTION:

Gas sensors use chemical and physical processes to turn gas into electrical signal output in order to determine the mixture and concentration of the gas. In the disciplines of flammable detection, explosive detection, poisonous and dangerous gas detection, and pollution monitoring, gas sensors are frequently utilized [1]. Gas sensors have been extensively used in several human-related disciplines. Because of their superior sensitivity, high selectivity, tunable dependability, low price, and other advantages, gas sensor materials have been receiving a lot of attention from scientific researchers. These materials were the primary aspects that affected the performances of different gas sensors. A promising technique to enhance the gas-sensing capabilities of a metal oxide semiconductor (MOS) was the development of nanostructures with a highly specific surface area [2]. MOS can have an electrical structure that is metallic, semiconductor, or insulator, and they have a broad range of physical and chemical characteristics as a consequence [2, 3]. Nanotechnology, a recently created technology built on the principles of quantum physics, material science, nanoelectronics, and computer engineering, is a method for creating advanced materials on the nanoscale [4].
Cobalt oxide (Co_3O_4) is a p-type semiconductor materials compound that is a mixed valence oxide of CoO and Co_2O_3 with a high oxygen concentration. The indirect band gap of Co_3O_4 is between 1.6 and 2.2 eV, making it a p-type semiconductor. P-type conductivity typically results from an oxygen level that is over stoichiometric in metal oxides [5]. Co_3O_4 has been extensively researched as a gas sensor material, as well as a super capacitors, catalysis, and electromagnetic device [5, 6]. Co_3O_4 has been synthesized by various techniques like CVD, RF sputtering, pulsed laser deposition, precipitation, electrochemical deposition, and physical vapour deposition method [7, 8]. Among them screen printing method is most suitable because of to its less expensive, low-temperature operating condition and freedom to deposit materials on a variety of substances [9, 10].
The current research work focus on the preparation of Co_3O_4 thick films by using screen printing technique and studied electrical, structural and gas sensing properties of Co_3O_4 thick films.

2. Experimental work

2.1 Preparation of thick films using screen-printing technique

Commercially available AR grade (99.99 % purity) Co_3O_4 powder was used for the preparation of films. Films were prepared on glass substrate. Initially, using acetone glass substrates were properly clean and then films placed under IR lamp. The 70-30 % ratio were used for organic and inorganic materials composition. In 70 % consist organic material (Co_3O_4) and 30% consist inorganic material (ethyl cellulose and BCA). Using mortar and pestle, thixotropic paste were made then prepared paste was used to deposit thick films on glass substrate using screen printing technique. The prepared thick films were kept under IR irradiation for 30 minutes to remove contamination. After, preparation of films, films were annealed at 400°C using muffle furnace for 2 hours. After that prepared films used for further research work.

2.2 Characterizations of Co_3O_4 thick film

2.2.1 Electrical characterizations:

The resistivity, TCR and activation energy at high and low temperature regions. The electrical properties of Co_3O_4 thick films were investigated using eequations 1, 2 and 3 for resistivity, TCR and activation energy respectively [12].

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

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.

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

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

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

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

2.2.2 Thickness measurement:

The thickness of Co_3O_4 films was determined by weight difference method using equation 4 [13].

$$t = \Delta m/\rho A \quad (4)$$

Where,
Δm is the difference in mass before and after deposition,
ρ = Density of the Co_3O_4, and
A= Area of the film.

3. RESULT AND DISCUSSION:

3.1 Electrical Properties:

3.1.1 Resistivity:

In MOS based sensors the resistivity of film is related to the concentrations of electron and hole as well as the mobility of charge carriers, these carriers plays very important role in gas sensing in another way we can say that resistivity plays vital role in the gas sensing mechanism of the film based sensors. The resistivity of the films may be change due to the doping, additives, annealing temperature and deposition technique of films.

The resistance (DC) of Co_3O_4 thick films was measured as a function of temperature using the half bridge method. In the temperature range of 30 to 350 °C, there is a downfall in resistance with increased surrounding temperature across the thick film of Co_3O_4 placed in electrical characterization system. The obtained plot shown in Figure 1, indicating semiconducting behaviour of Co_3O_4 thick films [11, 12]. The resistivity of films found to be 732.83 Ω-m.

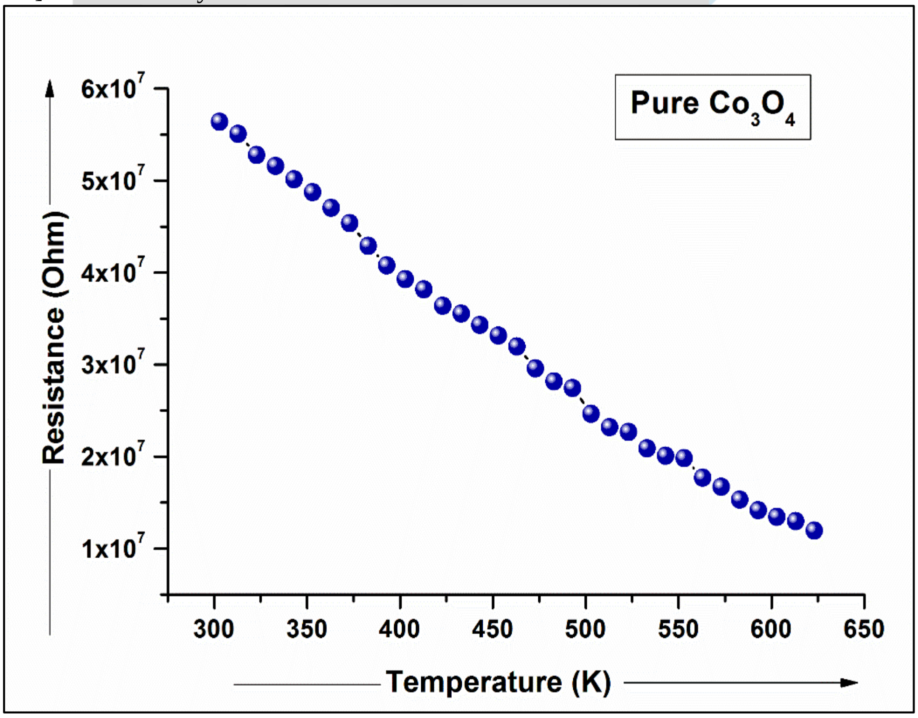

Figure 1 Resistance verses temperature plot of Co_3O_4 thick film

3.1.2 Temperature coefficient of resistance (TCR):

The temperature coefficient is important parameter in electrical characterization of thick as well as thin films. Temperature coefficient indicating the metallic or semiconducting properties of the films. If as surrounding temperature across the film is increased and the resistance of film increased its indicating positive temperature coefficient (PTC) and if resistance of film is decreased its indicating negative temperature coefficient (NTC). Basically negative sing of TCR indicating negative temperature coefficient nature of the film [13, 14]. In the present research work TCR for Co_3O_4 thick film was found to be -0.00241/°C.

3.3.3 Activation energy:

The activation energy is difference between two energy levels or in another term we can say that the amount of energy required to an electron migrate from valence band to conduction band. It is necessary to determine in case of semiconductor as well as MOS because the gas sensing mechanism is also based on this activation energy and forbidden energy gap. In this work activation energy is calculated on the principle Arrhenius equation [11, 15]. Figure 2 display the Arrhenius plot of log Rc vs. 1/T of Co_3O_4 thick film. The activation energy at higher temperature region was found to be 0.138752 eV and at lower temperature region was found to be 0.024554 eV.

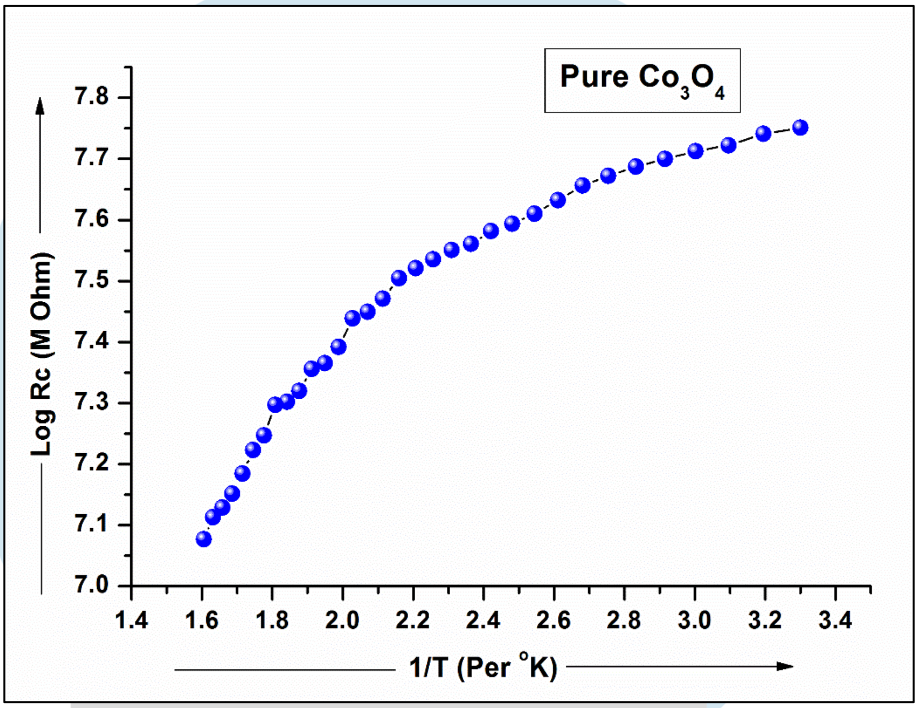

Figure 2 Log Rc vs. 1/T Arrhenius plot of Co_3O_4 thick film.

The thickness of Co_3O_4 thick film was calculated by using equation 4. The thickness of Co_3O_4 thick film was found to be 26 µm. All investigated electrical outcomes of Co_3O_4 thick film is tabulated in Table 1.

Table-1: Electrical outcomes of Co_3O_4 thick film.

Sample	Thickness (µm)	Resistivity (Ω-m)	TCR (/°C)	Activation Energy (eV)	
				HTR	LTR
Co_3O_4	26	732.83	-0.00241	0.138752	0.024554

3.2 Gas sensing properties of Co_3O_4 thick film:

The gas-sensing properties of Co_3O_4 thick film were investigated in this study using a static gas sensing system. The developed system was used to explore the selected gases such as ammonia (NH_3), Liquefied petroleum (LPG) Methanol and ethanol gases on the surface of Co_3O_4 thick film. The Co_3O_4 thick film has been used as a sensing element. At different operating temperatures, the resistance of Co_3O_4 thick film was measured in the surrounding conditions as well as in the presence of gas (at selected different ppm quantities).

3.2.1 Sensitivity

The sensitivity of gas sensor is calculated by the change in resistance of the film in absence of gas and in presence of gas [16, 17]. Figure 3 shows the sensitivity of Co_3O_4 thick film at various operating temperatures range (50, 100, 150, 200 and 250 °C).

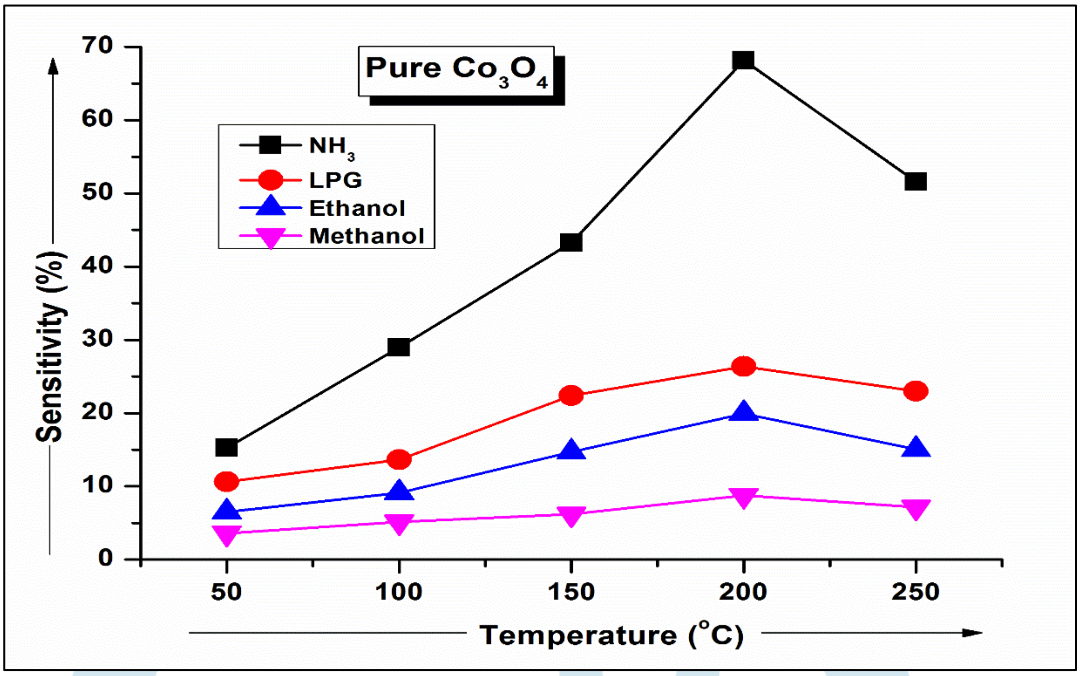

Figure 3 Sensitivity of Co_3O_4 thick film

The Co_3O_4 thick film shows maximum sensitivity to ammonia gas at operating temperature 200 °C and the ammonia gas concentration was 500 ppm. The maximum sensitivity to ammonia gas was found to be 68.13% as shown in figure 3. NH_3 gas shows maximum sensitivity as compared to other selected gases. From Figure 3, it is also observed that the Co_3O_4 thick film shows poor sensitivity to methanol gas. As operating temperature increased the sensitivity of the films also increased upto 200 °C then little sensitivity decreased it may be 200 °C is suitable operating temperature for NH_3 gas or it could be maximum gas and oxygen vacancies increased adsorption rate of reaction for gas sensing and hence sudden resistance of the film changes.

3.2.2 Selectivity

A key component of an effective gas sensor is its ability to differentiate between multiple target gases [17]. It was proven that a sensor's selectivity for a certain target gas can be measured at a specified operating temperature. Selectivity of the Co_3O_4 thick film shown in Figure 4.

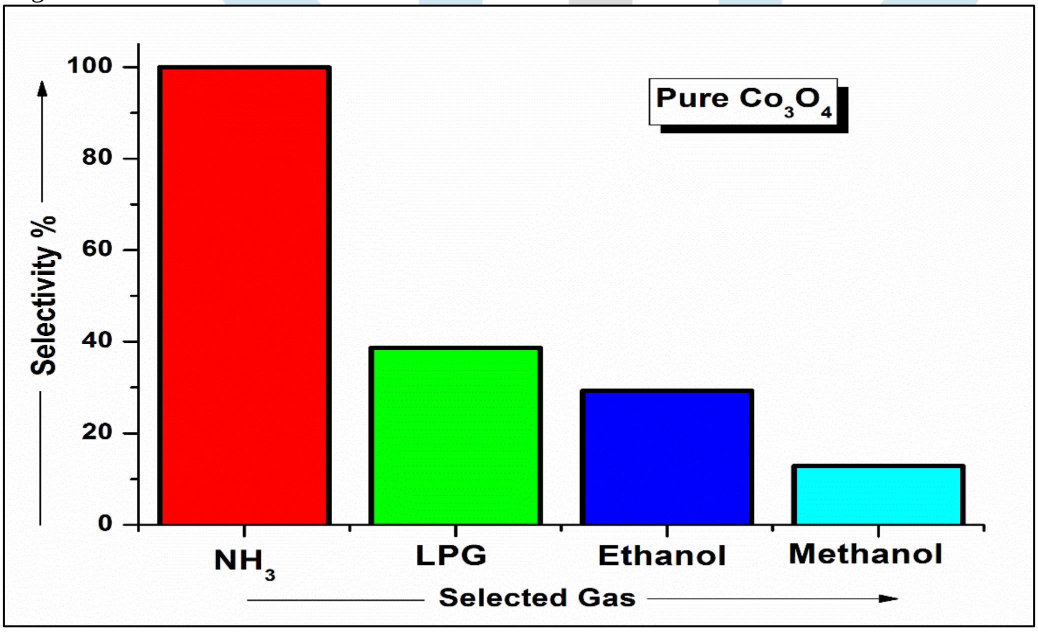

Figure 4 Selectivity of Co_3O_4 thick film at 200°C.

3.2.3 PPM variation:

The ammonia gas sensitivity were determined at different NH_3 gas concentrations (100, 200, 500 and 1000 ppm) using syringe (ml). Figure 5 reveals the maximum sensitivity found to be 500 NH_3 gas concentration among other selected.

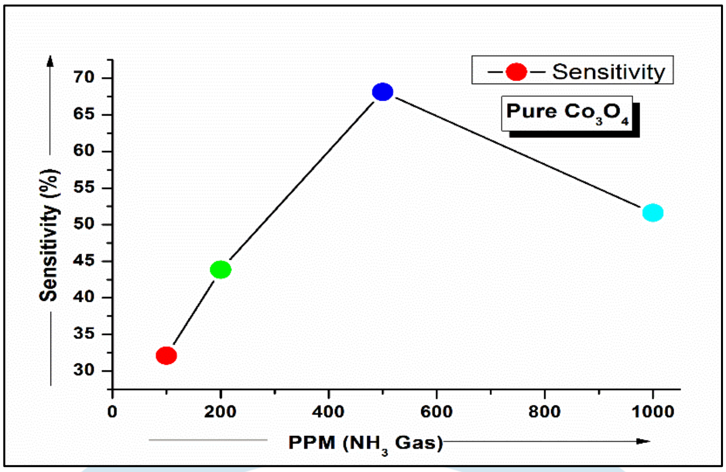

Figure 5 Sensitivity v/s ppm variation of NH3 gas at 200°C.

3.2.4 Response and recovery time of Co_3O_4 thick film:

The response and recovery time both are important parameters to determine for the performance of the any gas sensor. When gas is not explored in the static gas sensing system (chamber) the initially the resistance value of film the is near about constant (same) but after explored of gas in the chamber sudden resistance of the film changes in seconds that time is called as response time of films sensor and after some time the resistance of the film regret its initial resistance value called as recovery time of the film sensor [17, 18]. The response and recovery time of Co_3O_4 thick film is showed in Figure 6. The Co_3O_4 thick films shows quick response (~9) and recovery time (~22) in seconds to NH_3 at gas concentration was 500 ppm and operating temperature was 200 ºC.

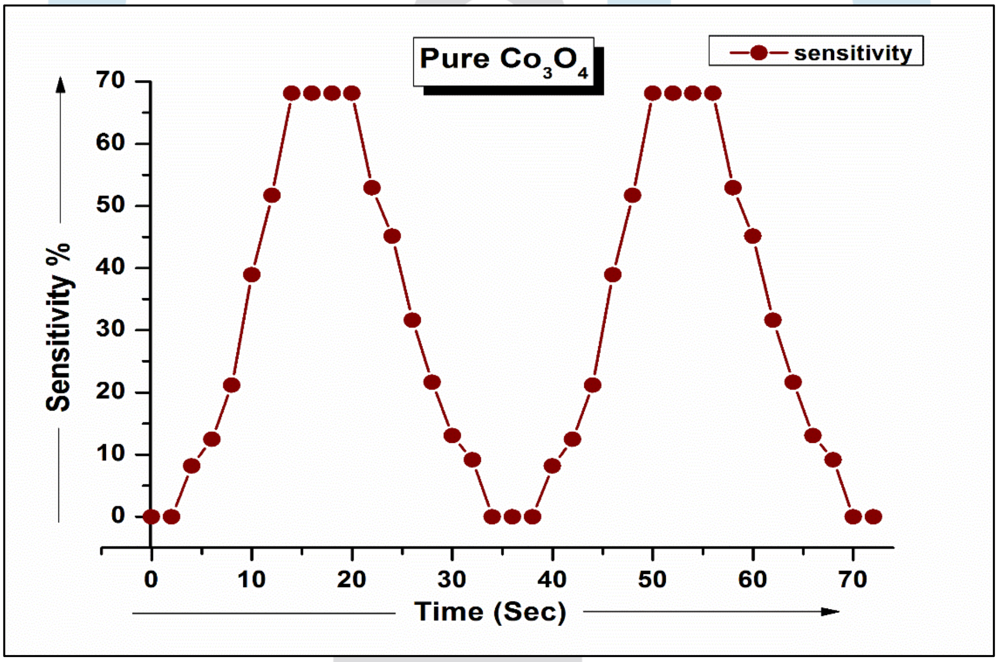

Figure 6 Response and recovery time of Co_3O_4 thick film for NH_3 gas.

3.2.5 Sensing mechanism Co_3O_4 thick films to NH_3 gas:

The kind of adsorbed that the sensor surface experienced had a significant impact on its ability to detect gases. Metal oxide base semiconducting materials may have different gas sensing adsorption processes depending on the amount of adsorption. Co_3O_4 is p-type semiconductor and p-type semiconductor has majority of holes (vacancies) and minority of electrons. Ammonia is reducing gas [18, 19]. When the surface of Co_3O_4 thick film is contact with reducing gas, leads to a decrease of the surface-trapped negative charges to produce a decreased electrical conductivity, hence the resistance of the Co_3O_4 thick film increased and film give good gas response in the form of sensitivity [19, 20].

Conclusions:

1. The Co_3O_4 thick films were successfully prepared by using screen-printing technique.
2. Temperature coefficient of resistance (TCR) is found to be negative.
3. Co_3O_4 thick films shows more sensitivity to ammonia gas.
4. Electrical and gas sensing properties successfully investigated in the current research work.

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References:

1. Zhou, Q., Zeng, W., Chen, W., Xu, L., Kumar, R. and Umar, A., 2019. High sensitive and low-concentration sulfur dioxide (SO2) gas sensor application of heterostructure NiO-ZnO nanodisks. Sensors and Actuators B: Chemical, 298, p.126870.
2. Guan, W., Tang, N., He, K., Hu, X., Li, M. and Li, K., 2020. Gas-sensing performances of metal oxide nanostructures for detecting dissolved gases: a mini review. Frontiers in chemistry, 8, p.76.
3. Godse, P., Sakhare, R., Pawar, S., Chougule, M., Sen, S., Joshi, P. and Patil, V.P., 2011. Effect of annealing on structural, morphological, electrical and optical studies of nickel oxide thin films. Journal of Surface Engineered Materials and Advanced Technology, 1(02), p.35.
4. Ge, L., Mu, X., Tian, G., Huang, Q., Ahmed, J. and Hu, Z., 2019. Current applications of gas sensor based on 2-D nanomaterial: A mini review. Frontiers in Chemistry, 7, p.839.
5. Xu, J.M. and Cheng, J.P., 2016. The advances of Co3O4 as gas sensing materials: A review. Journal of Alloys and Compounds, 686, pp.753-768.
6. Kim, H.J. and Lee, J.H., 2014. Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview. Sensors and Actuators B: Chemical, 192, pp.607-627.
7. Iravani, S. and Varma, R.S., 2020. Sustainable synthesis of cobalt and cobalt oxide nanoparticles and their catalytic and biomedical applications. Green Chemistry, 22(9), pp.2643-2661.
8. Wang, T., Ren, K., He, M., Dong, W., Xiao, W., Pan, H., Yang, J., Yang, Y., Liu, P., Cao, Z. and Ma, X., 2020. Synthesis and manipulation of single-crystalline lithium nickel manganese cobalt oxide cathodes: a review of growth mechanism. Frontiers in Chemistry, 8, p.747.
9. Li, M., Li, Y.T., Li, D.W. and Long, Y.T., 2012. Recent developments and applications of screen-printed electrodes in environmental assays—A review. Analytica chimica acta, 734, pp.31-44.
10. White, N., 2017. Thick films. Springer Handbook of Electronic and Photonic Materials, pp.1-1.
11. Tupe, U.J., Zambare, M.S., Patil, A.V. and Koli, P.B., 2020. The Binary Oxide NiO-CuO Nanocomposite Based Thick Film Sensor for the Acute Detection of Hydrogen Sulphide Gas Vapours. Material Science Research India, 17(3), pp.260-269.
12. Tupe, U.J., Patil, A.V., Zambare, M.S. and Koli, P.B., 2021. Stannous Oxide Thick Film Nanosensors Design by Screen Printing Technology: Structural, Electrical Parameters and H 2 S Gas Detection Study. Material Science, (1), pp.66-74.
13. Patil, A., Dighavkar, C. and Borse, R., 2011. Al doped ZnO thick films as CO2 gas sensors. Journal of Optoelectronics and Advanced Materials, 13(October 2011), pp.1331-1337.
14. Shinde, R.S., Khairnar, S.D., Patil, M.R., Adole, V.A., Koli, P.B., Deshmane, V.V., Halwar, D.K., Shinde, R.A., Pawar, T.B., Jagdale, B.S. and Patil, A.V., 2022. Synthesis and characterization of ZnO/CuO nanocomposites as an effective photocatalyst and gas sensor for environmental remediation. Journal of Inorganic and Organometallic Polymers and Materials, 32(3), pp.1045-1066.
15. Mohan, P.A. and Jayaraj, M.K., 2020. Metal Oxide Semiconductor Gas Sensors. In Nanostructured Metal Oxides and Devices (pp. 211-232). Springer, Singapore.
16. Subha, P.P., Mohan, P.A. and Jayaraj, M.K., 2020. Metal Oxide Semiconductor Gas Sensors. Nanostructured Metal Oxides and Devices: Optical and Electrical Properties, p.211.
17. Lad, U.D., Kokode, N.S. and Tupe, U.J., 2022. Study of pn Heterojunction Thin Films for Reducing Gas Sensing Application Fabricated by Thermal Evaporation Technique. In Advanced Materials Research (Vol. 1172, pp. 67-82). Trans Tech Publications Ltd.
18. Koli, P.B., Kapadnis, K.H. and Deshpande, U.G., 2019. Nanocrystalline-modified nickel ferrite films: an effective sensor for industrial and environmental gas pollutant detection. Journal of Nanostructure in Chemistry, 9(2), pp.95-110.
19. Shinde, V.S., Kapadnis, K.H., Sawant, C.P., Koli, P.B. and Patil, R.P., 2020. Screen print fabricated In3+ decorated perovskite lanthanum chromium oxide (LaCrO3) thick film sensors for selective detection of volatile petrol vapors. Journal of Inorganic and Organometallic Polymers and Materials, 30(12), pp.5118-5132.
20. Vetter, S., Haffer, S., Wagner, T. and Tiemann, M., 2015. Nanostructured Co3O4 as a CO gas sensor: temperature-dependent behavior. Sensors and Actuators B: Chemical, 206, pp.133-138.