Study of Electrical and Gas Sensing Properties of as Deposited Niobium Pentoxide (Nb_2O_5) Thick Films Fabricated by Screen Printing Method

Bhushan S. Pardeshi [1], Vasant G. Wagh [2], Arun V. Patil [3]

[1] Assistant Professor, Department of Electronic Science, K.A.A.N.M.S. Arts, Commerce and Science College, Satana, Nashik
[1] Department of Electronic Science and Research Centre, Loknete Vyankatrao Hiray Arts, Science and Commerce College, Panchavati
[2] Head of Department Physics, K.V.N. Naik College, Nashik
[3] Department of Physics, MGV's, Arts, Science and Commerce College, Manmad, Nashik

[1, 2, 3] Maharashtra, India

***Abstract*: Air pollution is the major issue in the world. Due to globalization of world, in the daily life human beings facing various types of problems as well as suffer from health issues. Hence there is need to develop gas sensors. The current research work dedicated on gas sensing and electrical properties of as deposited (un-annealed) niobium oxide thick films. Because of unique properties of niobium pentoxide (Nb_2O_5) like electrical, chemical and physical, it has been reported as a notable gas detection material. Thick films were fabricated using standard screen printing method. The glass substrates were used to fabricate films. The electrical properties of as deposited Nb_2O_5 thick film were study by resistivity, temperature coefficient resistance (TCR), and activation energy at high and low temperature region. The thickness, resistivity and TCR of thick film were found to be 38 µm, 2511.42 Ω-m and -0.0022434 /°C respectively. The gas sensing properties were investigated using sensitivity, selectivity, ppm variation, response time and recovery time of the films. The fabricated Nb_2O_5 thick films exposed to NH_3, CO_2, NO_2 and ethanol gases to determine sensitivity. The Nb_2O_5 thick films show a maximum sensitivity to NO_2 gas as compared to other targeted gases. The maximum sensitivity was found to be 62.03% to NO_2 gas at a concentration of 500 ppm and operating temperature was 200 °C. The films also show rapid response (~12) and recovery time (~34) seconds.**

Keywords: Niobium pentoxide, sensitivity, oxidizing gas, pollution.

1. INTRODUCTION:

Niobium pentoxide (Nb_2O_5) is n-type semiconductor oxide. Niobium (V) oxide (Nb_2O_5) which owns a high dielectric constant (200), high refractive index (2.4), and it has wide band gap of 3.2–4.0 eV. Nb_2O_5 can be used in various applications such as; gas sensor, capacitor dielectrics, biomedical, solar cells, catalysts, batteries, energy storage devices and optical sensor. Nb_2O_5 also used as a substitute to the traditional gate dielectric of SiO_2. Nb_2O_5 itself is a semiconductor which has exceptional field-switching qualities [1].

For semiconducting gas sensors, Nb_2O_5 has the potential to be a great material. The physical and chemical characteristics of this material could be advantageously tuned at different stoichiometries to generate significant sensitivity to specific target gas species. High surface to volume ratios, sufficient surface energies, and ideal spacing are all traits of highly organized nanostructured structures that allow interactions with multiple target gas molecules. In order to use the Nb_2O_5 in gas sensors, this has been studied. As a result of Nb_2O_5's high surface-to-volume ratios and quantum confinement effects, unique physical and chemical interactions can occur at the surface [3, 4].

Depending on whether the gas type is reducing or oxidizing, the interface of the types of gas molecules with the Nb_2O_5 films changes the amount of charge carriers and the depletion layer of the Nb_2O_5 films. These affect the films' physical and chemical properties in relation to the gas molecules that are exposed to the sensor. The sensing mechanism of this material is based on the reversible changing of electrical conductance in the presence of oxidizing or reducing gases [5, 6].

According to literature review, the thin films of Nb_2O_5 is prepared by different chemical and physical method such as physical vapour deposition, laser ablation, spray pyrolysis, spin coating technique and others. The thick films of Nb_2O_5 is prepared by screen printing technology [7].

The current research work emphasis on the fabrication of Nb_2O_5 thick films by using screen printing technique and studied electrical and gas sensing properties of as deposited Nb_2O_5 thick film.

2. Experimental work

2.1 Preparation of thick films using screen-printing technique

Commercially available AR grade (99.99 % purity) Nb_2O_5 powder was used for the fabrication of films. Glass substrates were clean using acetone. The organic and inorganic materials composition 70-30 % ratio was used. Thixotropic paste of Nb_2O_5 powder was made using BCA, EC, mortar and pestle. Screen printing set up was used to fabricate films on glass substrate. The fabricated thick films were kept under IR irradiation for 20 minutes to remove contamination. After that prepared films used for further research work. Figure 1 shows the flowchart of experimental work.

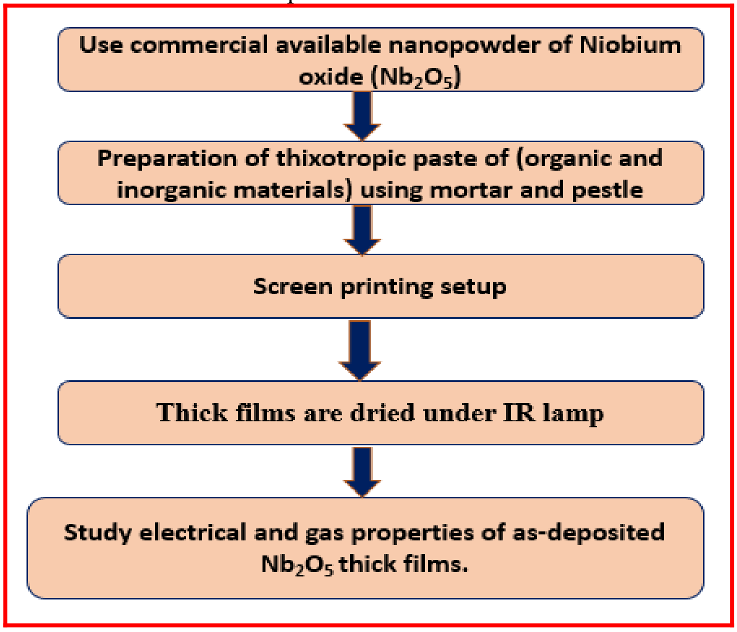

Figure 1: Flowchart of experimental work

2.2 Characterizations of as deposited Nb_2O_5 thick film

The electrical characterizations were carried out on the basis of resistivity, TCR and activation energy at high and low temperature regions. The electrical properties of as deposited Nb_2O_5 thick film were investigated using eequations 1, 2 and 3 for resistivity, TCR and activation energy respectively at higher and lower temperature regions [8-10].

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

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, ΔT = temperature difference, and R_o = Initial resistance of the film.

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

Where, ΔE = Activation energy, R = Resistance at raised temperature, R_0 = Resistance at room temperature.
The thickness of as deposited Nb_2O_5 thick film was determined by mass difference method using equation 4 [9].

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

Where, Δm is the difference in mass before and after deposition, ρ = Density of the Nb_2O_5, and A= Area (l x b) of the film.
The sensitivity and selectivity of the films were determined by equation 5 and 6 respectively.

$$\text{Sensitivity (\%)} = \frac{\Delta R}{R_{air}} = \left| \frac{R_{air} - R_{gas}}{R_{air}} \right| \text{ X } 100 \quad (5)$$

$$\text{\% Selectivity} = \left(\frac{S_{Target\ Gas}}{S_{Other\ Gas}} \right) x\ 100 \quad (6)$$

3. RESULT AND DISCUSSION:

3.1 Electrical Properties:

The Figure 2, indicating as temperature increases the resistance of the film decreases from 1.4×10^8 to 2.0×10^7. The decrease in resistance with raised temperature indicating the semiconducting behaviour of as deposited Nb_2O_5 thick film [8, 9]. The resistivity of films found to be 2511.42 Ω-m.

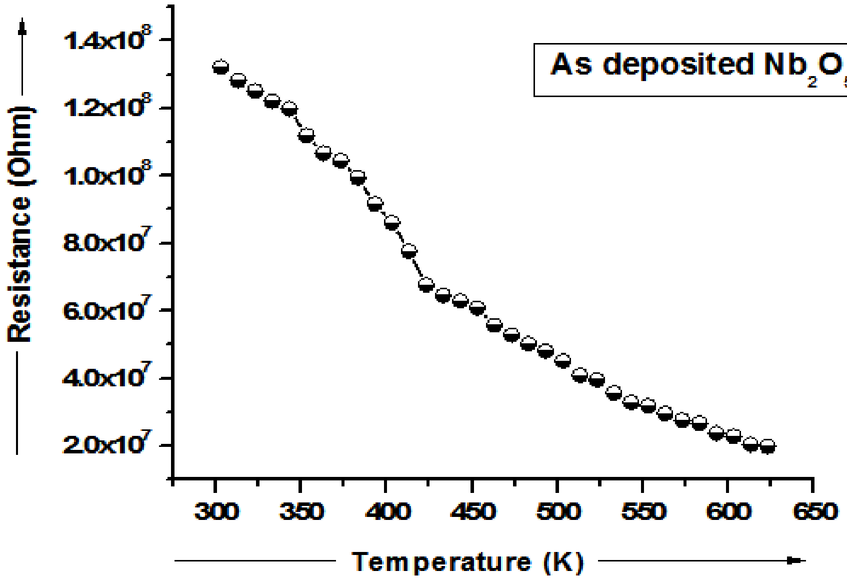

Figure 2: Resistance verses temperature plot of as deposited Nb_2O_5 thick film

The sample shows little nonlinear variations in the resistance versus temperature plot in figure 1, it may be due to films are not annealed at particular temperature. TCR for as deposited Nb_2O_5 thick film was found to be -0.0022434/°C. The negative sing indicating the negative temperature coefficient of as deposited Nb_2O_5 thick film. On the basis of obtained value of TCR, films shows semiconducting behavior because metal has positive temperature coefficient.

The difference between two energy levels, also known as the activation energy, seems to be what causes an electron to move from the valence band to the conduction band. Due to the fact that the gas sensing mechanism also relies on this activation energy and forbidden energy gap, it is important to establish this in the case of semiconductors and MOS. The Arrhenius equation is used in this work to estimate activation energy [10, 11]. Figure 3 illustrates the Arrhenius plot of as deposited Nb_2O_5 thick film. At higher temperatures, the activation energy was found to be 0.146045 eV, whereas at lower temperatures, it was found to be 0.0205551 eV.

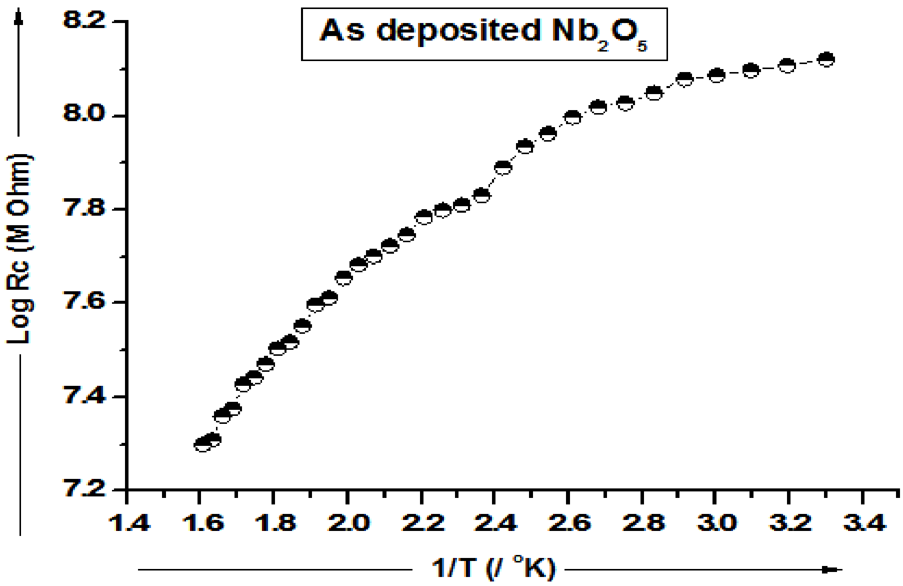

Figure 3: Log Rc vs. 1/T plot of as deposited Nb_2O_5 thick film

The film thickness is very important parameter for gas sensor. The thickness of the film changes the resistivity as well as TCR of films or any material. The thickness of as deposited Nb_2O_5 thick film was calculated by using equation 4. The thickness of film was found to be 38 µm. All studied electrical outcomes of as deposited Nb_2O_5 thick film are tabulated in Table 1.

Table-1: Electrical outcomes of as deposited Nb_2O_5 thick film.

Sample	Thickness (µm)	Resistivity (Ω-m)	TCR (/°C)	Activation Energy (eV)	
				Higher temperature region	Lower temperature region
Nb_2O_5	38	2511.42	-0.0022434	0.146045	0.020551

3.2 Gas sensing properties of as deposited Nb_2O_5 thick film:
The gas-sensing properties of as deposited Nb_2O_5 thick film were studied using a static gas sensing apparatus. The selected gases (NH_3, CO_2, NO_2 and ethanol) were explored on the surface of as deposited Nb_2O_5 thick film. At different operating temperatures (50,100,150, 200, and 250 °C) the sensitivity of film was tested.

3.2.1 Sensitivity
The change in resistance of films after and before exposing of gas was measured in the ambient conditions. Equation 5 is used to determine sensitivity [10]. Figure 4 displays the sensitivity of Nb_2O_5 thick film at various operating temperatures range (50, 100, 150, 200 and 250 °C).

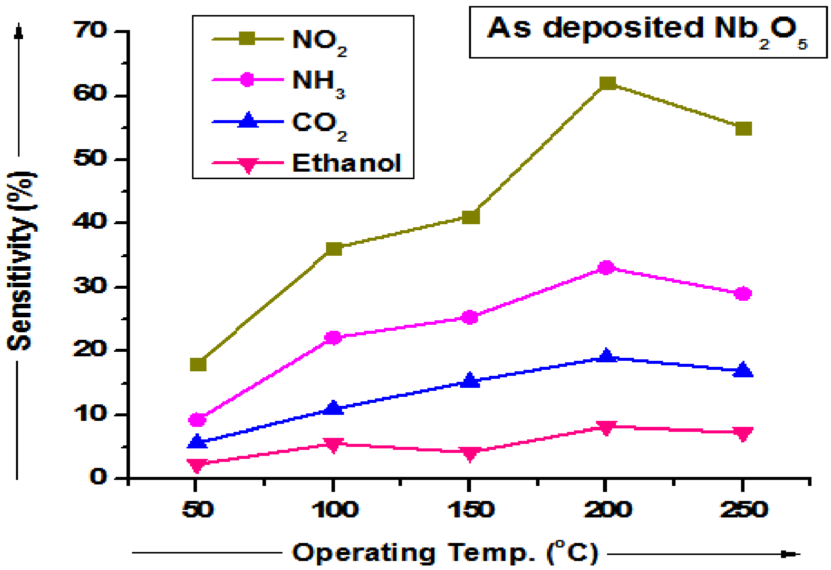

Figure 4: Sensitivity of as deposited Nb_2O_5 thick film.

The as deposited Nb_2O_5 thick film shows maximum sensitivity to NO_2 gas at operating temperature 200 °C and the gas concentration was 500 ppm. From Figure 4, it is also observed that the Nb_2O_5 thick film shows poor gas response to ethanol gas. It is also observed that the sensitivity of the films decreased at higher temperature at 250 °C to all selected gases. It may be due to the require oxygen vacancies presence maximum at 200 °C for gas sensing adsorption process and at 200 °C temperature it may be low. The response could be attributed to the adsorption – desorption type of sensing mechanism [10-12].

3.2.2 Selectivity: A gas sensor's selectivity refers to the material's preference for chemiresistive detection of one gas over another when two or more gases are present and the similar working circumstances. Selectivity of the as deposited Nb_2O_5 thick film shown in Figure 5. NO_2 gas shows maximum selectivity, while ethanol gas shows poor selectivity.

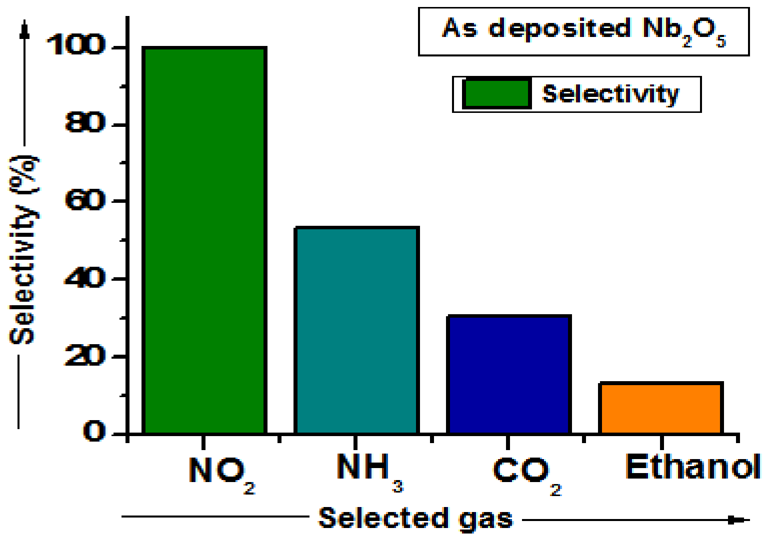

Figure 5: Selectivity of as deposited Nb_2O_5 thick film at 200°C.

3.2.3 PPM variation:

The as deposited Nb_2O_5 thick film shows more sensitivity to NO_2 gas hence in this work the sensitivity of Nb_2O_5 thick films were determined at different NO_2 gas ppm concentrations as shown in figure 6. Figure 6, it was observed that as NO_2 gas ppm concentration increases the sensitivity of the as deposited Nb_2O_5 thick film also increases.

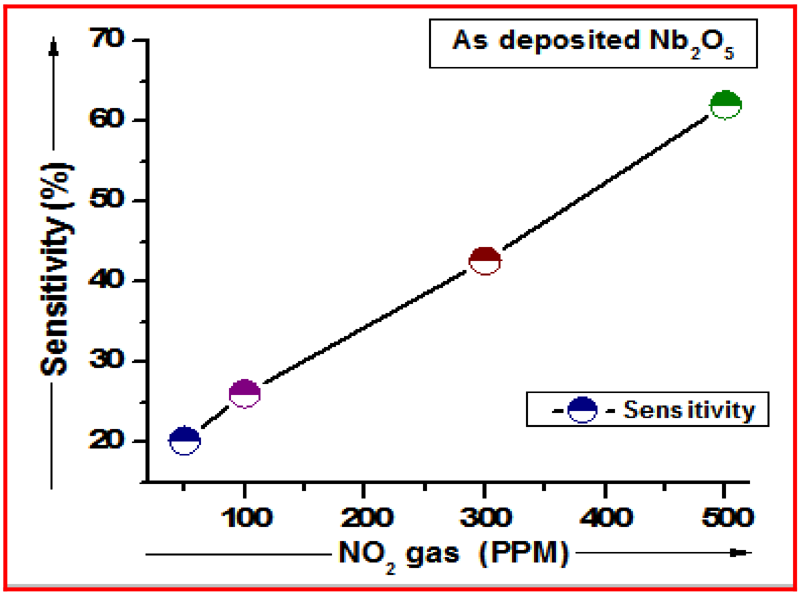

Figure 6: Sensitivity v/s ppm variation of NH3 gas at 200°C.

3.2.4 Response and recovery time of Nb_2O_5 thick film:

When a gas sensor is exposed to a target gas, response time refers to the amount of time it takes from the initial reaction to the stable end value once the signal has attained a specific percentage level. The sensing capabilities of the sensor are improved with a decreased response time. For target gas concentrations that are higher, the response time is quick. Because they could require a longer response time, hazardous gases at low concentrations should be monitored carefully [12, 13]. The amount of time a sensor needs to take to restore 90% of the baseline signal once the target gas has been evacuated and the sensor has been wiped with dry air. In order to use the sensor again, good sensor applications require for a sensor recovery time that is modest [13]. The response and recovery time of Nb_2O_5 thick film is showed in Figure 7. The Nb_2O_5 thick films shows fast response (~12) and recovery time (~34) in seconds to NO_2 at gas concentration was 500 ppm and operating temperature was 200 ºC.

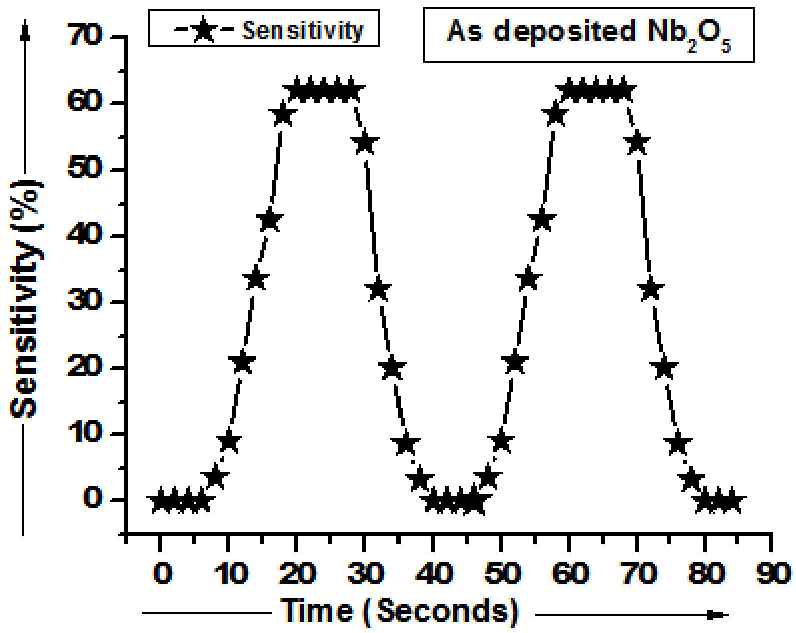

Figure 7: Response and recovery time of as deposited Nb_2O_5 thick film for NO_2 gas.

3.2.5 Sensing mechanism of as deposited Nb_2O_5 thick film to NO_2 gas:

The operating temperature for Nb_2O_5 based gas sensors and the amount of the molecules of NO_2 have been found to be directly correlated in the existing literature. According to the need for activation energy, there is a predictable initial rise in the extent of adsorption as the species are chemisorbed on the surface of Nb_2O_5 nanoparticles. However, at relatively high working temperatures, desorption of the analyte gas occurs, and the sensor response declines. Additionally, as operational temperature rises, O_2 adsorption becomes the main process, which significantly reduces Nb_2O_5 sensor responsiveness. The sensor's response showed a linear relationship with NO_2 molecules at the ideal operating temperature. The gas with the major influence in these reactions is NO_2 molecules, which is the target gas in this work. For this process, high temperatures (200 ºC) are usually needed for adsorption process [13, 15].

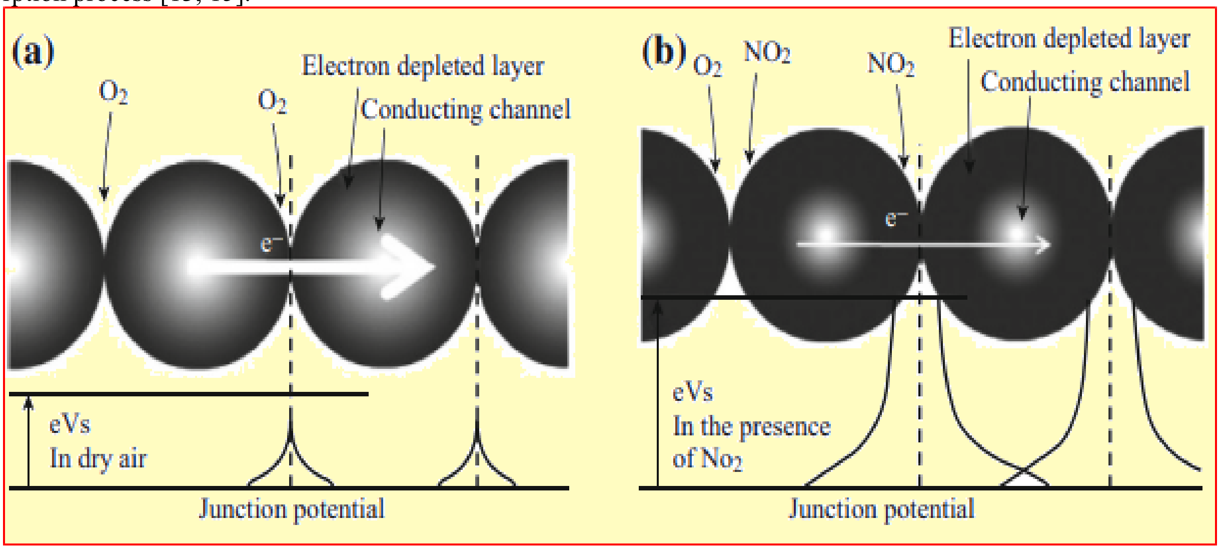

Figure 8: Schematic diagrams a) potential of Nb_2O_5 sensor with presence of air and b) potential of Nb_2O_5 sensor with presence of NO_2 gas.

Figures 8 a and b shows the schematic diagrams of shows potential of Nb_2O_5 sensor with presence of air and potential of Nb_2O_5 sensor with presence of NO_2 gas respectively. Both grain-boundary and neck interactions are thought to be essential forms of interactions. Regarding the connections between grain boundaries, the electrons cross the surface potential barrier for each border. As a result, the barrier height is varied, which also affects the sensor material's electric resistance. Nevertheless, the electrical resistance and operating temperature of the films affect the resistance and the gas response [13, 16].

Conclusions:

The Nb_2O_5 thick films were successfully fabricated by screen printing method. Temperature coefficient of resistance (TCR) is found to be negative. Activation energy was found to be high at high temperature region and low at lower temperature region.

Nb_2O_5 thick films shows more sensitivity to NO_2 gas. Electrical and gas sensing properties successfully investigated in the current research work.

Acknowledgment:
The authors thanks to Research Centre in Electronic Science, L. V. H. College Panchavati, Nashik, India, for providing laboratory facilities.

References:

1. Emeka, N.C., Imoisili, P.E. and Jen, T.C., 2020. Preparation and Characterization of Nb x O y Thin Films: A Review. *Coatings*, *10*(12), p.1246.
2. Graça, M.P.F., Saraiva, M., Freire, F.N.A., Valente, M.A. and Costa, L.C., 2015. Electrical analysis of niobium oxide thin films. *Thin Solid Films*, *585*, pp.95-99.
3. Zappa, D., Galstyan, V., Kaur, N., Arachchige, H.M.M., Sisman, O. and Comini, E., 2018. "Metal oxide-based heterostructures for gas sensors"-A review. *Analytica Chimica Acta*, *1039*, pp.1-23.
4. Lelevic, B., N. Fuschillo, and N. K. Annamalai. "Nonlinear high-field conductivity in Nb2O5 thin films." *Thin Solid Films* 23.2 (1974): 249-256.
5. Rosenfeld, Daniel. *Propriétés structurales et électriques de couches minces de Nb2O5 liées au fonctionnement d'un capteur d'oxygène*. No. THESIS. EPFL, 1995.
6. Greener, E. H., D. H. Whitmore, and M. E. Fine. "Electrical Conductivity of Near-Stoichiometric α-Nb2O5." *The Journal of Chemical Physics* 34.3 (1961): 1017-1023.
7. Pardeshi, B., Wagh, V., Patil A., "Niobium Oxide (Nb_2O_5) based Gas Sensor: A Literature Review." International Journal of Innovative Research and Creative Technology September-2022: Volume 8: Issue 5.
8. Patil, A., Dighavkar, C. and Borse, R., 2011. Al doped ZnO thick films as CO_2 gas sensors. *Journal of Optoelectronics and Advanced Materials*, *13*(October 2011), pp.1331-1337.
9. 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.
10. Dighavkar, C.G., Patil, A.V., Patil, S.J. and Borse, R.Y., 2009. Effect on H^ sub 2^ S Gas Sensing Performance of Nb_2O_5 Addition to TiO_2 Thick Films. *Sensors & Transducers*, *109*(10), p.117.
11. Patil, A.V., Dighavkar, C.G., Sonawane, S.K., Patil, S.J. and Borse, R.Y., 2010. Influence of Nb_2O_5 doping on ZnO thick film gas sensors. *Journal of Optoelectronics and Advanced Materials*, *12*(6), pp.1255-1261.
12. Shankar, P. and Rayappan, J.B.B., 2015. Gas sensing mechanism of metal oxides: The role of ambient atmosphere, type of semiconductor and gases-A review. *Sci. Lett. J*, *4*(4), p.126.
13. Kumar, R., Al-Dossary, O., Kumar, G. and Umar, A., 2015. Zinc oxide nanostructures for NO_2 gas–sensor applications: a review. *Nano-Micro Letters*, *7*(2), pp.97-120.
14. Wang, Y., Liu, C., Wang, Z., Song, Z., Zhou, X., Han, N. and Chen, Y., 2019. Sputtered SnO_2: NiO thin films on self-assembled Au nanoparticle arrays for MEMS compatible NO_2 gas sensors. *Sensors and Actuators B: Chemical*, *278*, pp.28-38.
15. Sonker, R.K., Sabhajeet, S.R., Singh, S. and Yadav, B.C., 2015. Synthesis of ZnO nanopetals and its application as NO_2 gas sensor. *Materials Letters*, *152*, pp.189-191.
16. Shishiyanu, S.T., Shishiyanu, T.S. and Lupan, O.I., 2005. Sensing characteristics of tin-doped ZnO thin films as NO_2 gas sensor. *Sensors and Actuators B: Chemical*, *107*(1), pp.379-386.