# Influence of annealing on electrical and optical properties of NiO thick film Sensors developed by screen printing technique

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***Abstract*: The current study present the preparation of NiO thick film sensors by using screen printing technique on glass substrate and study influence of annealing on electrical and optical properties of prepared thick films. Prepared films were annealed at in the range of 250°C to at 400°C using muffle furnace for 2 hours. Electrical properties of NiO thick film sensors were studied using resistivity, temperature coefficient ratio, and activation energy and optical properties were studied using FTIR and UV spectroscopy. It has been found that the resistivity of all prepared NiO thick film sensor decreased as annealing temperature increased. The energy band gap (Eg) of un-annealed and annealed at 250, 300, 350 and 400 °C NiO thick film sensors was found to be 3.25, 2.99, 2.81, 2.73, and 2.49 eV respectively. The change in optical band gap energy, reveals the impact of annealing on optical properties of the NiO films.**

***Keywords*: Annealing, muffle furnace, resistivity, FTIR and UV spectra.**

## 1. INTRODUCTION:

Metal oxide Semiconductors (MOS) have a wide range of structural topologies with an electronic structure that can be metallic, semiconductor, or insulator, giving them a wide range of chemical and physical properties [1]. As a result, metal oxide semiconductors are the most widely employed functional materials in chemical and biological sensing. Furthermore, their distinct and controllable physical features make them ideal candidates for electrical and optoelectronic applications. Because of their scientific relevance and prospective applications, nanostructured metal oxide semiconductors have been extensively researched [2, 3]. When MOS's reduced to nano-scale, there is increase in surface to volume ratio and so many materials exhibit unique structural, electrical and magnetic properties.

NiO is very well anti - ferromagnetic substance with a 3.6 eV band gap and is a metal-deficient p-type semiconductor [4]. NiO is a well-researched antiferromagnetic p-type semiconductor with good gas-sensing, catalytic, and electrochemical capabilities, and has gained importance in solid-state sensors, electrochromic devices, heterogeneous catalysts, and rechargeable batteries [5, 6]. Because of their exceptional chemical stability, nickel oxide (NiO) films have a variety of uses. Catalysts, electrochromic display devices, fuel cells, and gas sensors have all been employed with them [6, 7]. Among others preparation or synthesis methods like plasma deposition; electrochemical deposition, CVD, RF sputtering, pulsed laser deposition and physical vapour deposition method, screen printing method is most suitable because of to its low expensive, low-temperature operating condition and freedom to deposit materials on a variety of substances [8].

The fundamental disadvantage of NiO thin or thick films is that they have a higher resistance. Annealing NiO thin films is a popular method for overcoming the foregoing disadvantage and obtaining high pseudo capacitance. The association between the electrolytes ion and active sites, porous nature, surface area, electrical conductivity, and hydrophobicity of NiO thin films are all enhanced by annealing temperature, which improves the optimum performance of NiO films. As a result, post-deposition annealing is a significant step in improving structural, morphological, optical, and electrical properties of NiO films [9].

The current research work focus on the preparation of NiO thick films by using screen printing technique and studied electrical and optical properties of prepared NiO thick film sensors.

## 2. Methods and materials

### 2.1 Preparation of thick film sensor using screen-printing technique

Commercially available AR grade (99.99 % purity) NiO powder was for the preparation of films. Films were developed on glass substrate. Initially, glass substrates were properly clean using acetone then films placed under IR lamp. The 70-30 % ratio were used for material composition. In 70 % consist organic material (NiO) and 30% consist inorganic material (ethyl cellulose and BCA). Using mortar and pestle, thixotropic paste were formed 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 60 minutes to remove contamination. After, preparation of films, some films were annealed at in the range of 250°C to at 400°C using muffle furnace for 2 hours then un-annealed and annealed films were used for further study.

### 2.2 Characterizations of NiO thick film sensor:

#### 2.2.1 Electrical characterizations:

Using resistivity, TCR (thermal coefficient of resistance) and activation energy at high and low temperatures electrical properties of prepared thick films were studied. Equations 1, 2 and 3 were used to investigate resistivity, temperature coefficient of resistance (TCR), and activation energy, respectively [10].

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

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 between temperature $T_1$ and $T_2$,
$\Delta T$ = temperature difference between $T_1$ and $T_2$ and $R_o$ = Initial resistance of the film sample

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

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

**2.2.2 Optical characterizations:**
The optical properties of NiO thick film sensors were studied by FTIR and UV-Vis Spectra.
The optical band gap (Eg) of un- annealed and annealed NiO thick films is calculated on the basis of optical absorption spectra using the equation 4 [1].

$$\alpha = A\,(Eg\text{-}h\nu)^{n} / h\,\nu \qquad (4)$$

Where 'A' is a constant, 'Eg' is the semiconductor band gap and 'n' is a number equal to 1/2 for direct gap and 2 for indirect gap compound.

**2.2.3 Thickness measurement:**
The thickness of prepared films was calculated by weight difference method using equation 5 [1, 10].

$$t = \Delta m / \rho A \qquad (5)$$

Where, $\Delta m$ is the difference in mass before and after deposition, ρ = Density of the nickel oxide (6.67 g/cc$^2$), A= Area of the film.

## 3. RESULT AND DISCUSSION:

### 3.1 Electrical Properties:

#### 3.1.1 Resistivity:

Several factors influence the resistivity of film, including the preparation technique, surrounding parameters, doping agent, annealing temperature, and even measurement conditions. Equations 1 was used to calculate the resistivity of the fabricated NiO thick films. The resistance (DC) of prepared un-annealed and annealed at 250, 300, 350 and 400 °C NiO 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 decline in resistance with rising surrounding temperature across the thick film of NiO placed in electrical characterization system and films shows semiconducting properties by obeying Arrhenius equation [10, 11]. Because the ratio of surface area to bulk or the adsorbed oxygen concentration decreases with grain size, resistance decreases as annealing temperature rises [12, 13]. Figure 1 shows that the resistivity of all prepared pure NiO thick film sample decreased as annealing temperature increased, same result is reported by A. Madhavi, *et al*. (2016) [13]. It was also observed that the resistivity decreases with increase in temperature and supports the semiconducting nature of NiO films [4].

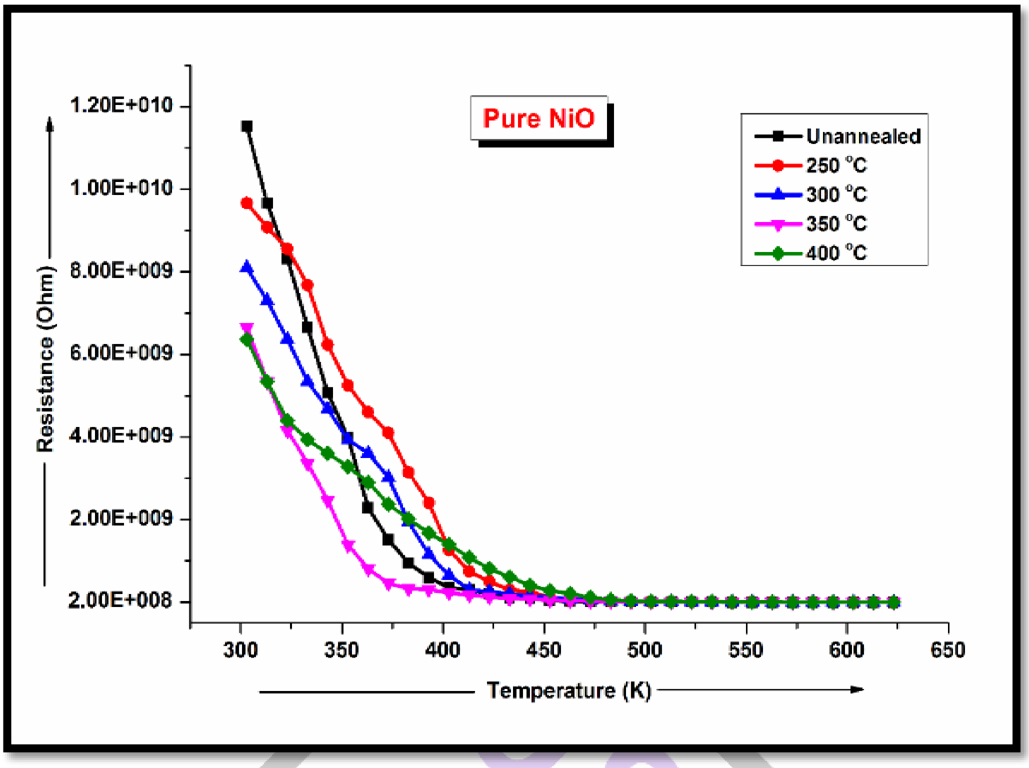


Figure 1 Resistance verses temperature of NiO thick film

### 3.1.2 Temperature coefficient of resistance (TCR):

The un-annealed and annealed at 250, 300, 350 and 400 °C thick films represented by S1, S2, S3, S4,and S5 respectively as shown in Figure 2. The TCR of un-annealed and annealed at 250, 300, 350 and 400 °C NiO thick film samples was found to be -0.01408 /°C, -0.012564 /°C, -0.53822 /°C, -0.01267 /°C, and -0.00051 /°C respectively. It is found that, as annealing temperature increase TCR also increase.

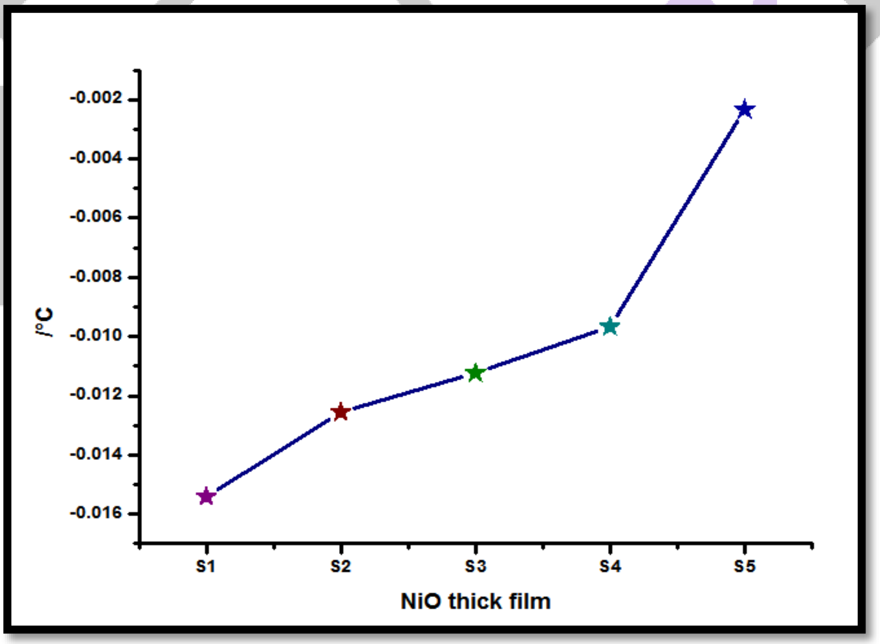


Figure 2 TCR plot of NiO thick films

### 3.3.3 Activation energy:

The activation energy lowers in this lower temperature region because a modest amount of thermal energy is sufficient to activate the charge carriers and allow them to participate in the conduction process. Because material travels from one conduction mechanism to another, the activation energy in the lower temperature region always seems to be less than the energy in the higher temperature region. The rise in conductivity at low temperatures is related to the mobility of charge carriers, which is determined by the defects. As a result, the region of low temperature conduction is often referred to as the conduction mechanism. The activation energy is higher in high-temperature regions than in low-temperature areas. This region is known as high temperature or intrinsic conduction because the electrical conductivity is mostly governed by intrinsic flaws. The high activation energy values seen in this location can be explained by the fact that the energy necessary to generate defects is significantly greater than the energy required to drift. As a result, the electrical conductance of the film samples is determined only at high temperatures due to intrinsic faults generated by thermal fluctuations [14, 15]. Figure 3 shows the Arrhenius plot of log R vs. 1/T of NiO thick film.

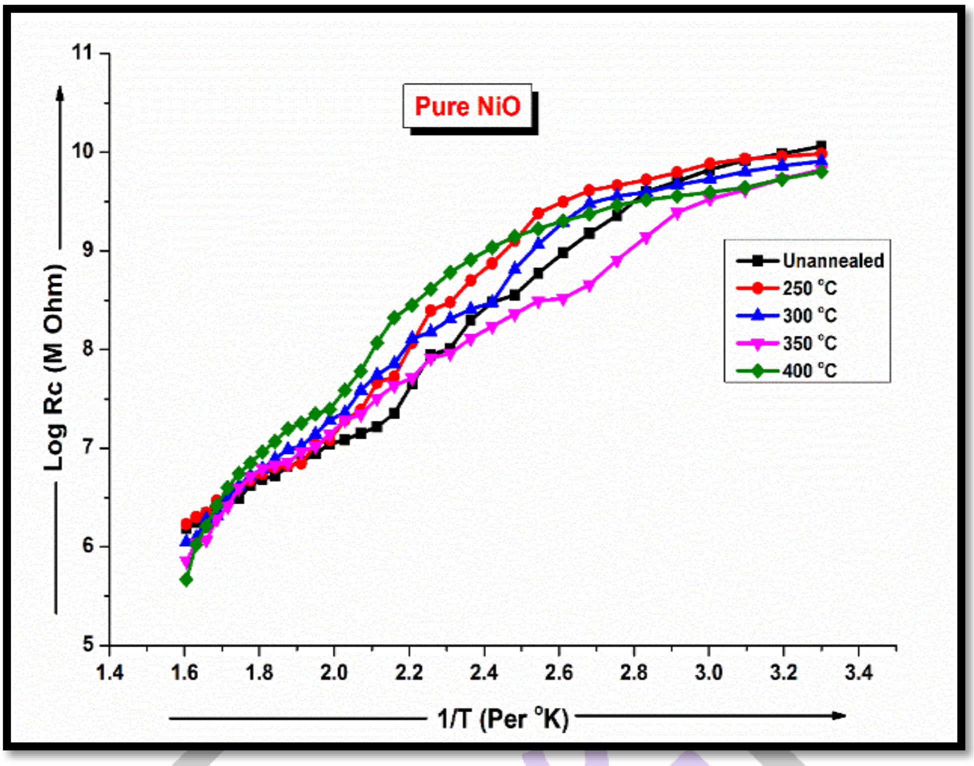


Figure 3 Arrhenius plot of log R vs. 1/T of NiO thick film

The thickness value was calculated by using equation 5 and was found to be 38, 36, 35, 34 and 32 µm for un-annealed and annealed at 250, 300, 350 and 400 °C thick films respectively. It was observed that increasing the annealing temperature resulted in a decrease in film thickness. The NiO thick film thickness is presented in Table 1.

**Table-1:** Influence of annealing on electrical properties of NiO thick film

| Sr. No. | Annealing Temperature (°C) | Resistivity (Ω.m) | Thickness (µm) | TCR / °C | Activation Energy (eV) | |
|---|---|---|---|---|---|---|
| | | | | | At LTR $x10^{-4}$ | At HTR $x10^{-4}$ |
| 1 | Un-annealed | 219040.76 | 38 | -0.01541 | 2.3644 | 3.48092 |
| 2 | 250 °C | 174013.54 | 36 | -0.01256 | 1.60113 | 5.8202 |
| 3 | 300 °C | 141716.89 | 35 | -0.01123 | 1.5788 | 5.7778 |
| 4 | 350 °C | 113163.33 | 34 | -0.00967 | 1.38511 | 9.3850 |
| 5 | 400 °C | 101967.66 | 32 | -0.00234 | 0.9577 | 12.091 |

### 3.2 Optical Properties:

The optical properties of prepared NiO thick films were studied by FTIR and UV spectroscopy.

#### 3.2.1 FTIR

At room temperature, FTIR measurements in the range of 4000–400 $cm^{-1}$ were taken to determine the main functional group present in the catalyst. The nickel oxygen bond stretching vibrations are visible in the FTIR spectra peaks around 443.54 and 563 $cm^{-1}$. At 443.54 $cm^{-1}$, the absorption bonds are linked to the Ni-O vibration bond. The crystalline form of the NiO catalyst is shown by the broadness of a peak [16, 17]. The FTIR plot of NiO thick films is shown in Figure 4.

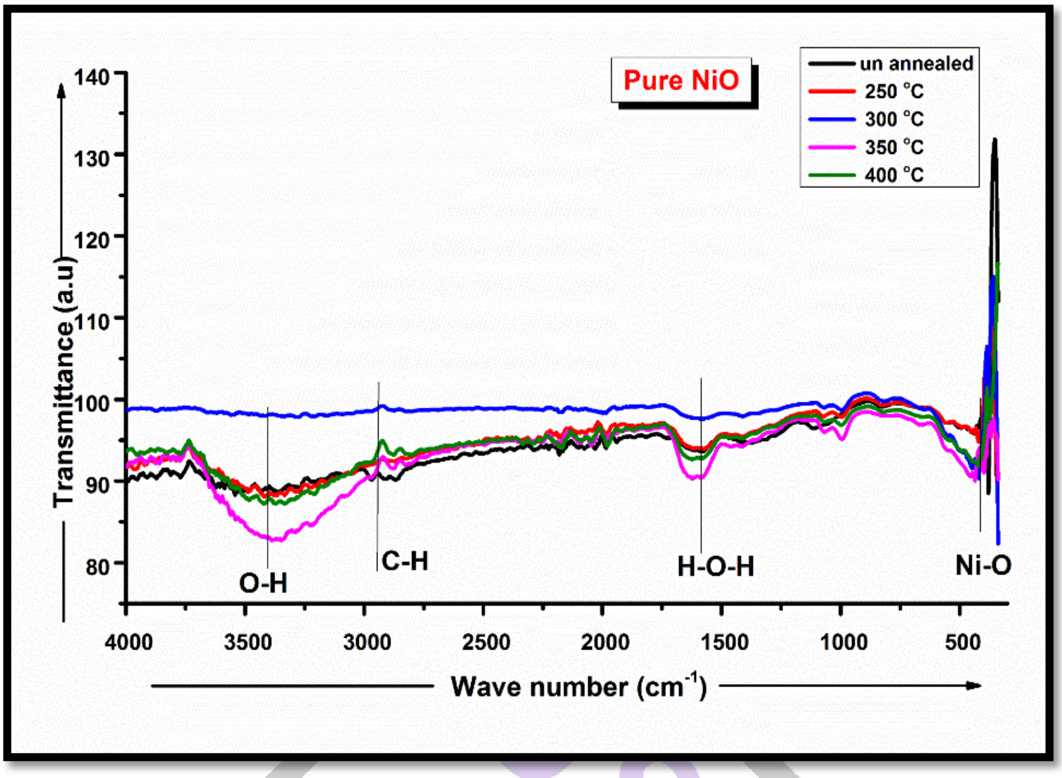


Figure 4 Transmittance versus wavenumber of Pure NiO thick films

The H–O–H bending vibration mode is relevant for the band at 1557, 1638 $cm^{-1}$ and suggests that the carbonates group exists. The hydroxyl group absorption at 1632$cm^{-1}$ and the bond at 2900 $cm^{-1}$ both correlate to the C-H stretching mode [18]. On the FT-IR spectra, the O-H bond has a peak about 3414-3651 $cm^{-1}$. Also, when FTIR analysis was performed, the broad peak at 3422.62 and 1398.44 $cm^{-1}$ could be due to stretching and bending vibrations of the–OH group absorbed on the catalyst surface from the atmosphere [18-20]. The presence of NiO nanoparticles was confirmed by FTIR data.

**3.2.2 UV spectra:**

A UV-Vis-NIR spectrometer was used to record the optical absorption spectrum of pure NiO thick films in the wavelength range of 400–800 nm. The optimum absorbance of films was found in the UV range (200-400 nm), after which the absorbance declined as the wavelength moved towards the visible and near-infrared regions. It's worth noting that NiO films were extremely transparent in the visible range. The energy band gap (Eg) of pure NiO thick film samples un-annealed and annealed at 250, 300, 350, and 400 °C was determined to be 3.25, 2.99, 2.81, 2.73, and 2.49 eV respectively. The effect of annealing on the optical characteristics of NiO films is revealed by the change in optical band gap energy. The plots of $(\alpha \cdot h\nu)^2$ versus hν of films un- annealed and annealed at 250˚C - 400˚C are shown in Figure 6.

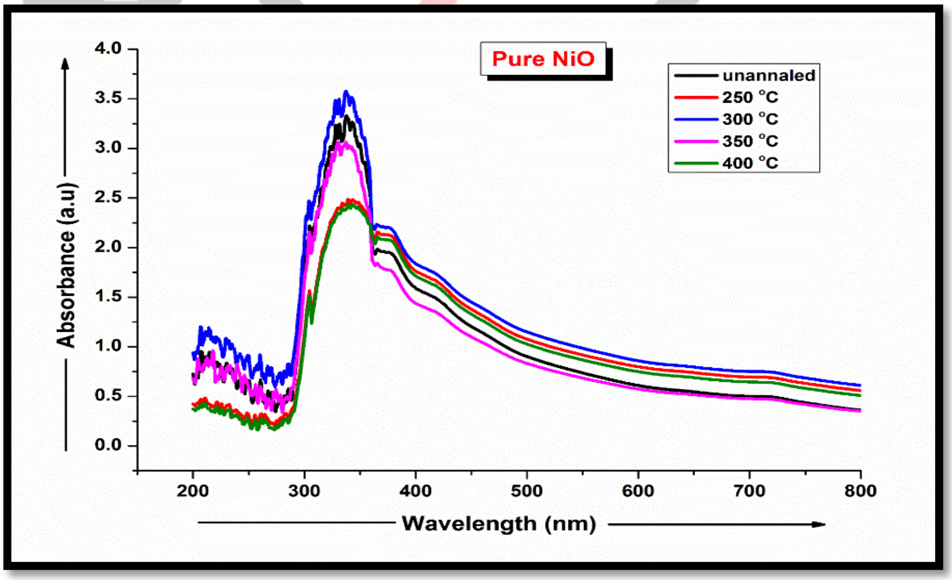


Figure 5 Absorbance versus wavelength of NiO thick films

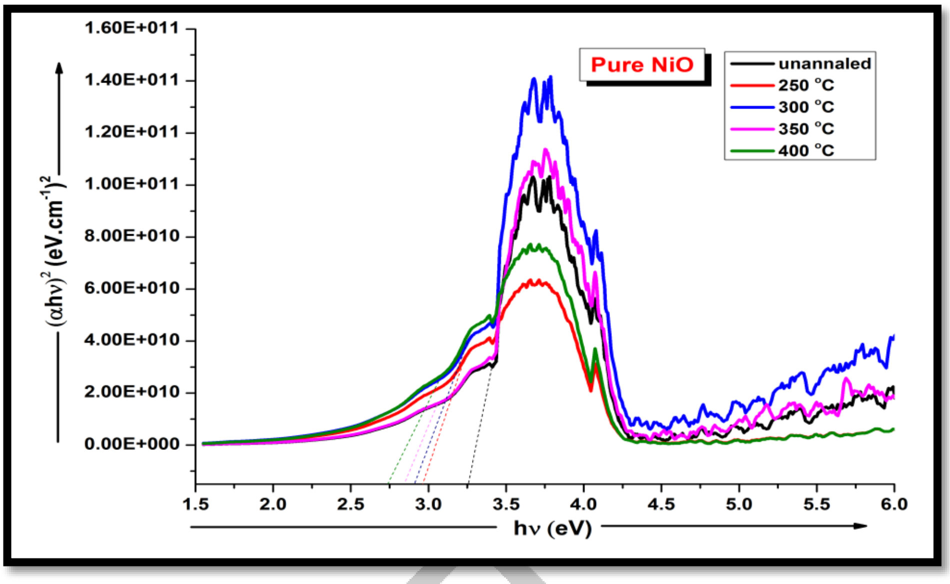


Figure 6 Optical band gap of NiO thick films

### 3.2.3 Study of Photoresponse of prepared NiO thick films

The light-dependent conductance variability of prepared thick films was investigated as an optical sensor. Using red, yellow, green, and blue colour filters and a photoresponse characterization system, the light sensing behaviour of prepared thick films at distinct wavelengths of 640, 550, 510, and 450 nm was investigated. The schematic diagram of a photoresponse characterization system is shown in figure 7. This system includes a light source (5 Watt), a distance adjustment function, a colour filter holder, and a sample holder, as well as a +5VDC fixed power supply unit. By changing the position of the source of light from thick film, the variation in current was examined with reference to light intensity in this setup. A Lux metre was used to measure the variation in current for a change in intensity over a distance range of 2 cm to 40 cm.

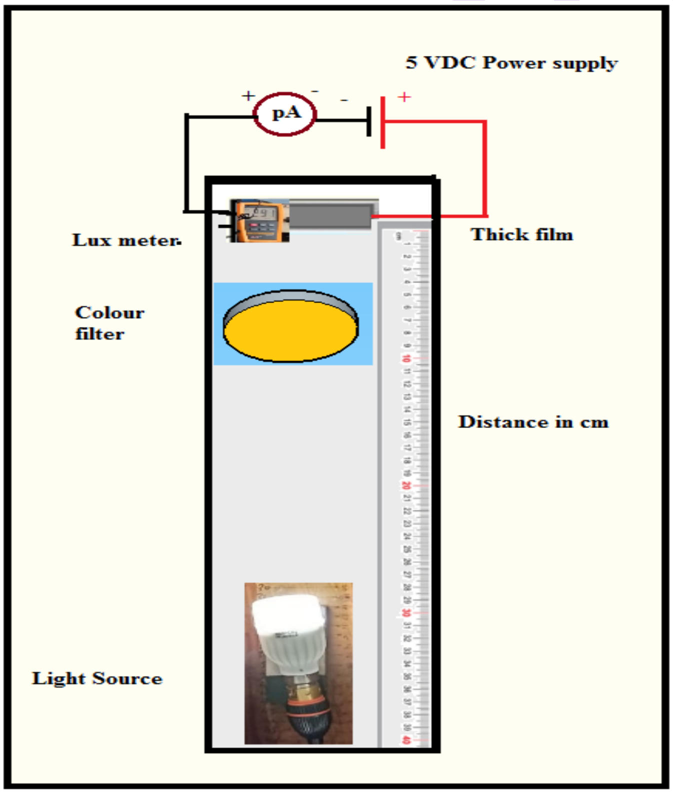


Figure 7 Schematic diagram of a photoresponse characterization system.

The position of prepared thick film samples was fixed in all subsequent steps, and one filter was utilised alternately during current or optical response measurements of the film. The light-dependent conductance variability of prepared pure NiO thick films was investigated as an optical sensor. Using red, yellow, green, and blue colour filters and a photoresponse characterization system, the light sensing behaviour of prepared thick films at distinct wavelengths of 640, 550, 510, and 450 nm was investigated. The pure NiO thick film annealed at 400 °C selected for study of optical sensing behaviour of prepared thick film samples because this films shows good optical properties like lower optical bad gap. The optical sensing behaviour of prepared NiO thick film were studied by using following steps.

i. Position of filter is fixed (near sample) and change the position (distance) of light source and measured response (current) through the prepared sample.

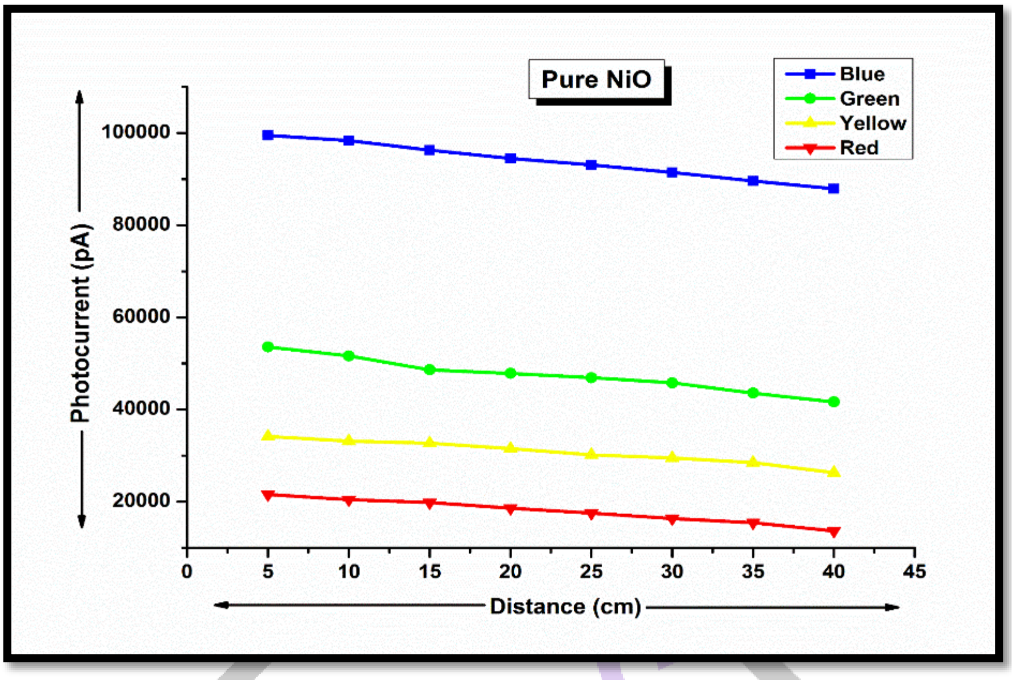


**Figure 3.8:** Distance versus photocurrent of NiO thick films

ii. The position of light source is fixed and change the position (distance- near sample, middle and way from the sample) of selected filter.

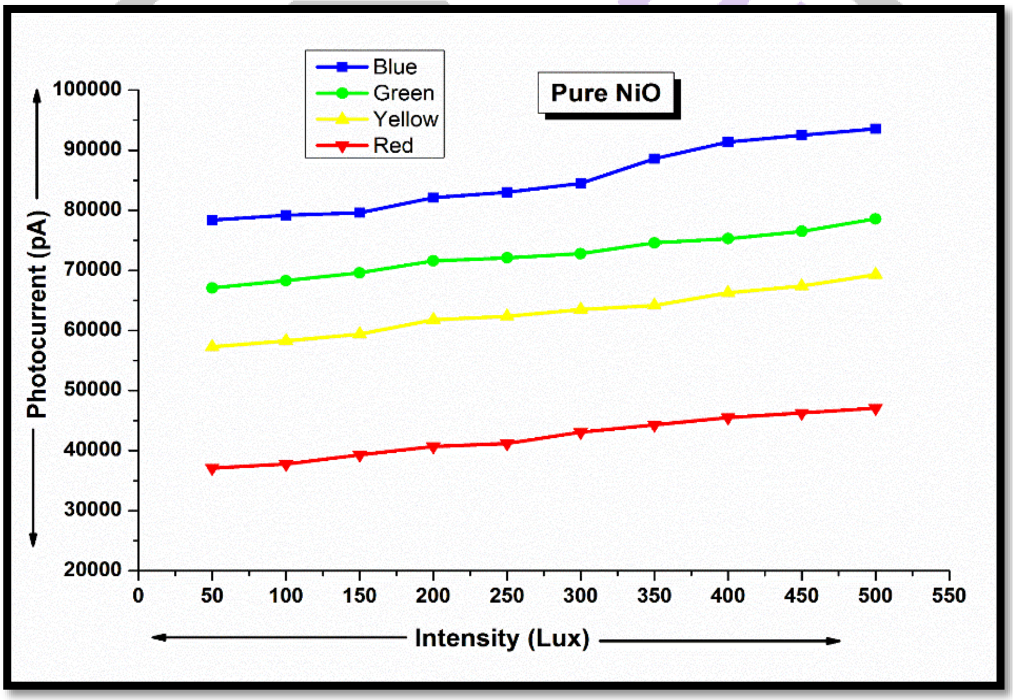


**Figure 3.9:** Intensity versus photocurrent of NiO thick films

iii. Change the intensity of light source using dimmer stat and measured response (current) through the prepared sample with filter and without filter (the position of filter near the prepared thick film sample.

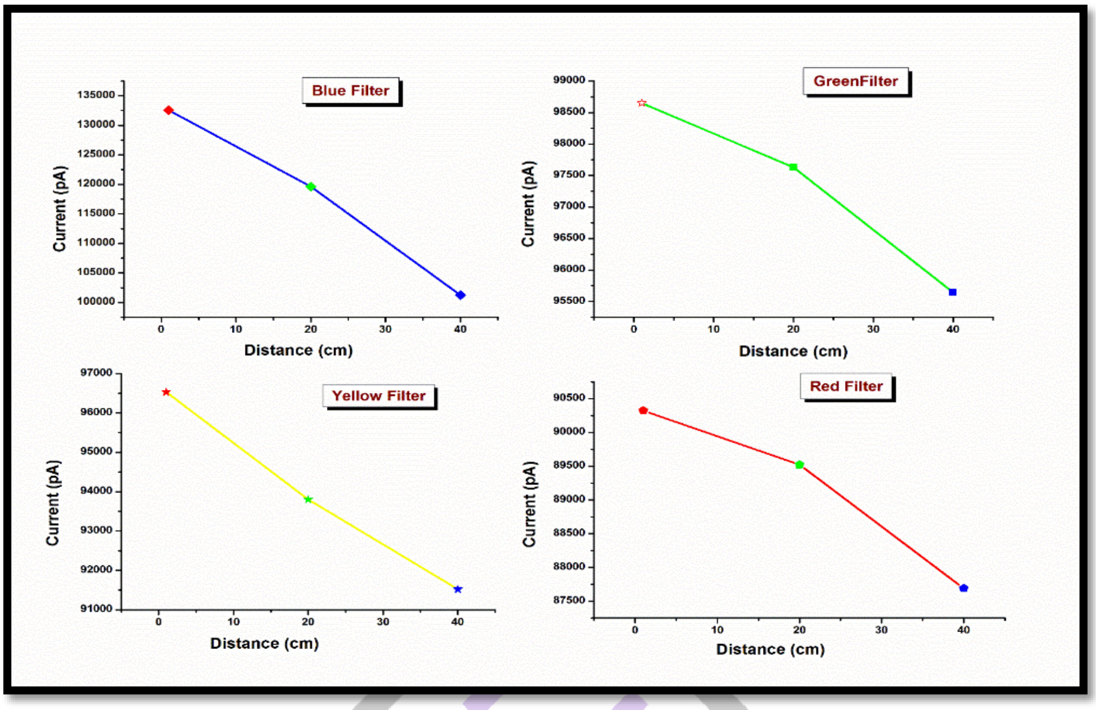


**Figure 3.10:** Optical response of prepared NiO thick films

The blue filter recorded the maximum output current, while the red filter provided the lowest output current. The output current increases as the wavelength decreases. Furthermore, the current for each wavelength decreases as the distance between the light source and the film increases.

**Conclusions:**

1. The NiO thick films were successfully developed by using screen-printing technique.
2. The annealing influence the electrical and optical properties of NiO thick films.
3. Thickness and resistivity of prepared thick films decreases with increase annealing temperature.
4. Temperature coefficient of resistance (TCR) increase as annealing temperature increase.
5. From FTIR, the broadness of a peak indicates that the NiO catalyst is crystalline in nature.
6. From UV spectra, the optical band gap of prepared thick films decreases with increase annealing temperature.
7. The blue filter shows the maximum photo response as compare to yellow, green and red filters because of low wavelength.

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