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COBALT CATALYZED-MULTI-WALLED CARBON NANOTUBES FILM SENSOR FOR CARBON MONO-OXIDE GAS

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The fabrication of cobalt (Co) catalyzed multi-walled carbon nanotubes (MWNTs) film sensor for the detection of carbon mono-oxide (CO) gas has been reported. Cobalt (Co) catalyzed carbon nanotubes have been synthesized on silicon oxide grown silicon substrate using low pressure chemical vapor deposition. The diameter of these multi-walled nanotubes (MWNTs) varies from 40-100 nm and the length is on the order of several tens of micrometers. To measure the gas sensing properties of this sensor, a typical pattern of gold electrodes has been thermally evaporated. The typical responses of MWCNTs gas sensor for different concentration (40, 100, 140 & 200 ppm) of sensing gas i.e. carbon mono-oxide (CO) have been studied. It is observed that this MWNTs gas sensor shows a quick response to CO gas with the fast recovery time. Temperature dependence of the resistance of this MWNTs-based film sensor has also been studied for a temperature range of 300-500K. It is found that the resistance decreases with the increase in temperature for all concentration of CO gas. The sensitivity and responsiveness has been estimated with respect to the time as well as temperature. The responsiveness increases whereas the sensitivity of this sensor decreases with the increase in temperature for all concentrations of CO gas. Some electrical parameters such as activation energy and pre-exponential factor have also been estimated to understand the electrical transport properties of this sensor.

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1. Introduction

Recently, gas sensors, or chemical sensors, have drawn a lot of attention due to their widespread applications in industry, environmental monitoring, space exploration, biomedicine, and pharmaceutics. The demand of today's sensing technology is the gas sensors with high sensitivity and selectivity, avoiding the leakage of explosive gases such as hydrogen, and allowing easy operation of real-time detection of toxic or pathogenic gases in industries. For monitoring and controlling our ambient environment, especially with the increasing concern of globe warming, we need highly sensitive gas sensors. Scientists at National Aeronautics and Space Administration (NASA) are seeking the use of high-performance gas sensors for the identification of atmospheric components of various planets.

The evolution of new materials and devices play a key role in the development of accurate and reliable devices such as sensors. During the last few decades, the technology of nanosensors has developed tremendously by joining many scientific achievements from various disciplines, offering challenges and opportunities. A lot of research work is focused on the fabrication of smaller devices capable of molecular level imaging and monitoring of pathological samples and macromolecules, particularly for remote monitoring, due to the increasing need for environmental safety and health monitoring [1-2].

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Several workers [3-6] used multiwalled carbon nanotubes (MWNTs) to sense polar as well as non polar gases such as carbon monoxide (CO), carbon dioxide (CO_2), ammonia (NH_3), water (H_2O), and ethanol (C_2H_5OH), helium (He) and nitrogen (N_2). In case of nanotubes, it is observed that the oxygen (O_2) molecules are electron acceptors with substantial adsorption energies and charge transference, whereas ammonia (NH_3), nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), water (H_2O), hydrogen (H_2) and argon (Ar) are electron donors [7]. The adsorption in nanotubes is determined by adsorption energy and availability of sites, with typically four different adsorption sites: external surface, grooves between carbon nanotubes on the bundle outside, pores inside carbon nanotubes, and interstitial channel between adjacent tubes inside the bundle [8-9]. Jhi et al. [10] reported that the electronic and magnetic properties of oxidized nanotubes and they concluded that the nanotubes have high potential for gas sensors. They further demonstrated that the sensing mechanism of as synthesized nanotubes is more related to oxygen doping than to intrinsic properties, and depends on the structural defects created during the synthesis of these nanotubes.

Many reports on different types of gas sensors are available in the literature [11-13]. These sensors generally operate on different principles and various gas sensing elements have been employed for these sensors, out of which resistive metal oxide sensors comprise a significant part. However, the metal oxide sensing elements typically operate at an elevated temperature for maximum performance, thereby, causing higher power consumption. This limits the application of these sensors in various fields such as wireless technology. Since their discovery [11], carbon nanotubes have drawn a lot of research interests due to their unique geometry, morphology, and properties. Their preparation, properties (such as electronic, mechanical, thermal, and optical properties), and applications on various fields are all studied intensely [12-17]. These properties make them potential candidates as building blocks of active materials in nanoelectronics, field emission devices, gas storage and gas sensors [18-20]. Among these, it has been reported [3, 21] that the carbon nanotubes show excellent room temperature gas sensing property for many applications. The large surface area provided by the hollow cores and outside walls in nanotubes gives them very large gas absorptive capacity. Interaction with any gas can change the electrical properties of CNTs at room temperature. Also, they have fast response and good reversibility [22]. Therefore, we set-out to study the carbon mono-oxide gas sensing properties of carbon nanotubes in the present manuscript. In the present work, a cobalt catalyzed multi-walled carbon nanotubes film sensor has been fabricated and the carbon mono-oxide gas sensing properties of this sensor has been studied.

2. Experimental

Carbon nanotubes (CNTs) were synthesized on cobalt catalyzed film using low pressure chemical vapour deposition system. These CNTs were grown by the catalytic deposition of C_2H_2 at 750^oC, at a chamber pressure of 100 Torr and the growth time was kept fixed at 5 minutes. Initially, nitrogen gas was passed for 10 mins. at a temperature of 700^oC, just after this process, the etching gases NH_3 and H_2 with flow rates of 100 sccm and 50 sccm respectively were passed through the reactor for 15 mins using mass flow controllers (MFC's). At the final stage, the hydrocarbon carbon gas C_2H_2 with a flow rate of 20 sccm was added for 5 minutes. Therefore, the final gas mixtures of NH_3:C_2H_2:H_2 with flow rates 100:50:20 sccm respectively, were used to grow the carbon nanotubes. The morphology of these carbon nanotubes (CNTs) were studied using Field Emission Scanning Electron Microscope (FESEM). Raman spectrum of as-grown CNTs was recorded using DXR Raman Microscope, Thermo Scientific with 532 nm laser as an excitation source at a power of 8 mW. A specially designed gas sensing set-up was used to study the gas sensing properties of these as-synthesized carbon nanotubes (CNTs) based sensor. An electrode pattern of gold was thermally evaporated on this film. To study the gas sensing properties of the as-prepared CNTs film sensor, the gas sensor was kept inside a stainless steel chamber and the resistance was measured using a Keithley 4200 I-V measurement system. The mass flow controllers were used to control the concentration of detecting gas. The Ag-Pt heater was used to heat and control the operation temperature of the sample. For measuring the gas sensing

properties, CNTs based sensor was kept inside the sample holder and probes were connected on the electrodes of CNTs film. The system was evacuated up to 10^{-6} Torr with the help of turbo molecular pump. After attaining the required degree of vacuum, the tubro and rotary pump valves were closed and air was purged with a flow rate of 2 l/min for 3 mins. Real time resistance was measured to obtain a baseline resistance. Once a baseline resistance was obtained, the detecting gas i.e. carbon mono-oxide with a set concentration was introduced into the sample holder. This gas was purged for 1-2 minutes to measure the change in resistance with time up to 2 minutes and after the time was over, the flow of detecting gas in to the sample holder was stopped and we measured the recovery time of the sensor. We repeated these cycles for different concentrations of carbon mono-oxide with respect to pure air to study the response of this CNT sensor for detecting carbon mono-oxide (CO). The sample gas flow time and the clean air reference flow time were fixed at 1 minute and 3 minutes, respectively. It should be noted that these switching intervals were selected so that the resistance change is at least 90% of the saturated value. The sensor resistance was sampled and recorded every second for subsequent analysis. The relative changes in the electrical parameters of the film were considered as sensor output. Typical response of this resistive sensor is measured with respect to time and temperature respectively.

3. Results and discussion

Figs. 1(a) & 1(b) represent the morphology of as-grown carbon nanotubes (CNTs). The diameter of these nanotubes varies from 40-100 nm and length of these carbon nanotubes (CNTs) is on the order of several tens of micrometers. TEM image of these CNTs is presented as Fig. 2. It is observed that these nanotubes are multi-walled and the diameter of inner and outer wall is 10 nm and 40 nm respectively. To verify the graphitic nature of as-grown carbon nanotubes, we have employed Raman Spectroscopy. Fig. 3 presents the Raman spectrum of as grown multi-walled carbon nanotubes (MWNTs). The presence of strong peak at 1580 cm^{-1} (G-band) in this spectrum clearly indicates the graphitized nature of these as-grown cobalt catalyzed multi-walled carbon nanotubes (MWNTs). The D mode (the disorder band) located between 1330 – 1360 cm^{-1}, is generally observed in CVD grown MWNTs. Here, the D-band peak observed at 1320 cm^{-1} seems to be less intense, which predicts that the less quantity of amorphous carbonaceous particles is adhered to MWNTs walls. In the present work, we have studied the typical resistive response of the cobalt catalyzed multi-walled carbon nanotubes (MWCNTs) gas sensor with respect to time and temperature.

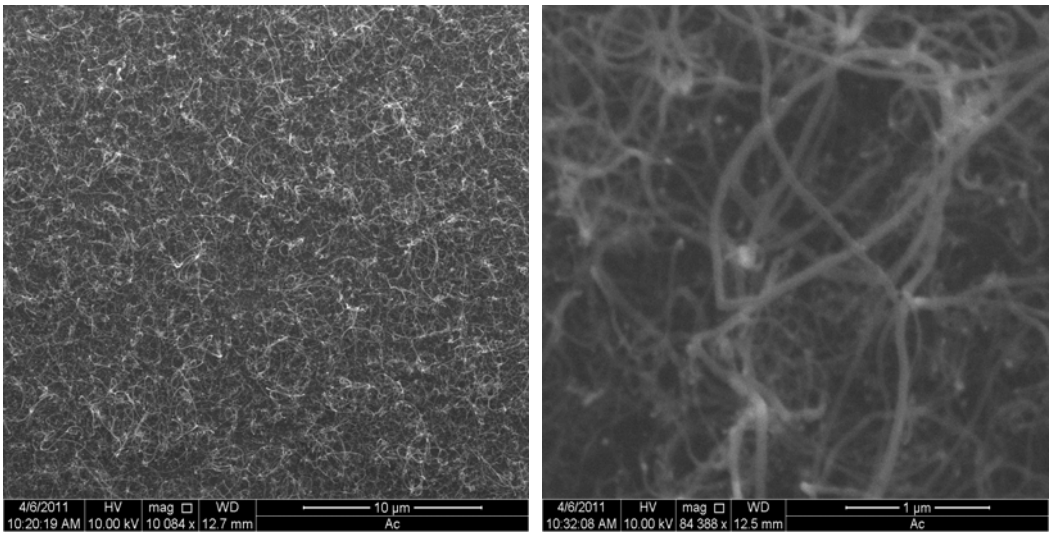

Fig. 1(a&b) FESEM images of Co-catalyzed CNTs.

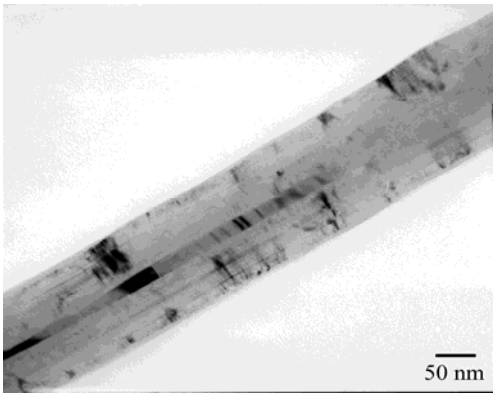

Fig. 2 TEM image of Co-catalyzed MWNT.

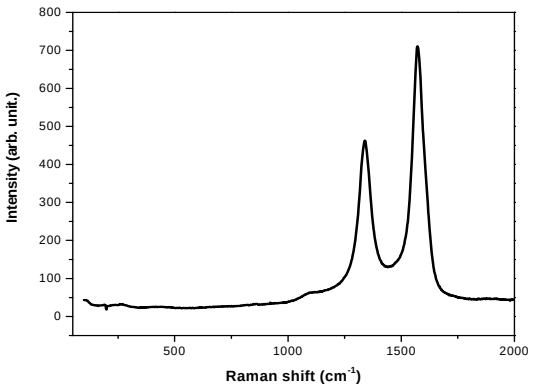

Fig. 3. Raman spectra of Co-catalyzed MWNTs.

3.1 Typical response on the basis of resistance versus time cycles

On the basis of resistance versus time cycles, typical response of this multi-walled carbon nanotubes (MWCNTs) gas sensor in the presence of carbon mono-oxide (CO) gas is presented in Fig. 4. It is observed that the resistance of the sensing materials increases on increasing the concentration of CO from 40 ppm to 200 ppm. This suggests that the CO is identified as an electron acceptor. It is also reasonable to propose that this behavior in the present sample may be due to the adsorbed CO molecules on the wall of these carbon nanotubes. CO has an unpaired electron and is known as oxidizer. Upon CO adsorption, a charge transfer is likely to occur from MWNTs to CO due to the electron-acceptor character of CO molecules inducing the formation of electronic levels in the semiconducting nanotube gap, very near to the Fermi level. Further increase in CO concentration may result in the interaction of a large number of CO molecules with the defective sites on the wall of the nanotubes, causing an increase in the electrical resistance. It is also well known that the carbon mono-oxide is a reducing gas and its absorption will result in injection of electrons to the CNTs and reduction in the number of holes in the material. As holes are the main charge carrier for p-type semiconductor, the reduction in the number of holes will result in an increase in resistance of the sample on the exposure of CO gas.

On the basis of the dynamical response (resistance-time (R-t) cycles) of this MWNTs film sensor, the response and recovery time has been calculated and the calculated values are given in Table 1. It is seen that the response time ($\tau_{res.}$) first decreases from 39.78 seconds to 33.06 seconds and then, it increases to 37.50 seconds with the increase in the concentration of carbon mono-oxide (CO) gas, whereas the recovery time ($\tau_{rec.}$) changes from 31.38 seconds to 43.14 seconds. Here, it may be suggested that this increase in the recovery time with the increase in CO concentration may be due to the increase in binding energy between MWNTs and CO. This overall increase in the response and recovery time may also be due to the increase in the adsorption/desorption process of gas molecules on MWNTs.

Table-1. Typical sensor parameters for the Co-catalyzed MWNTs-based film sensor

CO Concen-tration (ppm)	Resistance (Ohm)	Responsiv-eness [(R_{air}-R_{gas}) /R_{gas}]	Sensitivity (R_{air}/R_{gas})	Response Time (τ_{res}) (Sec.)	Recovery Time (τ_{rec}) (Sec.)	Activation energy (ΔE) (eV)	Pre-exponential factor (σ_o) ($ohm^{-1}.cm^{-1}$)
40	115.11	0.4645	0.8608	39.78	39.78	0.193	1.698
100	125.93	0.5094	0.8506	33.06	40.62	0.187	1.318
140	141.65	0.5645	0.7953	34.14	42.54	0.180	1.092
200	152.47	0.5949	0.7407	37.50	43.14	0.170	1.725
Air				-------	-------	0.190	3.196

To evaluate the sensitivity of this MWNTs gas sensor, we use the following relation;

$$\text{Sensitivity} = R_{air}/R_{gas} \quad (1)$$

Where, R_{air} is the sensor resistance in air and R_{gas} is the sensor resistance in the presence of a toxic species. The sensitivity of this gas sensor has been estimated for different gas concentrations. The sensitivity response with time for all the studied CO concentrations is shown in Fig. 5. The sensitivity of this MWNTs gas sensor decreases from 86.08% to 74.07% with the increase in gas concentration from 40 ppm to 200 ppm. This means the process of CNTs-hybridization reduces the gas sensitivity toward CO gas.

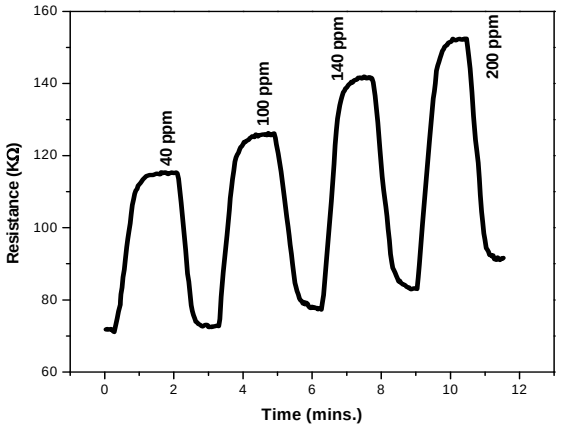

Fig. 4. Typical responses of Co-catalyzed MWCNTs gas sensor for different concentration of CO gas (40, 100, 140 & 200 ppm).

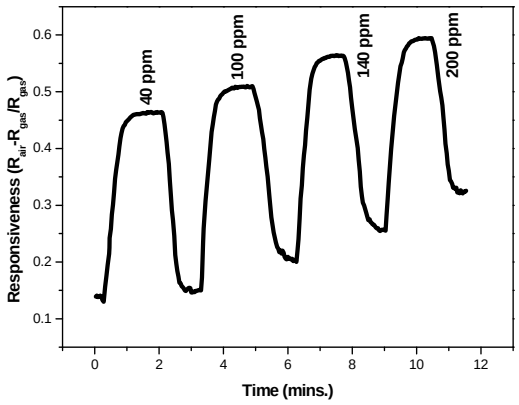

Fig. 5. Typical responsesiveness of Co-catalyzed MWCNTs gas sensor for different concentration of CO gas (40, 100, 140 & 200 ppm).

For quantifying the performance of a given sensor, we use the following relation to calculate the responsiveness (SR) of the sensor;

$$SR = (R_{air} - R_{gas})/R_{air} \quad (2)$$

It is defined as the ratio of the resistance change due to the exposure to the test gas and the sensor's baseline resistance in air. Using above relation (eq.2), the responsiveness of the present MWNTs sensor is calculated at different CO concentration and the values are presented in Table 1. It is clear from this table that this MWCNTs gas sensor could detect gas concentration as low as 40 ppm of CO. From the responsiveness time cycles (Fig. 6), it is found that the responsiveness increases from 46.45% to 59.49% as the gas concentration increases from 40 ppm to 200 ppm. It is therefore, suggested that this MWNTs sensor gives a good response to the different concentrations of CO gas.

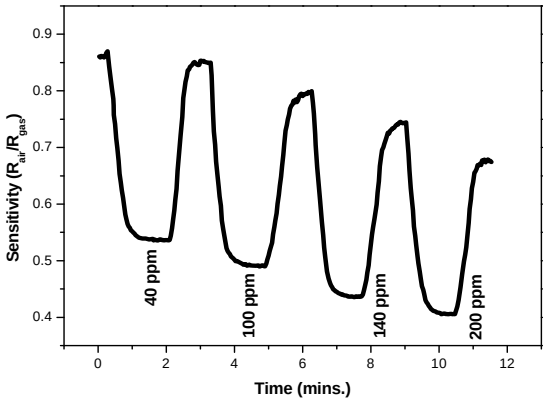

Fig. 6. Typical sensitivity of Co-catalyzed MWCNTs gas sensor for different concentration of CO gas (40, 100, 140 & 200 ppm).

In the present system, the electrical response to molecular adsorption in multi-walled carbon nanotubes (MWCNTs) may be explained on the basis of two sensing mechanisms namely (i) the adsorption resulting in direct charge transfer between a donor or acceptor type of molecule and MWNTs, which will lead to the shift in the Fermi level in the semiconducting tubes (intra-tube modulation), resulting in a change in resistance [23], (ii) the adsorption occurs in the interstitial space between MWNTs to form an MWNT-molecule-MWNT junction, which will result in a hopping kind of mechanism for inter-tube charge transfer between nanotubes. Therefore, an inter-tube modulation of the CNTs network may be responsible for the resistance change. This phenomenon is common for all types of molecules and for both metallic and semiconducting CNTs. This type of modulation is similar to that of the interaction between semiconductor metal oxides and donor or acceptor types of molecules, showing a nonlinear (power law) response [24].

3.2 Typical response on the basis of temperature dependence of resistance

Here, we have studied the variation of resistance with the temperature for different concentration of CO gas (40, 100, 140 & 200 ppm). Fig. 7 presents the temperature dependence of the resistance at different CO concentration for the present cobalt catalyzed MWNTs film sensor in the temperature range 300 to 500 K. It is observed that the resistance decreases exponentially with increasing temperature from 300 to 500 K, which suggests the semiconducting behavior of these MWNTs. At a particular temperature, the resistance is found to decrease with the increase in CO concentration. The variation of resistance with temperature for different concentration of CO (40, 100, 140 & 200ppm) is presented in Table 2.

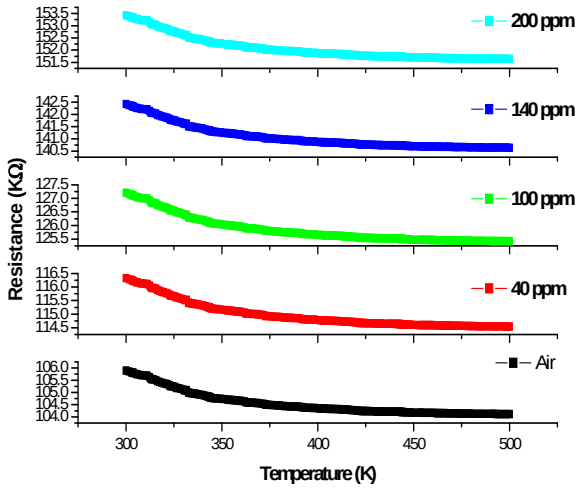

Fig. 7. Temperature dependence of resistance for the Co-catalyzed MWNTs-based film sensor in air and 40, 100, 140 & 200 ppm CO gas for the temperature range of (300-500K).

Table-2

Electrical parameters for the Co-catalyzed MWNTs-based film sensor

CO concent-ration	Resistance (kΩ) at different temperatures					Responsiveness [(R_{air}- R_{gas}) /R_{gas}] at different temperatures					Sensitivity (R_{air}/R_{gas}) at different temperatures					Activation energy (ΔE) (eV)	Pre-exponential factor (σ_0) ($ohm^{-1}.cm^{-1}$)
	300K	350K	400 K	450 K	500 K	300K	350K	400 K	450 K	500 K	300K	350K	400 K	450 K	500 K		
40 ppm	116.33	115.17	114.77	114.60	114.54	0.0897	0.0906	0.0909	0.0910	0.0911	0.9103	0.9094	0.9091	0.9090	0.9089	0.193	1.698
100 ppm	127.21	126.05	125.65	125.47	125.41	0.1675	0.1690	0.1695	0.1698	0.1699	0.8325	0.8310	0.8305	0.8302	0.8301	0.187	1.318
140 ppm	142.43	141.26	140.87	140.69	140.63	0.2564	0.2586	0.2593	0.2596	0.2597	0.7436	0.7415	0.7408	0.7404	0.7403	0.180	1.092
200 ppm	153.43	152.27	151.86	151.70	151.64	0.3098	0.3121	0.3129	0.3133	0.3134	0.6902	0.6879	0.6871	0.6867	0.6866	0.170	1.725
Air	----------					----------					----------					0.190	3.196

It is found that the entire experimental data for the temperature region (300- 500K) gives a best fit to the thermally activated process. Therefore, we have applied the thermally activated process for the temperature region (300-500K) to understand the conduction mechanism in the present sample of Co catalyzed MWNTs film,. The plot of lnσ Vs 1000/T for the temperature range of (300-500K) is presented in Fig. 8. The plot is a straight line, indicating that the conduction in this system is through the thermally activated process. The conductivity, is therefore expressed by the usual relation

$$\sigma = \sigma_0 \exp (- \Delta E / kT) \quad (3)$$

where, σ_0 and ΔE represents the pre-exponential factor and activation energy respectively, K is Boltzmann constant.

We may write equation (1) as,

$$\ln \sigma = \ln \sigma_0 - (\Delta E / kT) \quad (4)$$

or

$$\ln \sigma = -(\Delta E / 1000\ k)\ (1000/T) + \ln \sigma_0 \quad (5)$$

When we plot a graph between ln σ and 1000/T, a straight line is obtained having slope (ΔE/1000 k) and intercept ln σ_0.

We may calculate the activation energy (ΔE) and pre-exponential factor (σ_0) as follows,

$$(\Delta E) = 1000\ k \times \text{slope of straight line}$$
$$\sigma_0 = \sigma / \exp(-\Delta E / kT) \quad (6)$$

Using the above relations, the values of the activation energy and pre-exponential factor are calculated and these values are given in Table 2. On the basis of these calculated values, it is suggested that the conduction is due to thermally assisted tunneling of charge carriers in the localized states in band tails. The activation energy alone does not provide any indication as to where about of the conduction mechanism, whether it takes place in the extended states above the mobility edge or by hopping in the localized states. This is due to the fact that both of these conduction mechanisms can occur simultaneously. The activation energy in the former case represents the energy difference between mobility edge and Fermi level, (E_c- E_f) or (E_f - E_v). As compared to the initial value, an overall decreasing trend is observed for conductivity of this system with the increase in CO gas concentration. This decrease in conductivity could be caused by the increase in the defect states associated with the CO gas molecules [25]. In order to obtain a clear distinction between two conduction mechanisms, Mott and Davis [26] have suggested that the pre-exponential factor in equation (4) for conduction in the localized states should be two to three orders lower than the conduction in the extended states, and should become still lower for the conduction in the localized states near the Fermi level. Thus, in the present system, the value of pre-exponential factor (σ_0) is of the order of unity. On the basis of this value of σ_0, it is suggested that the conduction is taking place in the band tails of localized states. A significant change in the value of σ_0 is observed after exposing this MWNTs sensor to CO gas. This may be explained by using the shift of Fermi level after exposure to different concentration CO gas. Therefore, the change in the value of σ_0 may be due to the change in Fermi level with exposure of CO gas.

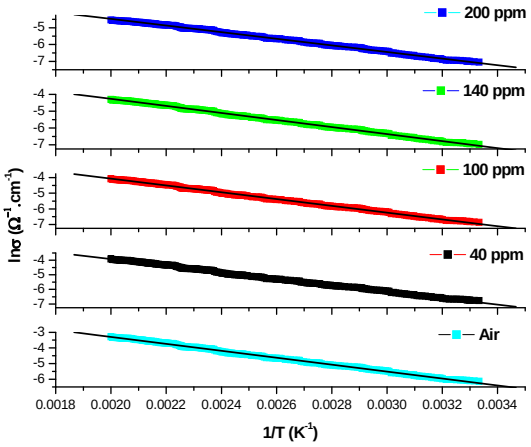

Fig. 8. lnσ versus 100/T for the Co-catalyzed MWNTs-based film sensor in air and 40, 100, 140 & 200 ppm CO gas for temperature range of (300-500K).

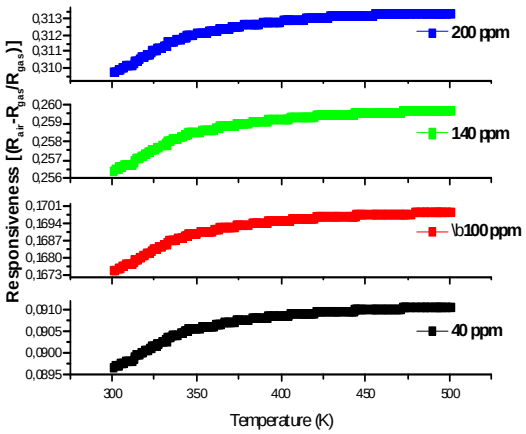

Fig. 9. Temperature dependence of responsiveness for the Co-catalyzed MWNTs-based film sensor in air and 40, 100, 140 & 200 ppm CO gas for the temperature range of (300-500K).

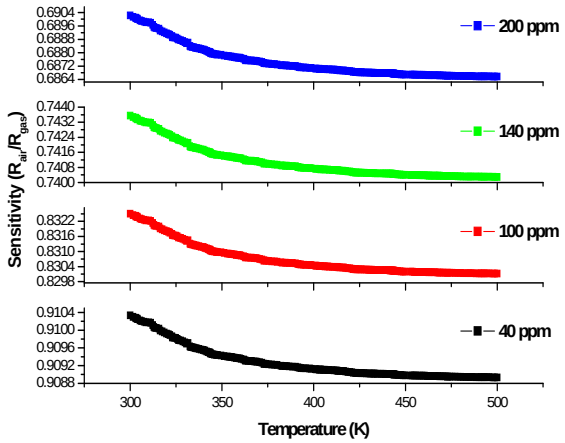

Fig. 10. Temperature dependence of sensitivity for the Co-catalyzed MWNTs-based film sensor in air and 40, 100, 140 & 200 ppm CO gas for the temperature range of (300-500K).

Fig. 9 presents the variation of responsiveness with temperature for different gas concentration. It is observed that the responsiveness of the presently studied sensor increases with the increase in temperature, suggesting that the sensor gives good response even at higher temperatures. Fig. 10 shows the variation of sensitivity with the temperature for different CO concentration. It is found that the sensitivity decreases with the increase in temperature. This indicates that the currently studied Co catalyzed MWNTs become more hybridized at higher temperature, thereby resulting in the decrease in sensitivity.

4. Conclusion

The dynamic response of electrical resistance with time suggests that the resistance of this cobalt catalyzed multi-walled carbon nanotubes (MWCNTs) sensor increases with the increase in the gas concentrations. An overall increasing trend is observed for the response time ($\tau_{res.}$) and the recovery time ($\tau_{rec.}$) with increasing gas concentration. This increase in response time ($\tau_{res.}$) and the recovery time ($\tau_{rec.}$) of this sensor with the increase in gas concentration may be due to the fast adsorption/desorption process of gas molecules on MWNTs. The sensitivity of multi-walled carbon nanotubes (MWCNTs) gas sensor decreases from 86.08% to 74.07% and the responsiveness increases from 46.45% to 59.49% as the gas concentration increases from 40 ppm to 200 ppm. Therefore, it is suggested that this MWNTs sensor gives a good response to the different gas concentration. From the temperature dependence of conductivity of this MWNTs sensor, it is observed that the conduction is though a thermally activated process in the band tails of localized states. The responsiveness of this sensor increases with the increase in temperature, whereas the sensitivity decreases for all the concentration of CO gas.

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