

# Study of plasma polymerized nanocrystalline thin film for detection of CO

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## Abstract

The key concern for environmental scientists is the detection and monitoring of hazardous species such as CO using quick, cost-effective, and highly specific equipment. The present detection methods are either indirect or time consuming and costly. These sensors work at high temperatures and have a very sluggish reaction time. Nanocomposite polymeric combinations have however shown to be effective sensors for detecting dangerous gases. Nanocomposite copolymers of aniline and formaldehyde produced by chemical polymerization using Fe-Al metal complexes have been discovered to be very selective and effective CO sensors. Thin films of Fe-Al doped nanocomposite copolymer evaporated under high vacuum on diverse substrates such as mica and glass were found to have good stability, sensitivity, selectivity, and a quick response reaction to CO vapors in the air. Optimization of doping (Fe-Al) in nanocomposite copolymer during synthesis results in high stability, sensitivity, selectivity, and specificity. These sensors are designed to work at ambient temperatures. This paper describes the production, optical, electrical, and structural characterization, and behavioral acceptance test on the gas detecting properties of these CO sensors.

**Keywords:** Copolymer; Semiconducting; Nanocomposite, Plasma, Thin film,

## 1. Introduction

Carbon monoxide (CO) is classified as a hazardous gas. The CO is generated widely, semiconductor, and chemical industries [1, 2]. It has been recognized as a workplace hazard with a short term exposure limit of 5 ppm. Because of the hazardous qualities of CO in both gaseous and aqueous forms, there is a high need for the detection of CO gas concentrations at sub-parts per million (ppm) levels.

The CO is a poisonous gas that is hazardous to both human health and the environment. It is produced by a number of sources, including power stations, industrial facilities, and automobiles. CO has been linked to respiratory issues, heart disease, and other health issues. It can also harm plants and contribute to acid rain.

As a result, it is critical to create sensitive and dependable sensors for CO detection. One potential sensing technology is plasma polymerized nanocrystalline thin sheets. These films are created by plasma polymerizing a thin layer of nanocrystalline material onto a substrate. The metal oxides, semiconductors, and polymers all these varieties of materials of may be used to create a nanocrystalline material.

There are advantages of using plasma polymerized nanocrystalline thin films over other forms of gas sensors. Such sensors are extremely sensitive to presence of CO and can function at variety of temperatures. Further these are also quite cheap to manufacture.

Currently existing CO detection technologies rely on sample drawing and analysis. These approaches are time-consuming, complex, and costly. The solid state sensors on the market are designed to work at high temperatures [3-6]. As a result, it is critical to monitor the amount of SO<sub>2</sub> in the location/area using a quick, easy, and cost-effective manner. As an alternative, there has recently been a notable increase in the creation of electro-active semiconducting polymer thin films for CO gas detection [7]. Electronic sensing devices based on polymeric semiconductors are an appealing alternative to traditional inorganic sensing devices due to possible cost savings, easier packaging, ease of processing, and compatibility with flexible substrates. The modifications in the doping level of the base polymer can alter the conductivity of these polymers from insulator to conductor [8-14]. Semiconducting thin films of aniline-formaldehyde nanocompolymer combined with iron and aluminum oxides were shown to have great sensitivity and selectivity, as well as a quick response when exposed to CO, and may be utilized to make sensors. The sensitivity of a sensor  $S_e$  is defined as the ratio of the magnitude of conductivity after gas exposure ( $S_e$ ) to that before gas exposure ( $S_o$ ). The great sensitivity and selectivity, as well as the quick reaction time, are obtained by appropriately changing the stoichiometric composition of the dopant. This paper describes the fabrication, characterization, and behavioral acceptability testing of plasma polymerized thin film CO gas sensors.

## **2. Experimental**

### **2.1. Materials**

Materials often employed in the manufacture of plasma polymerized nanocrystalline thin films for CO detection include:

The substrate is the substance over which the thin film is to be laid on. It is critical to select a substrate that is compatible with the plasma polymerization process and possesses desirable qualities related to electrical conductivity and thermal stability. Silicon, glass, and metal oxides are all common substrates.

Nanocrystalline substance: The sensor's sensing element is nanocrystalline material. It is in charge of detecting the presence of CO and producing a signal. Metal oxides, semiconductors, and polymers are common nanocrystalline materials utilized for CO detection.

For plasma polymerization a gas is utilized to generate the plasma that deposits the nanocrystalline material onto the substrate. Styrene, vinyl acetate, and nitrogen are common plasma polymerization gases. The particular materials utilized will be determined by the type of nanocrystalline material employed and the intended sensor qualities. If a metal oxide nanocrystalline material is utilized, for example, the plasma polymerization gas will normally be nitrogen. When using a polymer nanocrystalline material, the plasma polymerization gas is styrene or vinyl acetate.

Aside from the components listed above, a range of additional materials may be employed in the manufacture of plasma polymerized nanocrystalline thin films for CO detection. Electrodes, for example, can be put on the film to increase its electrical conductivity. To preserve the film from environmental damage, a protective coating may be added.

Here are some particular materials utilized in the manufacture of plasma polymerized nanocrystalline thin films for CO detection:

### **2.1.1. Substrates**

Silicon, glass and metal oxides (e.g., alumina, titania) as substrate.

### **2.1.2. Nanocrystalline materials**

Metal oxides (e.g.,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{WO}_3$ ), semiconductors (e.g.,  $\text{CdS}$ ,  $\text{GaAs}$ ), and polymers (e.g., polyaniline, polypyrrole) are examples of nanocrystalline materials.

### **2.1.3. Plasma Polymerization gas**

Styrene, vinyl acetate, and nitrogen are the plasma polymerization gases.

Aniline used was distilled twice, and the chemicals formaldehyde, CO, sodium hydroxide,  $\text{FeCl}_3$ , and  $\text{AlCl}_3$ , were analytical grade reagents that were used as purchased.

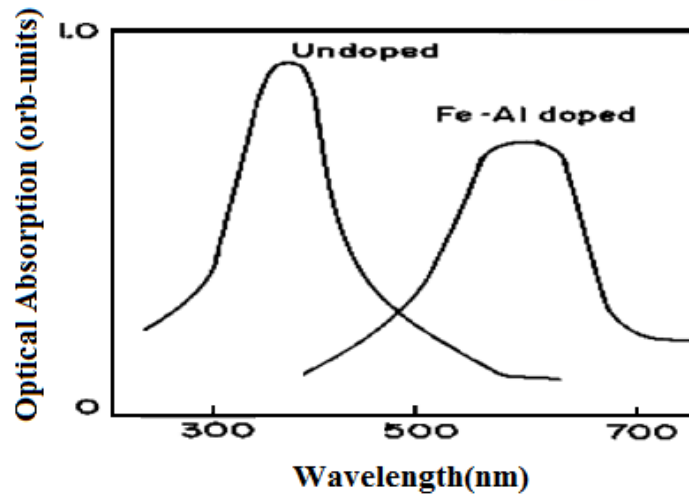
## **2.2. Synthesis of (aniline and formaldehyde) nanocomposites copolymer**

Using a synthetic approach which is previously described [12, 15], Fe-Al doped nanocomposites were generated in an aniline formaldehyde copolymer matrix. To generate a transparent solution of aniline hydrochloride, an aqueous solution of aniline (0.1 M) and hydrochloric acid (1 M) were mixed in 100 ml distilled water. This solution was mixed with a 35% formaldehyde solution for 2 hours at room temperature [16]. The resulting solution was left to stand until it turned a deep crimson hue. The solution was then combined with a second solution made by dissolving 9.6 g of anhydrous  $\text{FeCl}_3$  and 0.4 g of anhydrous  $\text{AlCl}_3$  in 50-100 ml of distilled water [17]. The resulting mixture was agitated for 50 minutes before being placed into a 10% NaOH solution. The resulting yellowish brown precipitate was filtered and rinsed with distilled water until it was alkali-free, and then dried. The resulting powder was used to make copolymer pellets. The pellets were employed for evaporation onto diverse substrates such as glass, mica,

and others at a high dynamic vacuum of 10K 5Torr. Thermal evaporation of the powder copolymer via the process of evaporation, conduction, and re-polymerization of polymer was used to create the films [11, 13, 17-21]. The film thickness was measured using a quartz thickness meter. The sensor element's size was optimized and regulated by suitable masking. The current-voltage (I-V) characteristics of these materials were examined in metal/polymer/metal sandwich and lateral structure configurations after CO exposure. The unique shift in current-voltage characteristics was used to subjectively and quantitatively identify CO.

## **Results and discussion**

The thermogravimetric analysis (TGA) of polyaniline formaldehyde powder copolymer with Fe-Al ratio (95:5) by weight polyaniline-formaldehyde copolymer in the temperature range 60-360°C shows that the copolymer dissociates and decomposes when heated beyond 280 °C. To preserve the conjugation of the polymer chain, the rate of evaporation is kept low (10 A/min) and the temperature of evaporation is kept below the decomposition temperature. This indicates that, in order to preserve the copolymer structure, thin films should not be heated over 270 °C while being prepared under vacuum. To generate a thin layer of copolymer, this powder was progressively heated at temperatures ranging from 165 to 175 °C under a high dynamic vacuum of 10K 5 Torr onto thermally appropriate substrate glass and mica. This process of evaporation, deposition, condensation, and re-polymerization lasted roughly 2 hours since the evaporation rate was kept low (10 A /min). For GPC, the molecular weight of the polyaniline copolymer was estimated to be 16,320. Ideally, a plasma layer should be more insulating and have a lower molecular weight, but in this situation, the observed higher molecular weight can be attributed to the presence of dopants Fe-Al [21]. This resulted in stoichiometrically homogeneous thin copolymer films on a glass substrate. For the preparation of sensing components of varying sizes, several masks were employed. The optical, electrical, and structural characteristics of the films were investigated [22, 23]. Figure 2 depicts the optical absorption spectra of undoped and Fe-Al doped (95:5) nanocomposite copolymer thin film in the 200-800 nm regions. The undoped nanocomposite thin film's optical absorption spectra show absorption at 375 nm [11, 15, 17]. When this nanocomposite is doped with Fe-Al (95:5), the peak moves to 625 nm. When doped with metal complex, the optical absorption peak broadens as well. This discovery suggests that doping the copolymer has a significant influence on the optical and hence on electronic properties of the copolymer, which are directly connected to charge carriers and polymer properties.



**Fig.1.UV-visible spectra of nanocomposite thin film.**

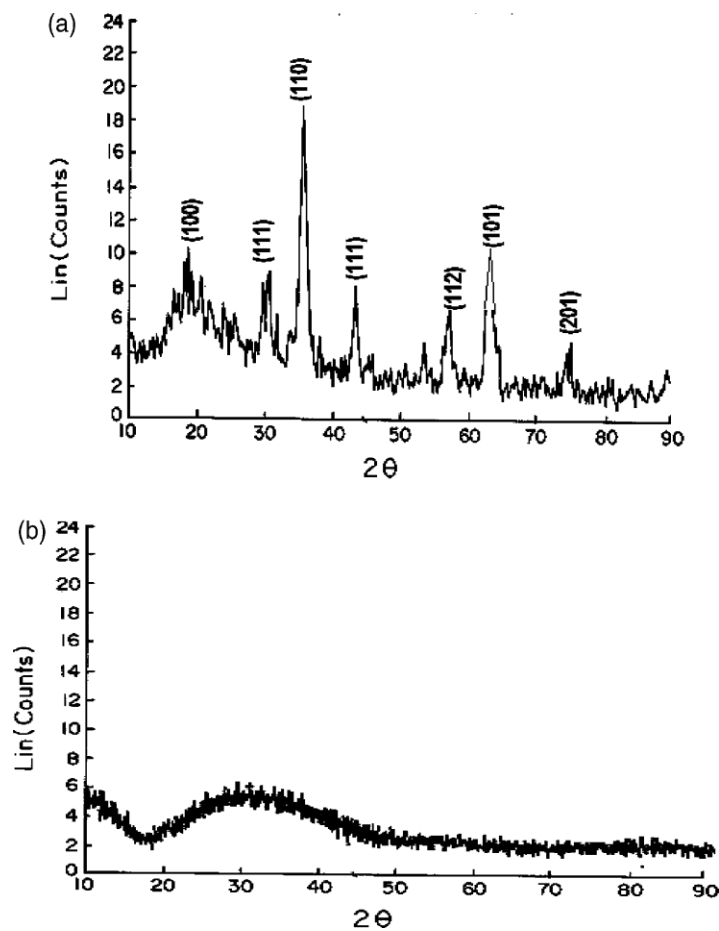
Doping with Fe-Al had a notable influence on the absorption spectra, lowering absorption and significantly moving the absorption peak to 625 nm. Plasma semiconducting copolymer thin films are created via evaporation-condensation-repolymerization of the base material, as well as modification of the conjugation by the dopant [11, 13, 15]. The X-ray diffractograms of Fe- Al doped and undoped polyaniline copolymer thin films on glass is shown in Figs. 3(a) and (b). Peaks in (a) indicate a high degree of crystallinity (peaks for Fe at  $35/2q$ ). The thin film's basal structure appears to be amorphous, but the existence of a high number of peaks indicates the presence of tiny crystals potentially generated around nanocomposite. The Fe-Al doped polyaniline thin film clearly displays the development of crystallization in the film. The presence of a Fe-Al ion complex composite in the polyaniline matrix caused crystallization. The XRD results show that Fe- Al doping is critical for increasing the sensitivity of polyaniline thin films. The X-ray diffraction of an undoped polyaniline thin film formed on glass is shown in Fig. 3(b). The X-ray diffraction pattern is characteristic of a polyaniline film that is entirely amorphous.

SEM was used to examine the surface topography of a metal complex doped with aniline and formaldehyde (Fe- Al). The SEM micrographs (Fig. 4(a) and (b)) show distinct form crystallites with a considerable range in size (b) and without doping (a). This establishes the thin film's nanocrystallite. SEM micrographs show that the grains in the Fe-Al doped polyaniline film are tiny, whereas the deposition of pure polyaniline thin film is smooth and homogeneous. EDAX determined the quantitative analysis of components present in thin films to ensure that the base material stoichiometry is transmitted to thin film. The film was EDAX analyzed, and the elemental composition is presented in Table 1.

For evaporation, the closely similar elemental analysis of the base composite powder was employed. The evaporation, condensation, and re-polymerization processes utilized to

generate this nanocomposite thin film do more than just transmit the polymer conjugation.

Figure 5 depicts the sensor structure. To prepare sensors, glass substrates 1x1 cm<sup>2</sup> were thoroughly cleaned with trichloroethylene, methanol, and distilled water using an ultrasonic technique. Vacuum evaporation of doped and undoped polyaniline resulted in thin films of thickness ( $\approx 1000$  Å) covering the whole surface of the glass plate. Plasma gold contacts were installed on the films.

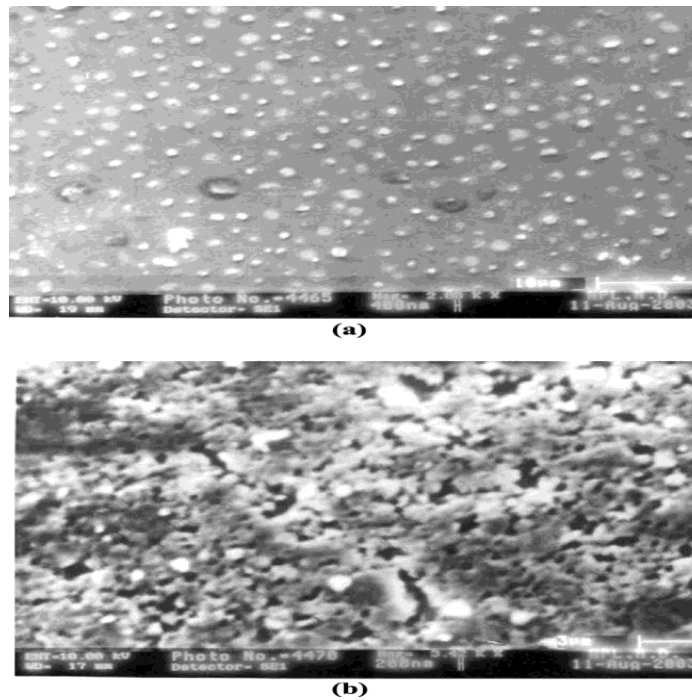


**Fig.2. (a) and (b) X-ray diffraction of polymeric thin film.**

**Table1**

**EDAX elemental composition of doped copolymer**

|       |        |
|-------|--------|
| Total | 100.00 |
|-------|--------|



**Fig.3. (a) and (b) Surface topography of the thin film sensor.**

The thin film sensor's sensitivity has been tested as a function of changes in the conductivity of the film after CO exposure. As a result, the sensitivity  $S$  may be defined as the ratio  $se/s_0$ , where  $se$  is the conductivity after CO exposure and hence the dark conductivity. Figure 6 depicts the change in conductivity of the polymeric thin film after exposure to CO at concentrations ranging from 0.01 to 100 ppm, as well as the voltage across the sensor. The highest change in conductivity may be observed at a voltage of 3.5 V. This is due to the fact that significant current flows are permitted by lowering intercrystallite grain barriers at 3.5 V, which appears to be an ideal working voltage for this design. This 5.5 V curve has been seen experimentally to begin at the value depicted in Fig. 6. Because of the crossing of the intercrystalline barrier at this field value, the conductivity increases. Under these conditions, a sensitivity of around 800 was selected.

Figure 4 depicts the reaction time of these polymeric sensors with changing CO concentrations ranging from 0.2 to 20 ppm. The CO gas was combined with air before being sent through the sensor. Within around 5 seconds, there was an initial surge, then saturation was attained. The gas flow was then interrupted, and the sensor's current output dropped exponentially. As a result, the overall time was around 8-10 s. The sensor's current output increases proportionally as the amount of CO gas increases, as does the reaction time. However, one sensor specimen remained steady during operation, and the reaction time did not rise. The sensor may be reused once the current output decayed, with a base value of 5-10 s. This means that there is no chemical interaction between and the polymeric thin films, simply physical CO adsorption on the copolymer. This is backed further by the fact that the gases they are exposed to alter the oxides, as oxide-based sensors typically work at temperatures ranging from 250 to 300 8C. The copolymers of a nanocomposite thin film sensor function at room temperature with no chemical interaction between the polymer and the gas. As previously stated, the sensitivity of polymeric thin film sensors results from physical absorption of the gas, which is afterwards disorbed, resulting in a rapid recovery of the sensor's initial stage. Polymeric sensors can therefore be reused and stable for several years (thousands of charge discharge cycles). The polymers are non-biodegradable, have a low environmental impact, and are hence stable.

Plasma polyaniline copolymer is semiconducting and behaves as a p-type semiconductor. The hopping transport of polarons and bipolarons causes conduction in copolymer thin films. In a sensor arrangement, polarons and bipolarons are mobilized by the action of an electric field. These charge carriers travel inside the chain, across the chain, and via intercrystallites. Conduction occurs in copolymer thin films by charge carriers passing across via the intercrystallite boundaries (Fig. 8), which act as a charge barrier [18, 19]. When this thin film is exposed to CO, the barrier height at the intercrystallite grain boundary decreases, resulting in an increase in charge carriers flowing through the intercrystallite grain borders and a rise in current output. The amount of gas absorbed by the thin layer and hence the increase in sensor output is directly proportional to the reduction in barrier height [20].

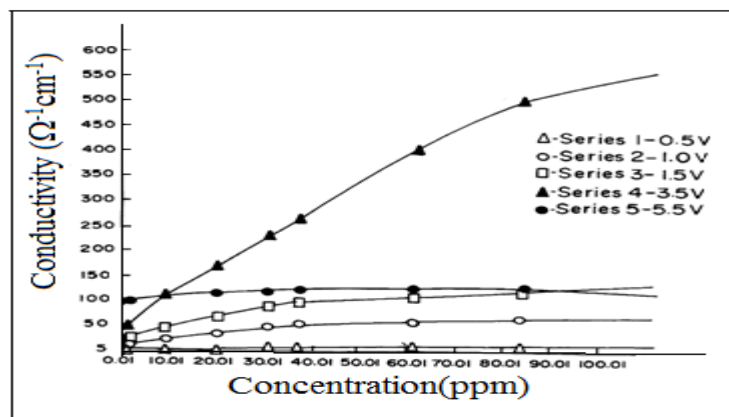
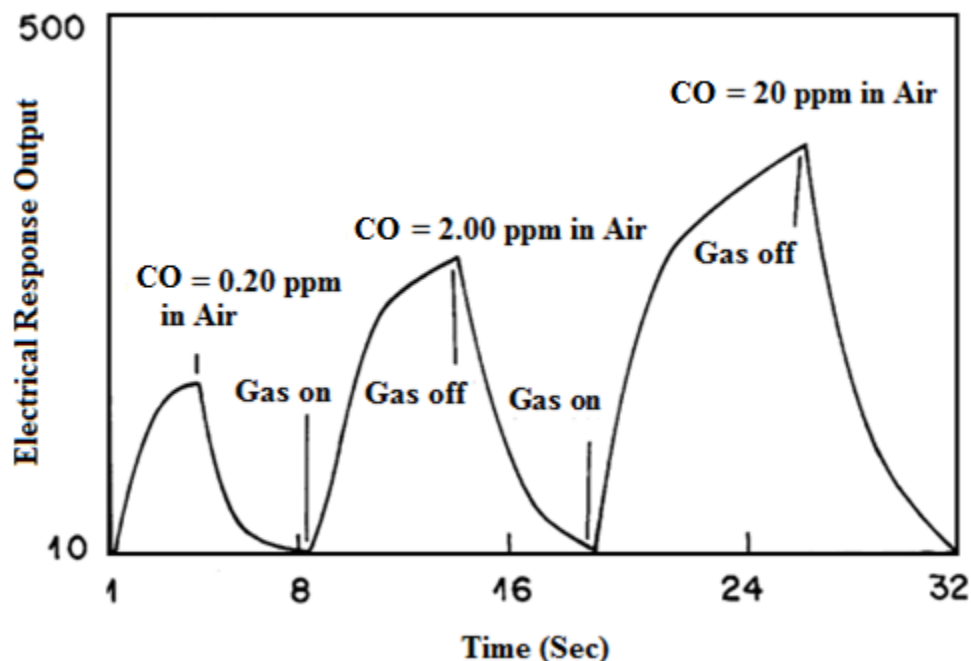


Fig. 4. I-V characteristic of the sensor.

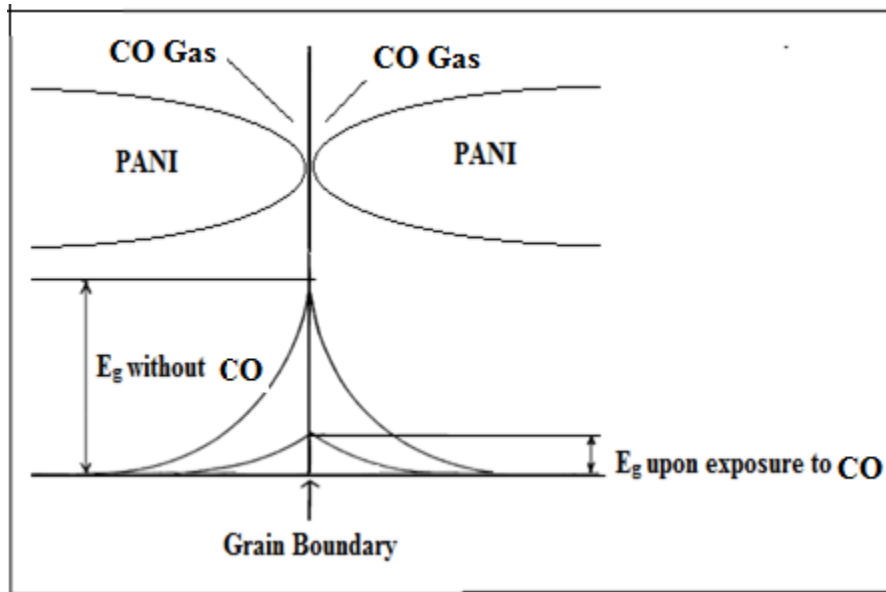


### 3. Conclusion

Plasma deposition may be used to create high-quality doped polyaniline copolymer nanocomposite thin films. These films have the potential to be effective sensors for the detection of harmful gases such as CO. These nanocrystalline coatings acts like granular metallic crystallites immersed in a nonconductive medium. By appropriately doping the polyaniline during synthesis, high sensitivity (order 400-800), specificity, and selectivity may be attained. A stoichiometric composition of Fe-Al (95:05) has been discovered to be appropriate for CO detection. The sensor has a reaction time of around 10 seconds, whereas inorganic sensors (oxide base) have a response time of roughly 1-2 minutes. Because there is no chemical interaction between the polyaniline thin film and the gas, the sensor is reusable. The sensor operates at room temperature and does not require heating of the sensor materials, which significantly increases the sensor's lifespan. According to the behavioral acceptability tests, plasma polyaniline thin film sensors are best suited for online detection and continuous monitoring of CO. The sensors can be placed remotely to offer an audiovisual alert when CO levels exceed the safety limits. We've created sensors with varied compositions and doping that are sensitive and selectively specific to other gases. The findings of these sensors will be communicated as soon as possible.



**Fig.5.** Response time of the sensor.



**Fig.6.** Effect of exposure to CO on the grain boundary.

#### 4. References

- [1] De-Castro CSC, De-Azevedo ACP, Monteiro EEC, Pinho RR, De- Souza GGB. PolymDegrad Stab 2001; 71:233–7.
- [2] Zimmerling R, Dammgen U, Kusters A, Grunhage L, Jager HJ. Environ Pollut 1996; 91:139–45.
- [3] Supriyatno H, Yamashita M, Nakagawa K, Sadaoka Y. Sens Actuators B: Chem 2002; 85:197–204.
- [4] Martinelli G, Carotta MC, Ferroni M, Ferroni M, Traversa E. Sens Actuators B: Chem.1999; 55:99–110.
- [5] Kemp NT, Flanagan GU, Kaiser AB, Trodahl HJ, Chapman B, Partridge AC, Buckley RG. Synth Met 1999; 101:434–5.
- [6] Morales JA, Cassidy JF. Sens Actuators B: Chem 2003; 92:345–50.
- [7] Choi HJ, Kim JW, To K. Synth Met 1999; 101:697–8.
- [8] Macdiarmid AG, Chiang JC, Halpern M, Huang WS, Mu SL, Nanayakkara LDS, Wu W, Yaniger SI. MolCrystLiqCryst 1985; 121: 173–80.

- [9] Han JS, Bredow T, Davey DE, Yu AB, Mulcahy DE. *Sens Actuators B: Chem* 2001; 75:18–23.
- [10] Xu B, Choi J, Caruso AN, Dowben PA. *ApplPhysLett* 2002; 80: 4342–4.
- [11] Misra SCK, Ram MK, Panday SS, Malhotra BD, Chandra S. *ApplPhysLett* 1992; 61:1219–21.
- [12] Vadera SR, Tuli A, Kumar N, Sharma BB, Gupta SR, Chanda P, Krishan P. *J Phys IV* 1997;7:C-1549–C-1554.
- [13] Misra SCK, Beladakere NN, Pandey SS, Ram MK, Sharma TP, Malhotra BD, Chandra S. *J ApplPolymSci* 1993; 50:411–4.
- [14] Sharma SK, Misra SCK. *Int J Light Electron Opt (Germany)* 2002; 113:351.
- [15] Misra S C K, Pant R P, Pandey J, Kumar L N. *J Magn Magn Mater* 2002; 252:20–2.
- [16] Sharma DR, Mathur R, Vadera SR, Kumar N, Kutty TRN. *J Alloys Compd* 2003; 358:193–204.
- [17] Kajii H, Araki H, Yoshino K, Zakhidov AA, Onada M. *Synth Met* 1999; 103:2388–91.
- [18] Jeon D, Kim J, Gallagher MC, Willis RF. *Science* 1992; 256:1662–4.
- [19] Berggren M, Bergman P, Fagerström J, Inganäs O, Andersson M, Weman H, Granström M, Stafstrom S, Wennerstrom O, Hjertberg T. *Chem Phys Lett* 1999;304:84–90.
- [20] Misra S C K, Mathur P, Srivastava B K. *Sens Actuators A: Phys* 2004; 114:30–5.
- [21] Abe M, Ohtani A, Ohmoto Y, Akazuki S, Ezoe M, Higuchi H, Nakamoto K, Okunood A, Noda Y. *J ChemSoc, ChemCommun* 1989;1736–8.
- [22] R Kumar, S Singh, A.K. Mishra *J. Polym. Mater.* Vol. 27, No. 4, 2010, 369-377.
- [23] R Kumar, S Singh, A.K. Mishra *Journal of Minerals & Materials Characterization & Engineering*, Vol. 9, No.11, 2010, pp.997-1006,