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CHARACTERIZATION OF PLASMA POLYMERIZED NANOCOMPOSITE THIN FILMS FOR DETECTION OF SO_2

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ABSTRACT
Monitoring and detection of hazardous gases prevailing in the environment is a big challenge for environmental scientists. SO_2 is one of these gases to be monitored. Methods being used for its detection are time consuming and indirect. These methods are effective only at high temperatures, hence have limited applicability. Nanocomposite polymers have proved to be good detectors in several respects. Fe/Al doped polymer thin films prepared by plasma polymerization are found to be very good detectors. These films have wide application with different substrates. In this paper the preparation and characterization of such thin films is presented. Which is going to have wide acceptability for detection of SO_2 under different environments with changing conditions.

Keywords:
Nanocomposite, Polymer, Plasma Polymerization, Thin film.

1. Introduction
Sulphur dioxide (SO_2) is widely generated in chemical industries in manufacture of semiconductors [4,26] and in other social activities. Being hazardous it has harmful impact having exposure limit of 5 ppm (parts per million). As it is hazardous in gaseous as well as in aqueous forms, it is very much needed to detect it up to sub ppm levels.
Automobile industries, power stations, and industries etc. are other sources which produce SO_2. It is harmful to respiratory system, heart, lungs and different other health aspects. Plants are badly effected by it and also contributes to acid rain.
Looking into these it is essential to have sensitive sensors to detect SO_2. Plasma polymerization is a potential technique to create thin films by depositing thin layers of nanocrystalline materials on suitable substrate.
Polymers, semiconductors and metal oxides are different ingredients used for creation of nanocrystalline material.
Plasma polymerized nanocrystalline thin films used as sensors have advantage over other forms of gas sensors [9,10,18,19,20,23]. These can work in a wide range of temperature and are very sensitive to the presence of SO_2.
These are also cheaper in manufacture. Current sensing techniques for detection of SO_2 are based on sample drawing and its analysis, which are costly complex and time consuming. Solid state sensors available, work at high temperatures [3,8,12,17]. Hence it becomes crucial to locate and monitor SO_2 in the sites using easy, quick and cost effective methods. Recently electroactive semiconducting polymer thin films have notably being created as an alternative to sense and detect SO_2 [11]. Polymeric semiconducting devices are cost saving, compatible, easy in packaging and processing, fabricated with flexible substrates and present fruitful alternative over traditional inorganic sensors. Conductivity of polymers can be altered from insulator to conductor by altering doping level of base polymer [5,13,14,16,22,24,25]. When iron and aluminium oxides are added with aniline formaldehyde, nano

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co-polymer semiconducting thin films, show quick response, sensitivity and selectivity to the exposure of SO_2. These features lead to make sensors. The sensitivity of a sensor is the ratio of its conductivities after and before gas exposure. By appropriate change of stoichiometric composition of the dopant, amazing quick reaction time, selectivity and sensitivity are obtained. With all these recent features, this paper puts forward the fabrication of plasma polymerized thin films with their characterization in respect of their application as SO_2 gas sensors.

2. Experimental

2.1 Materials:

The ingredient materials used in the synthesis of nanocrystalline thin films by plasma polymerization for detection of SO_2, are-

There is a need of substrate over which the film is formed. It is very critical to select a substance which fulfills the desired qualities like thermal stability and electrical conductivity and compatible with the process of plasma polymerization. Metal oxides glass and silicon are common materials which fulfill the above mentioned qualities. While detecting the existence of SO_2 the nanocrystalline material produces a signal. Commonly used nanocrystalline materials for detection of SO_2 are polymers, semiconductors and metal oxides.

In the process of plasma polymerization in the reactor, a gas generates the plasma, which deposits the nanocrystalline material over the substrate. Nitrogen, Styrene, and Vinyl acetate are commonly used gases for this purpose. Selection of the material depends on the type of nanocrystalline material and qualities of sensors.

For example nitrogen is normally utilized as plasma polymerization gas for metal oxide nanocrystalline material and styrene is used as gas for polymer nanocrystalline material which we have used in our process.

In addition to above materials, other components may be utilized for manufacturing thin films for detection of SO_2.

An example of such components is the addition of electrodes with thin films to enhance their electrical conductivity. Protective coating is added to isolate the film from environmental influences.

Some particular materials suitable in the manufacture of nanocrystalline thin films for detection of SO_2 are given hereafter.

2.1(a) Substrates:-

Metal oxides (e.g. Alumina, titania), glass and silicon are uses as substrate.

2.1(b) Nanocrystalline materials:-

Commonly crystalline material are polymers (e.g. polypyrrole, polyaniline), semiconductors (e.g. GaAs, CdS) and metal oxides (e.g. WO_3, ZnO, SnO_2).Polyaniline (PANI) is the material in this process.

2.1(c)Plasma polymerization gas:-

The plasma polymerization gases are nitrogen, vinyl acetate and styrene.

Analytical grade of $AlCl_3$, $FeCl_3$, NaOH, SO_2, Formaldehyde and Aniline distilled twice.

3. Synthesis of nanocomposite copolymer of aniline

With the approach of early workers [14, 21], nanocomposites of aniline formaldehyde with Fe-Al doping were obtained. As plasma polymerization is a versatile technique with inherent advantages. The ionization of gaseous molecules through electronic impacts forming radical cations leads to the formation of the polymer. A transparent solution as 0.1M aniline and 1M HCl mixed with 100 ml distilled water and 9.6g anhydrous $FeCl_3$ and 0.4g anhydrous $AlCl_3$ is prepared [6,7]. This is mixed and vigorously stirred with formaldehyde solution.

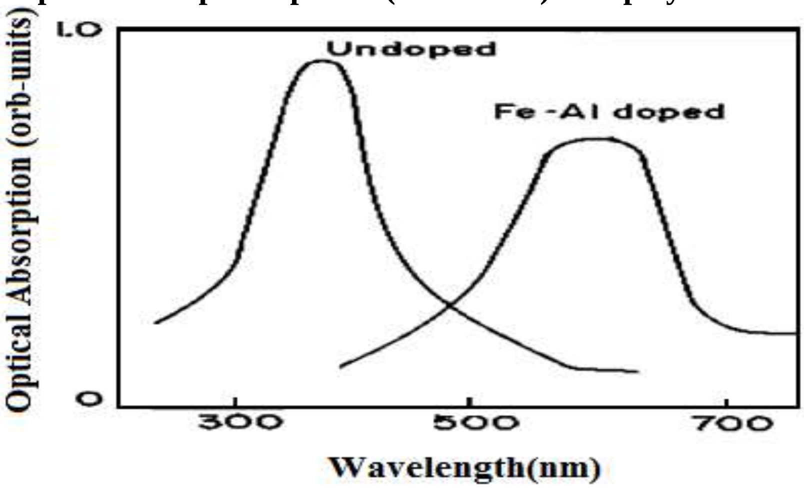
This solution was injected into the reaction chamber above anode which arrives in the plasma zone in vapour state, is distributed uniformly. The deposition of material over the glass substrate takes place in the form of thin film [1,2,6,15,22,24]. Quartz thickness meter was used to measure thickness of the film. The (I-V) characteristics of the prepared film were studied in metal/polymer/metal sandwich with the exposure of SO_2. These characteristics could be used for detection of SO_2 concentration in desired environment.

4. Result and discussion

In our process doping of Fe-Al in the ratio 95:5 by weight in the polymeric formaldehyde copolymer decomposes and dissociates beyond 280º C. To preserve polymer structure in the process of plasma deposition temperature should be below 270º C. To develop the film the copolymer was injected into the reactor chamber and plasma was generated. Film was deposited over glass substrate. Films were deposited first for undoped copolymer and then Fe-Al doped copolymer. Molecular weight of plasma layer should be low, we found it to be 16.320. This is due to the presence of heavier dopants of Fe-Al [1].

Electrical, structural and optical absorption characteristics are studied in our present work. Absorption spectra are depiction in fig.1, in 200-800nm region.

Fig.1. Optical absorption spectra (UV-visible) of copolymer thin films



The peaks are observes in undoped and doped copolymer at 375nm and 625nm with doping of Fe-Al in the ratio 95:5.

Figures 2(a) and (b) show the x-ray diffractograms of Fe-Al doped and undoped films. Peaks in the diagrams show high degree of crystallinity. The amorphous character is shown by thin films, however presence of small crystals around nanocomposite shows the existence of sufficient peak radicals. Increase in the crystalline character is expected due to Fe-Al doping. Fig.(2) shows x-ray diffraction patterns of entirely amorphous polyaniline composite film.

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

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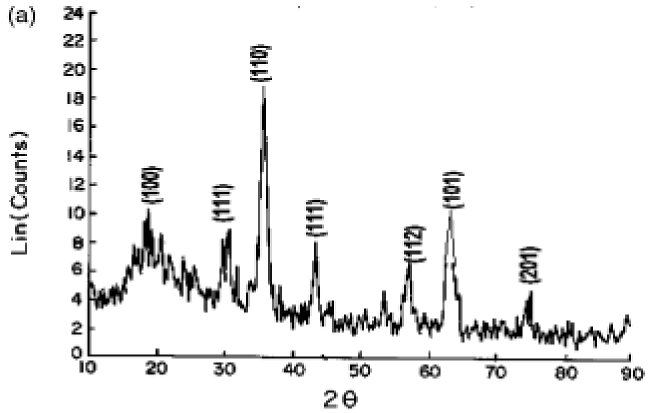
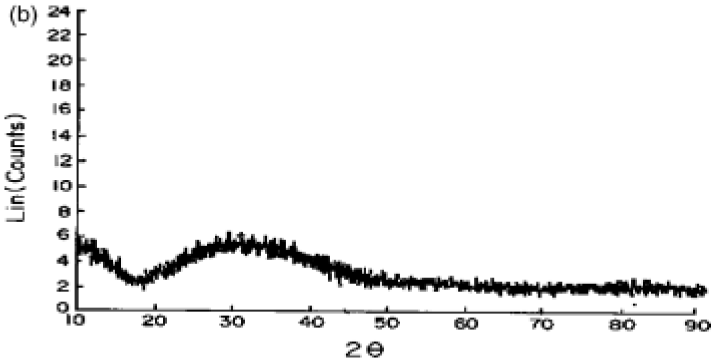




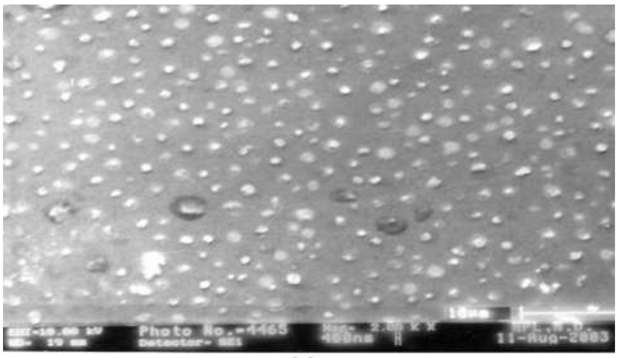
Structure of films is also characterized by Scanning Electron Microscopy (SEM) technique, the photographs of which are shown in fig.3(a) and 3(b) for doped and undoped films respectively. Both show crystallites distinct with considerable size and range. SEM results of Fe-Al doped variety show small size grains while for the undoped variety it is homogeneous and smooth. The analysis of relative quantities for various elements was done by EDAX, presented in table.1.

Table.1

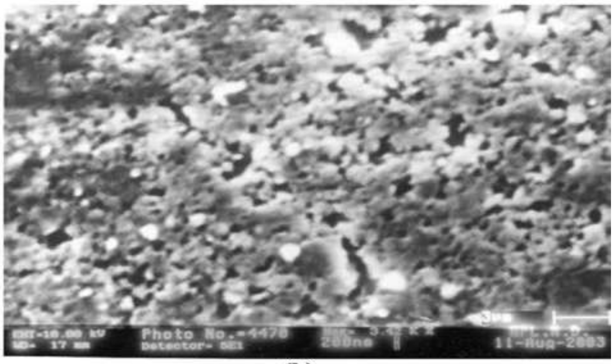
EDAX analysis of doped copolymer films

S. No.	**Element**	**Spect. Type**	**Element %**
1.	C	ED	59.43
2.	Fe	ED	18.65
3.	O	ED	16.85
4.	Cl	ED	2.66
5.	Al	ED	0.98
6.	Na	ED	0.50
7.	Ca	ED	0.36
8.	Si	ED	0.26
9.	Mg	ED	0.21
10.	Cu	ED	0.10
	Total		**100.00**

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



(a)



(b)

The glass substrate was thoroughly cleaned with trichloroethylene distilled water and methanol by an ultrasonic technique to preserve sensors. The sensor structure is depicted fig.5.

5. Fabrication of Sensor

Polymer thin films are prepared suitable for fabrication of sensors. Glass substrate properly cleaned with distilled water, methanol, and trichloroethylene are used for deposition of film around 1000A° in thickness. Electrodes were installed over the film covering entire glass surface.

Response and sensitivity of sensors:

Conductivity changes were tested for sensitivity of sensors for exposure of SO_2. The rates of conductivity after the exposure of SO_2(S_e) and before the exposure of the same(S_o) is called sensitivity factor i.e.

$$S = \frac{Se}{So}$$

For different concentrations of SO_2 in air ppm the I-V characteristics of the sensors is studied depicted in fig.4. DC Voltage is varied from 0.5V to 5.5V for different series from 1 to 5. Graph for series 4 at 3.5V shows highest selectivity which is because of significant currents flows due to lowering of inter crystalline grain barriers as 3.5V. Therefore 3.5V is proved as real voltage in respect of sensor. The sensitivity factor which is the measure of quality of sensor is as high as 800.

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

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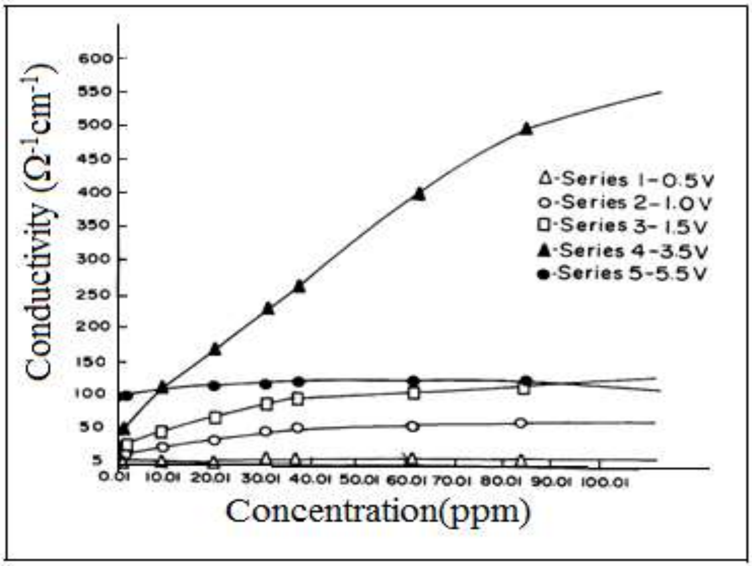
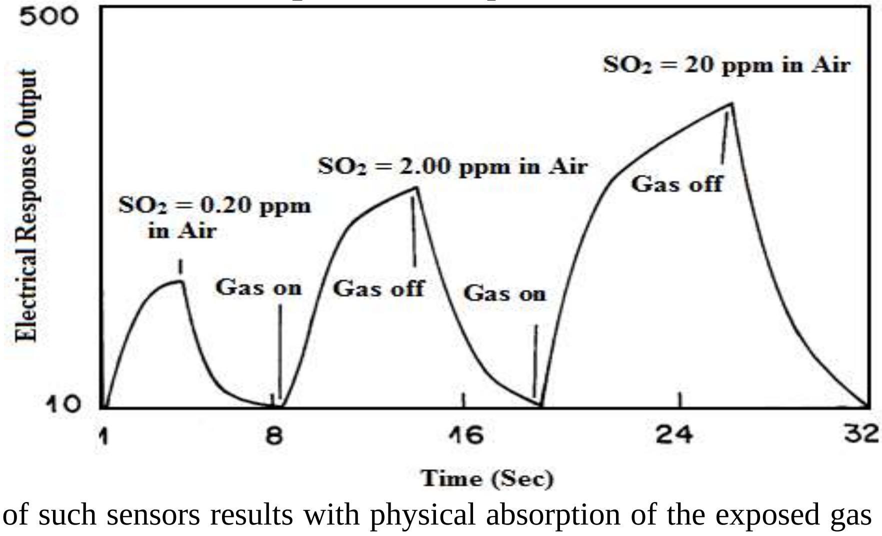


The reaction time of polymeric sensors changes with SO_2 concentrations. Fig. 5 depicts reaction time for concentrations 0.2 to 20ppm ofSO_2. Air SO_2 combination was used for sensing through the sensor. For initial 5 seconds an initial surge is observed before reaching saturation. After the gas flow was interrupted sensors current dropped exponentially resulting overall time around 8-10sec. With increase of SO_2 in air current output increases exponentially, also the reaction time. With steady sensor specimen reaction time did not rise. Reuse of sensor with current decay with 5-10sec shows there is no chemical reaction with thin film with sample absorption.

Fig.5. Sensor response time.



The sensitivity of such sensors results with physical absorption of the exposed gas on the surface of polymeric film. After de-absorption of gas the sensor is recovered. These observations show that sensors can be reused for years after different charge-discharge cycles. Being non biodegradable and having low environmental impact the polymers are stable. Behaviour of plasma polyaniline copolymer is as p-type semiconductor. The action of an electric field mobilizes polarons and bipolarons which travel across the chain via inter crystallite boundaries (fig.5) which act as charge barrier [2,15] with the exposure of SO_2 barrier height of this boundary decreases resulting increase in charge flow across grain borders and current output increases. Reduction of barrier height is directly related to amount of gas absorbed and sensor output.

6. Conclusion

As in our work described above polyaniline copolymer nanocomposite thin films are synthesized with high quality and better response. These films are very useful for the detection of harmful gases like

SO_2 by their fabrication as sensors. Film coatings work as granular metallic crystallites in nanoconductive medium. High sensitivity (order 400-800), selectivity and specificity may be achieved by proper doping of polyaniline in the process of synthesis. Fe-Al composition has been found very appropriate with (94:06) to (95:05) for the detection of SO_2. This stoichiometric combination is used to fabricate sensors which have reaction time around 10 seconds. Whereas inorganic sensors (oxide based) show response time around 1 to 2 minutes. These sensors are reusable and adapt at room temperature. Sensors life span is increased with this feature. The behavioural acceptability of plasma polymerized polyaniline film sensors suits, continuous monitoring of SO_2 and its online detection.
These sensors are useful for audiovisual alerts (remotely) for detection of safety levels and limits of SO_2. Our sensors have selectivity, sensitivity with varied composition of doping, useful for detection of other gases. With their wide application, the other response of these sensors will be brought into notice for the benefit of research and development in this field.

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7. References

[1] Abe M., Ohtani A., Ohmoto Y., Akazuki S., Ezoe M., Higuchi H., Nakamoto K., Okunood A., Noda Y. (1989) J ChemSoc, ChemCommun 1989, 1736–8.
[2] Berggren M., Bergman P., Fagerstro¨m J., Ingana¨s O., Andersson M., Weman H., Granstro¨m M., Stafstrom S., Wennerstrom O., Hjertberg T. (1999), ChemPhysLett 1999, 304:84–90.
[3] Choi H.J., Kim J.W., To K. (1999), Synth Met 1999, 101:697–8.
[4] De-Castro C.S.C., De-Azevedo A.C.P., Monteiro E.E.C., Pinho R.R., De-Souza GGB. (2001), PolymDegrad Stab 2001, 71:233–7.
[5] Han J.S., Bredow T., Davey D.E., Yu A.B., Mulcahy D.E. (2001),Sens Actuators B: Chem 2001, 75:18–23.
[6] Jeon D., Kim J., Gallagher M.C., Willis R.F. (1992), Science 1992, 256:1662–4.
[7] Kajii H., Araki H., Yoshino K., Zakhidov A.A., Onada M. (1999), Synth Met 1999, 103:2388–91.
[8] Kemp N.T., Flanagan G.U., Kaiser A.B., Trodahl H.J., Chapman B., Partridge A.C., Buckley R.G. (1999), Synth Met 1999, 101:434–5.
[9] Kumar R., Singh S., and Mishra A.K. (2010), "Electrical, optical and Structural Characterization of Polyaniline Thin Film Prepared by Pulsed-plasma Polymerization", J. Polym, Mater, Vol. 27, No. 4, 2010, 369-377.
[10] Kumar R., Singh S., and Misra A. K. (2010), "Development of NO_2 Gas Sensor Based on Plasma Polymerized Nanostructure Polyaniline Thin Film", Journal of Minerals and Materials Characterization and Engineering, Vol. 9,No. 11, 2010, pp.997-1006.
[11] Macdiarmid A.G., Chiang J.C., Halpern M., Huang W.S., Mu S.L., Nanayakkara L.D.S., Wu W., Yaniger S.I. (1985), MolCrystLiqCryst 1985, 121: 173–80.
[12] Martinelli G., Carotta M.C., Ferroni M., Ferroni M., Traversa E., (1999),Sens Actuators B: Chem. 1999, 55:99–110.
[13] Misra S.C.K., Pant R.P., Pandey J., Kumar L.N. (2002), J MagnMagn Mater 2002, 252:20–2.
[14] Misra S.C.K., BeladakereN.N., Pandey S.S., Ram M.K., Sharma T.P., Malhotra B.D., Chandra S. (1993), J ApplPolymSci 1993, 50:411–4.
[15] Misra S.C.K., Mathur P., Srivastava B.K. (2004), Sens Actuators A: Phys 2004, 114:30–5.
[16] Misra S.C.K., Ram M.K., Panday S.S., Malhotra B.D., Chandra S. (1992),ApplPhysLett 1992, 61:1219–21.

[17] Morales J.A., Cassidy J.F. (2003),Sens Actuators B: Chem 2003, 92:345–50.
[18] Nadekar B., Khollam Y.B., Shaikh S. F., Trimukhe A., Deshmukh R., Pandit B., and S. P. (2024), “Impact of plasma polymerized Iodine-Doped thiophene films for enhanced sensing response towards industrial VOCs”, Journal of Photochemistry and Photobiology, A:Chemistry 446 (2024) 115125.
[19] Nastase C., Prodan G., and Nastase F. (2022), “Plasma-Polymerized Aniline-Diphenylamine Thin Film Semiconductors”, Coatings 2022, 12(10), 1441.
[20] Park C-S., Jung E.Y., Jang H., and Bae G.T. (2019), “Synthesis and Properties of Plasma-Polymerized Methacrylate via the Atmospheric Pressure Plasma Polymerization Technique”, Polymers 2019, 11, 396.
[21] Sharma D.R., Mathur R., Vadera S.R., Kumar N., Kutty T.R.N. (2003),J Alloys Compd 2003, 358:193–204.
[22] Sharma S.K., Misra S.C.K. (2002), Int J Light Electron Opt (Germany) 2002, 113:351.
[23] Supriyatno H., Yamashita M., Nakagawa K., Sadaoka Y. (2002), Sens Actuators B: Chem 2002, 85:197–204.
[24] Vadera S.R., Tuli A., Kumar N., Sharma B.B., Gupta S.R., Chanda P., Krishan P. (1997), J Phys IV 1997, 7:C-1549–C-1554.
[25] Xu B., Choi J., Caruso A.N., Dowben P.A. (2002), ApplPhysLett 2002, 80: 4342–4.
[26] Zimmerling R., Dammgen U., Kusters A., Grunhage L., Jager HJ. (1996),Environ Pollut 1996, 91:139–45.