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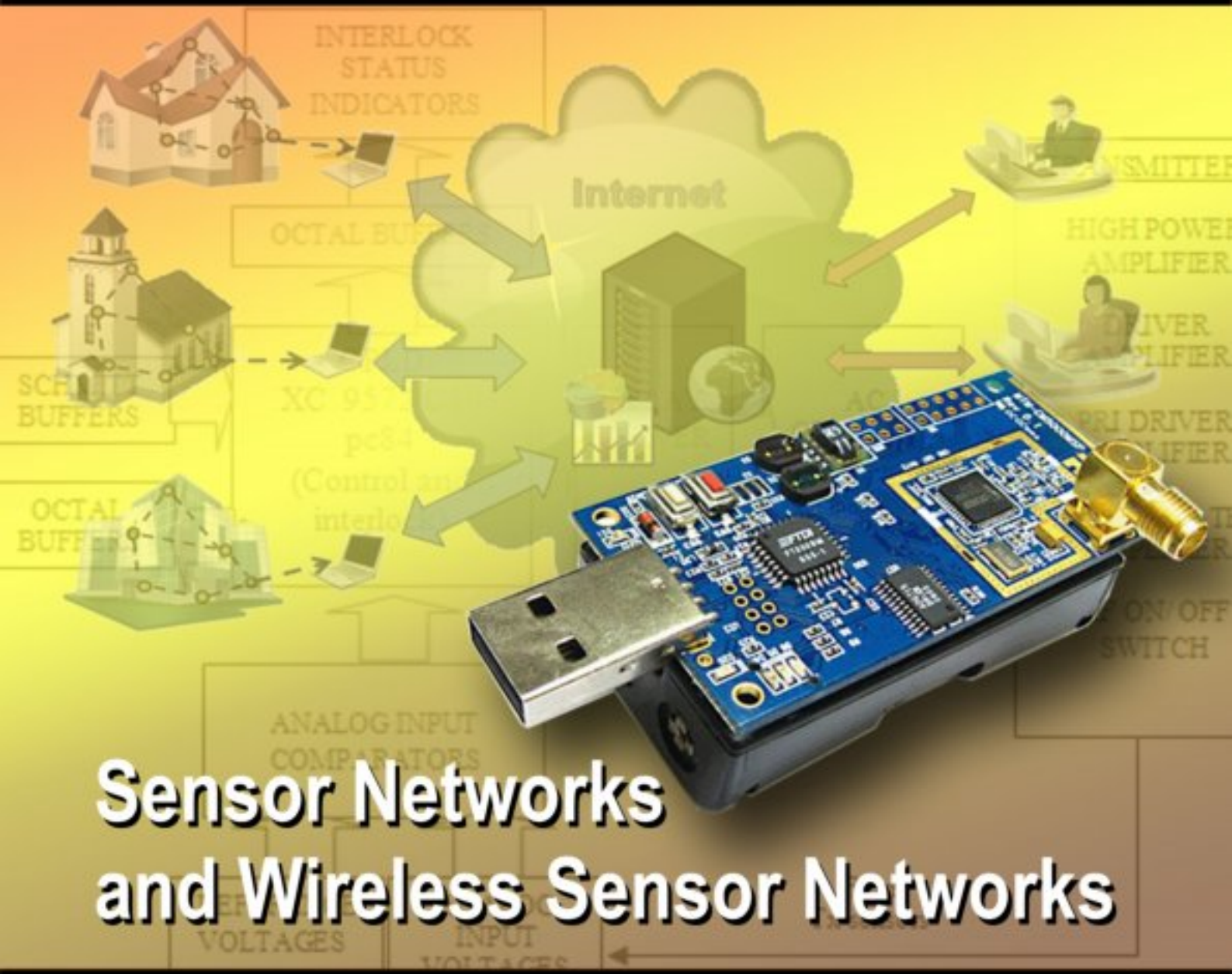

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Improvement in the Sensitivity of PbO Doped Tin Oxide Thick Film Gas Sensor by RF and Microwave Oxygen Plasma Treatment

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Abstract: In the present work efforts have been made to analyze the effect of oxygen plasma and PbO doping on the sensitivity of SnO_2-based thick film gas sensor for methanol, propanol and acetone. The effect of substrate temperature on the response of dual frequency (RF and microwave) plasma treated thick film sensor array has also been studied. To achieve this, three sensor arrays (each with four tin oxide sensors doped with different (1 %, 2 %, 3 % and 4 % PbO) concentrations) were fabricated by thick film technology and then treated with oxygen plasma for various durations (5 min, 10 min. and 15 min.). The plasma treated sensors were found to possess appreciably high sensitivity at room temperature in comparison to untreated sensor. The sensitivity showed the increasing trend with plasma exposure time and 15 minutes exposure time was found to be most suitable as the sensitivity of the plasma treated sensors for this duration were high towards all the chosen vapors with maximum (97 %) value for propanol. The sensitivity of the sensors were found to be increasing gradually as PbO concentration was varied from 1- 4%. *Copyright © 2010 IFSA.*

Keywords: Tin oxide, Thick film, Sensitivity, Oxygen plasma, Microwave

1. Introduction

Chemical sensors have attracted considerable attention owing to their application in environmental and safety control of gases. Semiconductor metal oxide sensors are the most promising due to simple

implementation, low fabrication cost, fast sensing response and adaptability to a wide variety of toxic and inflammable gases [1–3].The thick film technology is most widespread for industrial applications because its costs are lower when small/medium series of sensors are fabricated [4]. Additionally, thick film technology is more flexible when small amounts of catalysts or sensitizers need to be included in the gas sensitive film [5-7].

SnO_2 is a representative gas sensing material [8]. There has been intensive research on improving the gas sensitivity and selectivity by controlling the particle size [9], nano-structures [10, 11], sensing temperature [12], surface structure [13], and catalysts [14].

A thick film tin oxide gas sensor operates on the principle of change in the conductance due to chemisorptions of gas molecules on the sensor surface [15]. For gas sensing, SnO_2 is heated to 200–450° C, and an electron depletion layer is formed near the surface of the nano-sized particles due to oxygen adsorption with a negative charge, which establishes the core (semiconducting)–shell (resistive) structure in each particle as well as the potential barrier between the particles [8]. After exposing the sensor to reducing gas, the negatively-charged surface oxygen is consumed in the oxidation of reducing gas and the released electrons are injected back to the semiconducting core region. This leads to a decrease in resistance as a function of the gas concentration. Nanosized SnO_2 particles are generally used to get the advantages of low operating temperature and high sensitivity [16, 17]. However, significant aggregation between nanosized particles is inevitable due to the Vander Waals attractions. This makes it difficult for a gas to diffuse through the nanoscale pores in the aggregates, which hinders the gas sensing reaction [18].

Treatment of the tin oxide sensor surface by various gas plasmas to improve the sensing performance is well known and has been attempted by the several workers [19-20]. Surface activation consists in grafting chemical functions (plasma active species) on the material surface in order to give it specific properties by varying its surface energy. For example, an argon–oxygen plasma leads to the grafting of polar and hydrophilic functions (oxygen groups), which increase the material surface energy [21] and consequently improves the sensing performance. However, RF plasma has been used by previous workers [19-20] for surface treatment.

In present work, an attempt has been made to utilize the microwave plasma in addition to RF plasma for surface treatment of sensor as microwave plasma has some unique features such as: high degree of ionization resulting in rapid growth rate, sustenance of plasma over a wide pressure range from as low as 10^{-5} Torr and development of low self bias at the substrate eliminating radiation damage due to ion bombardment [22]. Additionally, Single-frequency systems are generally limited in the amount of control over reaction kinetics where as dual frequency systems allow control of electron density and ion flow separately, thus enabling easier control over film parameters [23]. The aim of this work is to characterize and understand the effect of microwave oxygen plasma treatment on the sensitivity of PbO doped tin oxide thick film gas sensor array towards methanol, propanol and acetone.

2. Experimental

Tin oxide based gas sensors were fabricated by the thick film screen printing technique. The gas sensitive tin oxide paste was developed in our laboratory. The SnO_2 nanoparticles were synthesized using Sol-gel method. Here, pure SnO_2 powder was prepared by slow reaction of $SnCl_4.5H_2O$ with ammonia water (NH_4OH). After some time, tin hydroxide, in the white precipitated form, was obtained. The precipitate was then washed with distilled water so as to remove excess ammonium chloride. The precipitate is then filtered and dried in an oven at about 150 ^{0}C. The powder so obtained is the tin hydroxide which when calcined at 400 ^{0}C for four hours, yields the tin oxide desired for sensor development. Doped SnO_2 powder was obtained by mechanically mixing the appropriate

amounts of PbO. This mixture was ball milled for 15 hours to get homogeneous powder and was then sintered at 600 ^{0}C for 2 hours in a furnace. To get a proper paste, PbO-doped tin oxide powder was mixed with lead glass powder and the organic binder followed by ball milling for one hour, then α-terpineol and Diethyl glycol monobutyl ether were added to the mixture and kept at 80 ^{0}C for 24 hours. Three set of sensor arrays (each consisting of four different (1 %, 2 % 3 % and 4 %) PbO doped sensors) were prepared in our laboratory and they were exposed to oxygen plasma for three different durations of time (5 min., 10 min and 15 min.)

Oxygen plasma was generated at low pressure by using dual frequency PECVD (plasma enhanced chemical vapor deposition) system (made in National Physical Laboratory (NPL), New Delhi).The pressure in the chamber was maintained at 0.06 Torr and oxygen flow rate was kept at 99 sccm/min. The surface of the sensing layer was bombarded by oxygen plasma. The top electrode was driven by microwave power (200 W) operated at 2.45 GHz while the bottom electrode at which the substrate is kept was driven by RF power (20 W) operated at13.56 MHz The entire experiment was performed in an air ambient at a relative humidity around 40 %. The fabricated sensor was then exposed to varying concentration of acetone, methanol and propanol in a locally developed test chamber of volume 2047cm^3 having placed at the metal base. The change in resistance of sensor is measured using KEITHELY 195 A multimeter.

3. Results and Discussions

Fig. 1a-L show the experimental plot of sensitivity vs. the concentration for acetone methanol and propanol for different durations (5, 10 and 15 min) of O-plasma exposure for sensor arrays consisting of 1 %, 2 % 3 % ad 4 % PbO doped sensors at room temperature.

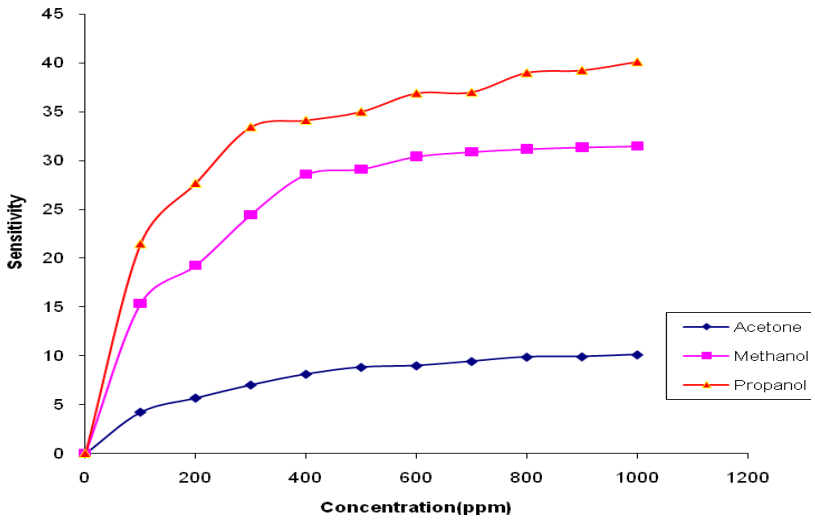

Fig. 1a. Sensitivity variation of O-plasma treated (200 W, 5 min) 1 % PbO doped sensor with concentration of methanol, propanol and acetone.

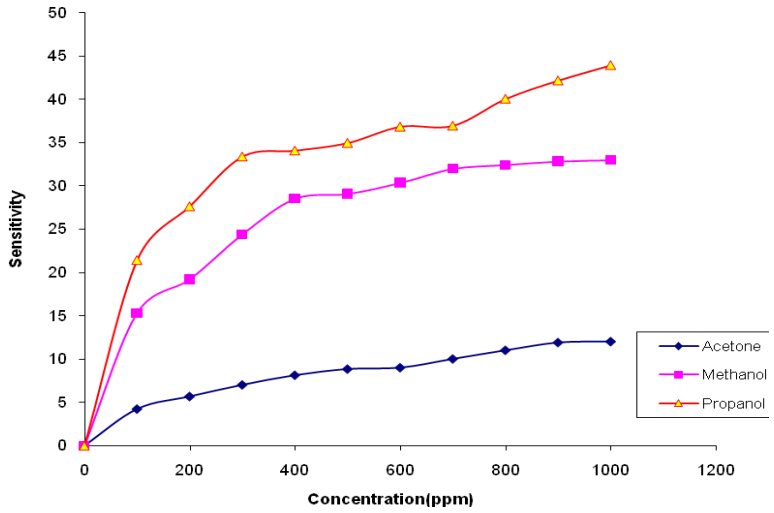

Fig. 1b. Sensitivity variation of O-plasma treated (200 W, 5 min) 2 % PbO doped sensor with concentration of methanol, propanol and acetone.

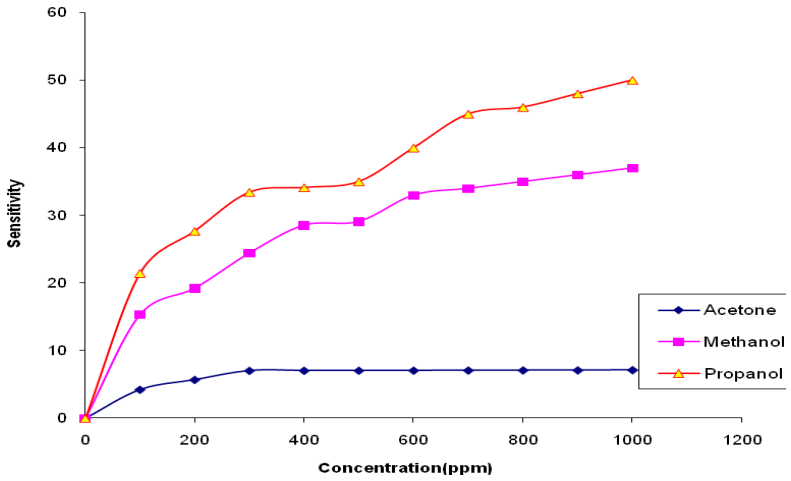

Fig. 1c. Sensitivity variation of O-plasma treated (200 W, 5 min) 3 % PbO doped sensor with concentration of methanol, propanol and acetone.

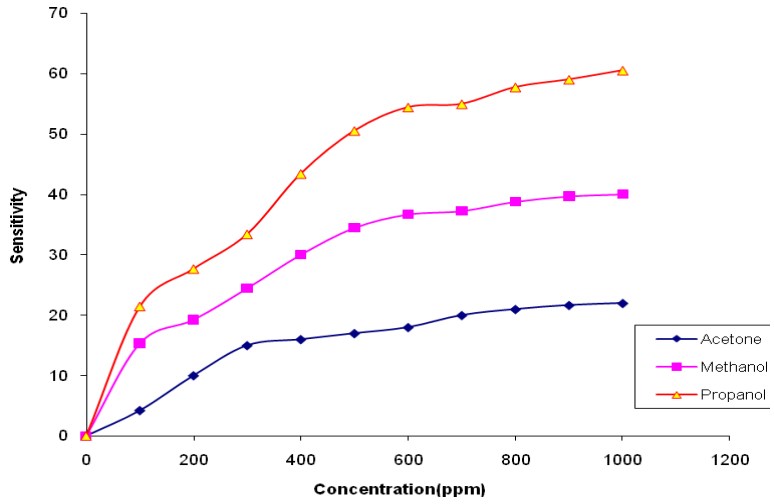

Fig. 1d. Sensitivity variation of O-plasma treated (200 W, 5 min) 4 % PbO doped sensor with concentration of methanol, propanol and acetone.

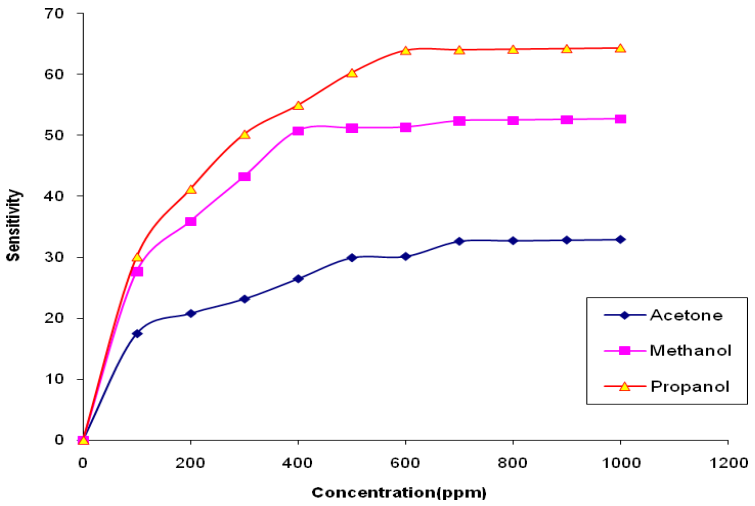

Fig. 1e. Sensitivity variation of O-plasma treated (200 W, 10 min) 1 % PbO doped sensor with concentration of methanol, propanol and acetone.

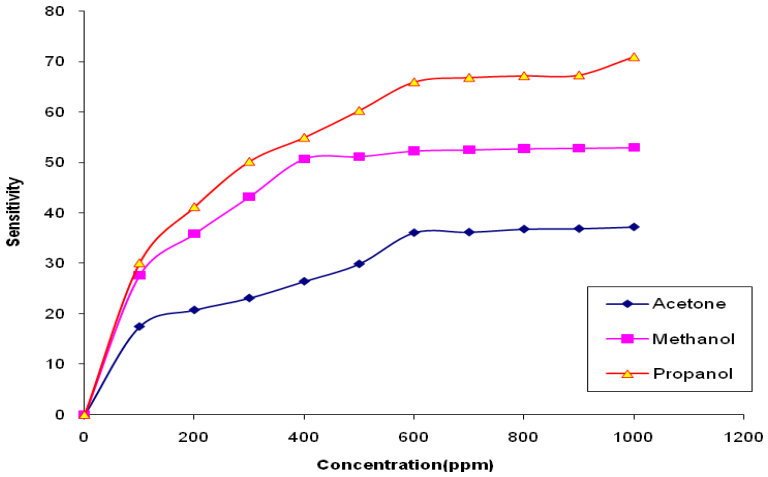

Fig. 1f. Sensitivity variation of O-plasma treated (200 W, 10 min) 2 % PbO doped sensor with concentration of methanol, propanol and acetone.

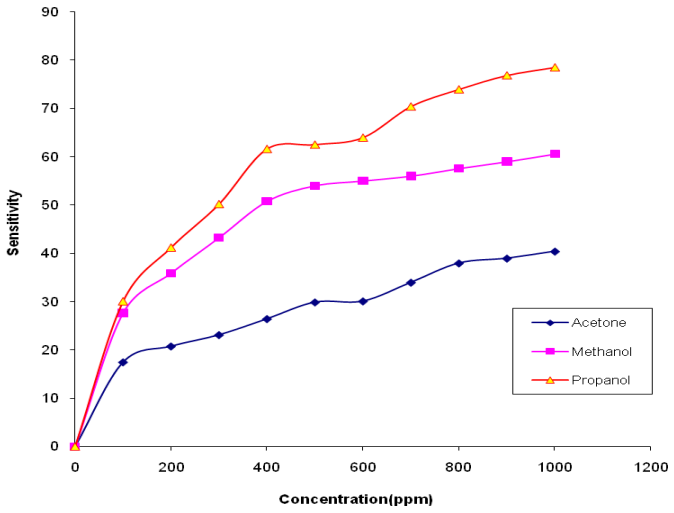

Fig. 1g. Sensitivity variation of O-plasma treated (200 W, 10 min) 3 % PbO doped sensor with concentration of methanol, propanol and acetone.

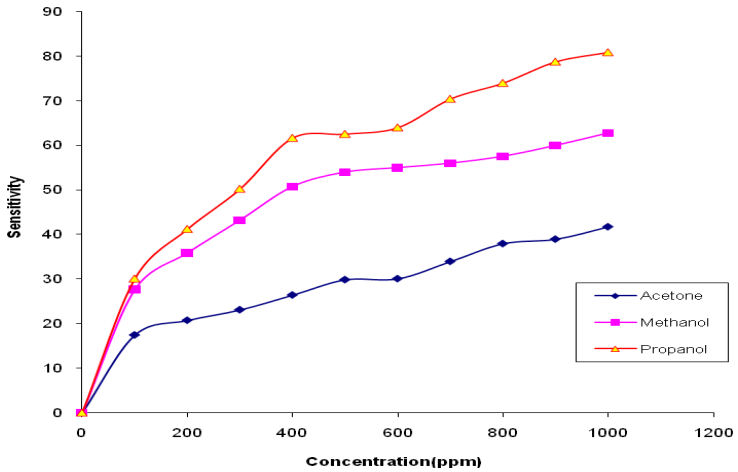

Fig. 1h. Sensitivity variation of O-plasma treated (200 W, 10 min) 4 % PbO doped sensor with concentration of methanol, propanol and acetone.

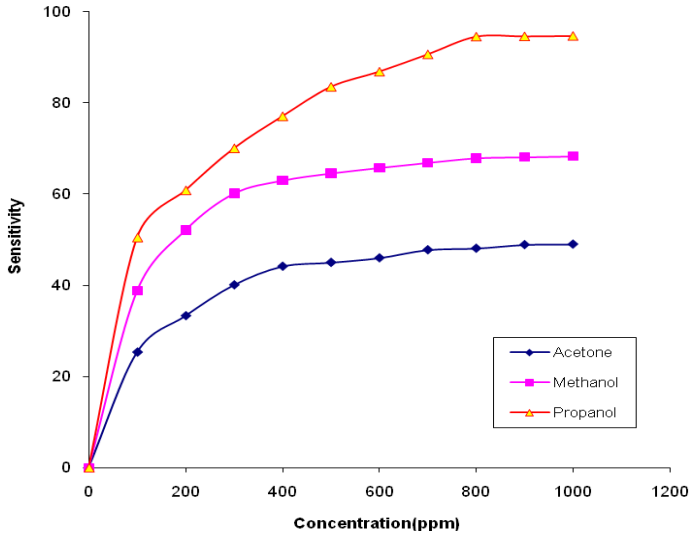

Fig. 1i. Sensitivity variation of O-plasma treated (200 W, 15 min) 1 % PbO doped sensor with concentration of methanol, propanol and acetone.

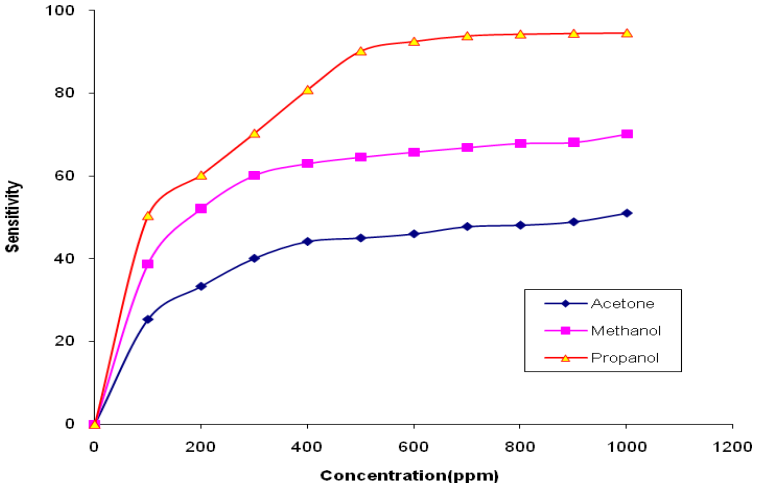

Fig. 1j. Sensitivity variation of O-plasma treated (200 W, 15 min) 2 % PbO doped sensor with concentration of methanol, propanol and acetone.

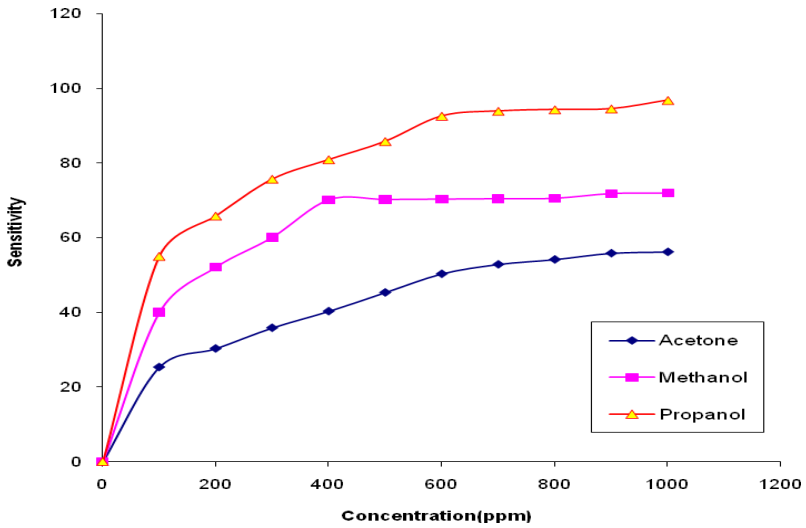

Fig. 1k. Sensitivity variation of O-plasma treated (200 W, 15 min) 3 % PbO doped sensor with concentration of methanol, propanol and acetone.

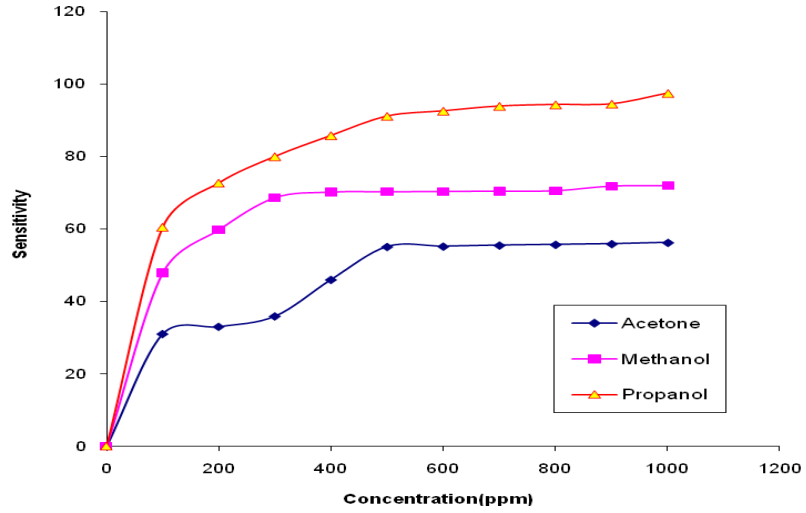

Fig. 1L. Sensitivity variation of O-plasma treated (200 W, 15 min) 4 % PbO doped sensor with concentration of methanol, propanol and acetone.

It is evident from these results that sensitivity of all the sensors increases with concentration of the gases and attain the saturation after some time. Each of the sensors possessed the highest sensitivity for propanol irrespective of O- plasma exposure time. The sensor array that was annealed in O-plasma for 15 minutes found to give the best performance for all the chosen gases with maximum sensitivity (97 %) for propanol. At fixed plasma exposure time, the effect of the concentration of the dopant (PbO) on the sensitivity seems to be very feeble i.e. each of the sensors in a particular plasma treated sensor array has more or less the same sensitivity (Table 1).

The sensitivity is found to be maximum in case of plasma treated sensor due to the release of a greater no. of conduction electrons on interaction with the adsorbed gas molecules [19]. It has been reported [24] that plasma exposure reduces tin oxide to increase its non-stoichiometry. For all conc. of methanol, propanol and acetone the sensitivity trend is similar. The increase in sensitivity is believed to be caused by the change in non-stoichiometric composition of tin oxide.

The primary role of plasma is to produce chemically active species which subsequently react with each other and produce ions and free radicals. Hence it is a mixture of several single, multiple, positive, negative charge species and electrons [25]. When these charge species interact with each other surface state charge present are increased and the no. of active sites of adsorption are also modulated. In the case of oxygen plasma, species present are O^-, O^{2-}, O^{3-}, O^{4+}, O^{3+}, O^{2+},O^+ etc. and electrons [26]. The adsorbed gas molecules interact with single or multiple species present on the surface because of plasma treatment and release more conduction electrons. Since microwave plasma has higher plasma density (number of charged particles per unit volume) but lower ion impact energy than RF plasma [27] which consequently should give rise to availability of higher no. of charged species on the tin oxide surface and also the release of more conduction electrons. This seems to be responsible for dramatic improvement in the sensitivity of microwave plasma treated sensor at room temperature.

Table 1. Effect of Plasma exposure time and PbO doping on the sensitivity of the sensor to methanol, propanol and acetone.

Doping concentr.	**Methanol**			**Propanol**			**Acetone**		
	Plasma exposure time								
	5 min	**10 min**	**15 min**	**5 min**	**10 min**	**15 min**	**5 min**	**10 min**	**15 min**
1 % PbO	31.44	40.56	68.3	44.03	64.46	92.01	10.11	32.31	49.01
2 %PbO	33.24	52.7	71.06	46.89	71.39	94.72	12.14	37.09	52.05
3 % PbO	37.52	53.49	73.17	52.44	78.09	96.25	12.45	40.53	57.45
4 % PbO	40.11	63.09	70.44	60.65	80.27	97.45	22.09	42.87	60.23

4. Conclusion

It is concluded that the oxygen plasma treated sensors can be used to sense organic vapors like methanol, propanol and acetone very effectively at room temperature. The 15 min exposure time for the plasma treatment was found to be best for obtaining high sensitivity with highest sensitivity (97 %) for propanol. Other plasma treated sensors (5 mi. 10 m exposure) are also found to exhibit the highest sensitivity for propanol though lesser than 15 min treated sensors at room temperature. At fixed plasma exposure time, the effect of the concentration of the dopant (PbO) on the sensitivity seems to be very feeble. The increase in the non stoichiometry in the tin oxide is attributed for high sensitivity of plasma treated sensor.

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- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
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