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Study of Ag doped SnO2 film and its response towards aromatic compounds present in tea

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Study of Ag Doped SnO_2 Film and Its Response Towards Aromatic Compounds Present in Tea

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***Abstract*— The work presented here focuses on the synthesis of Ag doped SnO_2 based metal oxide semiconductor gas sensor using co-precipitation method and its performance evaluation towards some vital compounds responsible for the appealing aroma in tea. The sensor is tested to evaluate its response towards four noteworthy compounds (linalool, geraniol, methyl salicylate and trans-2-hexenal) present in the aroma matrix of black tea under diverse working temperature conditions. The prepared Ag doped SnO_2 gas sensor exhibits improved sensitivity at a comparatively lesser working temperature (150^0C) than the undoped SnO_2 gas sensor. The proposed Ag doped sensor yields the highest sensitivity towards methyl salicylate(64.69%), an organic ester naturally synthesized by tea plants and is found in green, oolong and black tea. The physical characterization of the sensing material is carried out using XRD(x-ray diffraction), EDS(Energy dispersive X-ray spectroscopy) and SEM (scanning electron microscope). This research will aid in selecting an appropriate sensing material for detection of methyl salicylate which could help in the quality determination of tea.**

Keywords—gas sensor, co-precipitation, MOS, tea, aroma, methyl salicylate.

I. INTRODUCTION

Tea is a universally demanded stimulating drink and one of the most commonly consumed brews in the world, holding a noteworthy stake in the worldwide commercial market. The pleasant flavor along with its stimulating effects undeniably fetches the popularity of tea. Tea plant, (Camellia sinensis) a viable beverage production plant, is composed of a number of different elements and compounds in its leaf which are responsible for its colour, taste and aroma[1]. The fermentation level of the manufacturing process is used to categorize tea into unfermented (green), semi-fermented (oolong), and fermented (black) tea[2]. The researchers working in the esteemed Tocklai tea research association of Assam, India, has recognized the concentration of volatiles responsible for aroma as only 0.01 – 0.02 % dry wt. in the chemical composition of Fresh Tea Shoot. Although these volatiles are present in such minute percentage, they have immense impact on its aroma. Tocklai researchers have classified the major aromatic biochemical compounds responsible for black tea aroma in five categories[3]:

- sweet(Linalool, Linalool oxide)
- floral(Geraniol, Phenylacetaldehyde)
- fruity(Methylsalicylate, Nerolidol, Benzaldehyde, Phenyl ethanol)
- fresh(Trans-2-Hexenal, n-Hexanal, Cis-3-Hexenol)
- grassy(b-Ionone)

Volatile constituents contribute to aroma attribute and non-volatile constituents decide on the taste which together governs the quality gradation of tea.

Linalool, Geraniol, Methyl salicylate and Trans-2-Hexenal are among the substantial volatile component that adds considerably to the smell of brewed, dry or extracted tea and are estimators of good quality of black, green and oolong tea. Therefore, sensing these components is considered as very important for quality estimation of tea.

Tea quantification is carried out by "human tasters" which is highly subjective, laborious, inconsistent and time-consuming and hence sensor-based quantification could be very helpful for the tea industry. There are reports where tea aroma sensing and quantification is analyzed based on commercially available various metal oxide semiconductor (MOS) gas sensors of Figaro Engineering Inc.[6]. Fabrication of Quartz crystal microbalance (QCM) sensors and thier exposure to linalool [4], geraniol[7], methyl salicylate[5] and trans-2-hexenal[8] is also reported. However, MOS based sensor dedicated to tea aroma sensing is not reported in the literature to the best of our knowledge. In this work, we investigate the development of Ag doped SnO_2 based gas sensing material and its response to linalool, geraniol, methyl salicylate and trans-2-hexenal which were procured from Sigma Aldrich. The sensors were prepared using a simple non- expensive wet chemical procedure where SnO_2 was doped with 5wt% of Ag. This work will definitely pave way for selection of a sensing material for detection of methyl salicylate and henceforth, objective quality evaluation of tea aroma.

The sensing mechanism of MOS gas sensing material includes surface chemical adsorption/desorption process of gas molecules and charge transfer mechanism where conductance of the sensing film increases when exposed to a reducing gas. SnO_2 is an n-type MOS material which is widely accepted as an effective gas sensing material and due to its unique gas sensing abilities, it is the earliest to be made into a commercial gas sensor [9]. Doping noble metals enhance properties of the SnO_2 film such as morphology, surface-to-volume ratio, active center of the material, reduction in band gap energy, reduction in working temperature which has great importance in gas sensing. There are several reports of doping MOS material with noble metals (Au, Ag, Pt, Pd, etc.) for improving gas sensing properties[10-13]. Co-precipitation synthesis is best suited for a low cost means to dope metals into sensing materials with atomic precision and uniformity. In this work, the sensitivities towards four different aromatic vapours are carried out at four different temperatures where

Ag doped sensor yields the highest sensitivity for methyl salicylate at an optimum temperature of 150^0C.

II. SENSOR PREPARATION

A. *Material synthesis*

A 0.1M solution of stannic(IV)chloride-pentahydrate ($SnCl_4.5H_2O$) was prepared in de-ionized water. To this solution, 1mol/L ammonium hydroxide aqueous solution was added dropwise under vigorous stirring at 500r.p.m. for 1hour to get a white precipitate of pure SnO_2 and maintaining the pH value at 10. The precipitated material was washed with ethanol and DI water alternatively to remove NH_4^+ and Cl^- ions and to get pure SnO_2. Silver nitrate test was done to ascertain the removal of Cl^- from the solution. This precipitate was dissolved in a 1M aqueous solution of $AgNO_3$ under vigorous stirring of 500r.p.m (the amount of $AgNO_3$ dissolved was calculated such that a mass ratio of 5wt% of Ag ions was integrated in the solution). An Ammonium hydroxide aqueous solution of the same concentration was again added to the solution dropwise under constant stirring of 500r.p.m. for about 1 hour until the pH reaches 10. The mixture was filtered, washed with ethanol and DI water alternatively and kept for 1hour ageing. The precipitate was then mixed with DI water to obtain a colloidal form which is ready to be deposited onto the substrate.

B. *Substrate preparation and sensor fabrication*

A p-type (100) silicon wafer was cleaned by the standard Radio Corporation of America (RCA) method. A 0.5µm layer of SiO_2 was uniformly deposited on the wafer employing plasma enhanced chemical vapour deposition method (*pressure: 0.8 torque; temperature: 250^0C; time:150s*). Thereafter, a 2cm ×1cm rectangular piece of the SiO_2 deposited wafer was used as the substrate for the sensor. After that, Au electrode (*shape: interdigitated with 0.5µm finger spacing; thickness: 0.5µm*) was deposited on the substrate by thermal evaporation (*model: HHV BC-300; pressure: 10^{-9} mbar and current:80A*). The deposition of the synthesized material was carried out by drop and dry coating method (5 times). A profilometer(*Taylor Hobson (model S100)*) was employed to determine the thickness of the surface film and was found to be 20.8 µm. The prepared sensor was dried for 1hour in the air at 120^0C and subsequently calcined at 500^0C for another hour in a muffle furnace.

III. PHYSICAL CHARACTERIZATION OFTHE SENSOR

A. *XRD analysis*

Powder X-ray diffraction(XRD) was employed to ascertain the crystalline structure of the samples at 40 kV and 30 mA in the scanning angle (2θ) from 10^0 to 70^0 with a scan speed of 0.020/s. Fig. 1(a) and 1(b) shows the XRD patterns of the Ag doped and undoped SnO_2 material respectively. All the diffraction peaks complemented with the typical tetragonal rutile structure of SnO_2 as per the JCPDS card no 41-1445 and the diffraction pattern of Ag exhibited a cubic phase as per the standard JCPDS card no. 07-0483. Comparing Fig. 1(a) and 1(b), the influence of Ag doping in SnO_2 can be clearly seen. The average particle size is calculated by the Debye-Sherrer formula [14]. The first major peak SnO_2 (110) was used to estimate the SnO_2 crystallite size according to the peak broadening analysis and was found to be 9.43nm, while the crystallite size of the doped nanoparticles based on Ag (200) peak was found to be 37.2nm.

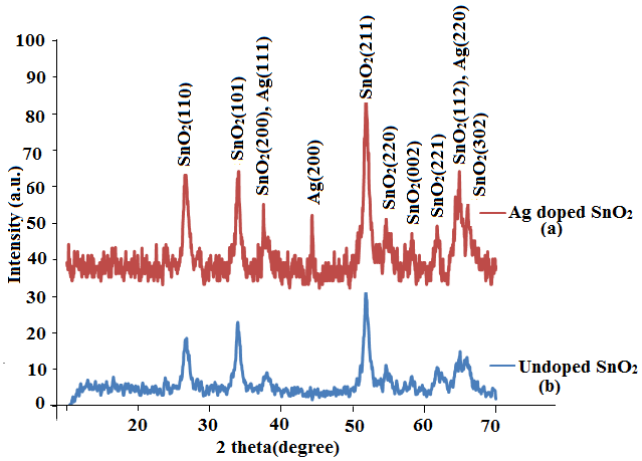


Fig.1: XRD pattern of (a) Ag doped SnO_2 (b) Undoped SnO_2

B. *SEM analysis*

Fig.2 shows the SEM image of the fabricated Ag doped SnO_2 sensing material. Careful inspection of the image exhibits fiber-like morphology agglomerated all over the surface of the sensor.

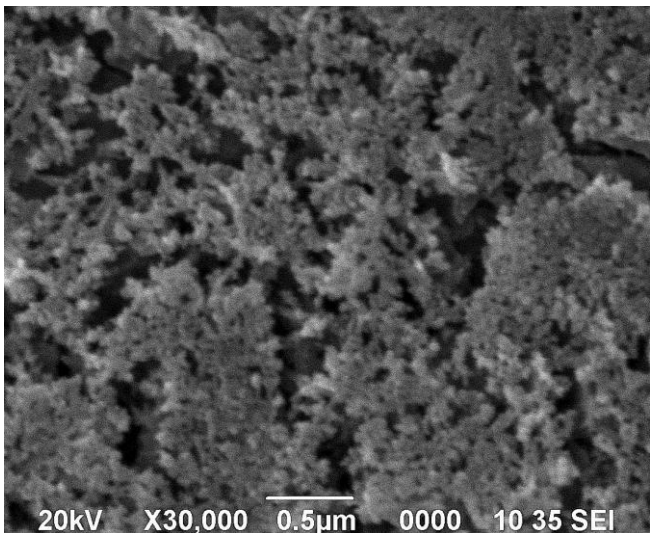
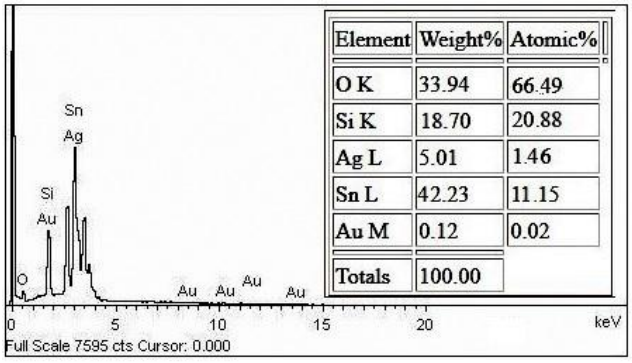


Fig.2: SEM images of Ag doped SnO_2 sensor

C. *EDS analysis*

Fig.3 shows the EDS spectra which confirm the chemical composition of the synthesized sensor. The crests of five elements O, Si, Ag, Sn and Au were detected. The incorporation of Ag in the MOS material was hence verified and also no peak due to chloride ions was observed in the EDS spectra. The Au electrodes integrate the occurrence of Au as seen in the spectra. The percentage of Si is due to the Si/SiO_2 substrate.



Element	Weight%	Atomic%
O K	33.94	66.49
Si K	18.70	20.88
Ag L	5.01	1.46
Sn L	42.23	11.15
Au M	0.12	0.02
Totals	100.00	

Fig.3: EDS spectra of Ag doped SnO_2 sensor

IV. ELECTRICAL RESPONSES OF THE SENSORS TOWARDS THE AROMATIC COMPOUNDS

An airtight enclosed test chamber of 200ml with a heating arrangement via a hot plate was taken to hold the sensor during the course of measurement using a two probe measurement technique. The measurement set up used for sensor evaluation is shown in Fig. 4(a) while Fig. 4(b) shows the electrical circuit for sensor performance measurement. A constant voltage (V_S= *2V*) was supplied by a voltage source and an electrometer (Keithley 2100) was used to monitor the output voltage (V_0) on exposure to gases at different temperatures. The load resistance, R_L=1KΩ was connected to the circuit across which the output voltage was measured. R_S, here denotes the sensor resistance. There is one inlet in the sensor chamber for micropippetting the VOCs into it, another inlet for pumping in fresh air to refresh the sensor to its baseline and one gas outlet fitted with a pump for pumping the gas out of the chamber.

The sensors were exposed to vapours of the four aromatic compounds (viz. geraniol, methyl salicylate, linalool and trans-2-hexenal) one at a time via micropippetting at four different operating temperatures(50^{0}C, 100^{0}C, 150^{0}C and 200^{0}C). The change in V_0 was noted as shown in Fig.5 where a gradual increase in V_0 is seen on exposure to the gases at all temperatures. It can also be noted that as the temperature is increased, there is an increase in the baseline voltage of the sensor. The % sensitivity variation shown in Fig. 6(a), substantiates 150^{0}C as the optimum operating temperature for gas sensing at which there is a considerable divergence in sensitivities towards the four exposed gases beyond which there is only a small increase when the temperature is further increased to 200^{0}C. The sensitivity is defined by equation (1) as:

$$S(\%) = (V_g - V_a)/V_a \times 100\% \qquad (1)$$

where V_g is the voltage measured across the load while the sensor is under exposure to analyte gas and V_a is the voltage measured across the load while the sensor is kept in fresh air condition. Fig. 6(a) shows the sensitivity curves of the Ag doped sensor, which is very much improved as compared to the sensitivity curves of the undoped SnO_2 sensor shown in Fig. 6(b). The Ag doped sensor shows the highest sensitivity towards methyl salicylate(64.69% at 150^{0}C) amongst the four tested gases.

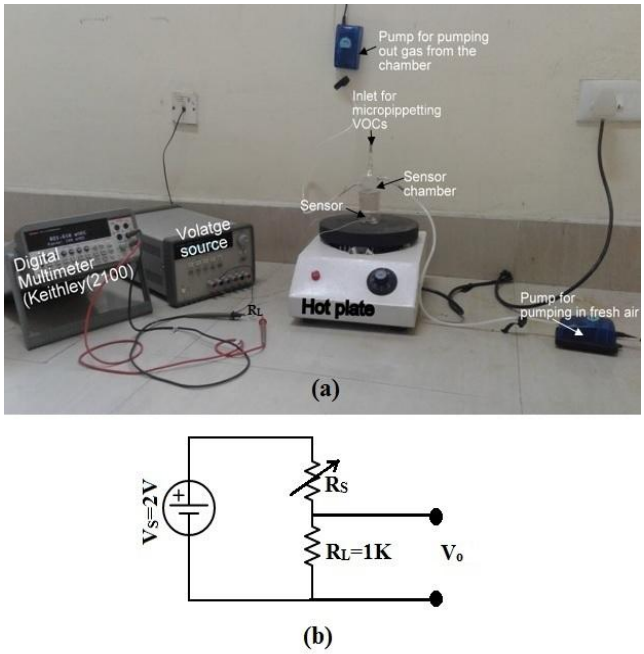


Fig.4: (a) Sensor performance measurement set up
(b) Electrical circuit for measurement

The sensing and purging time are also calculated and are found to be comparatively lower at 150^{0}C as compared to the other tested temperatures. Among the tested gases at different operating temperatures, for the Ag doped sensor, methyl salicylate has the lowest sensing time of 100s both at 150^{0}C and 200^{0}C and the purging time is lowest (110s) for geraniol both at 150^{0}C and 200^{0}C. A histogram depicting the sensing and purging time for the four different aromatic compounds at different operating temperatures is shown in Fig.7.

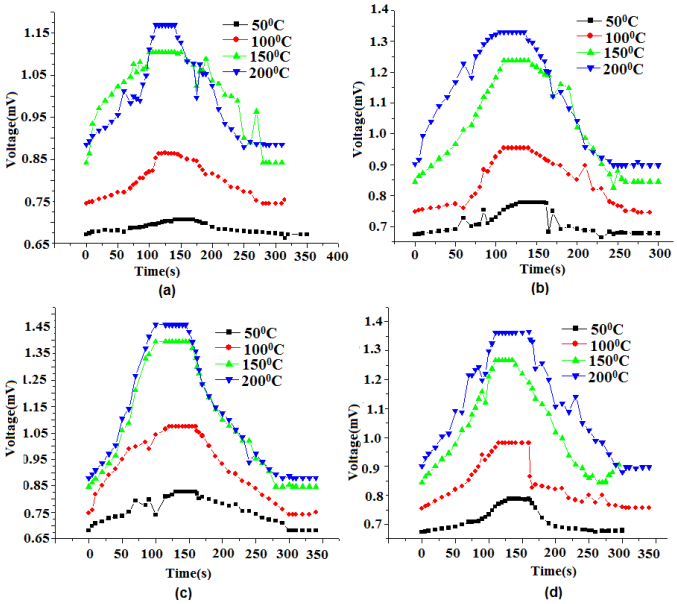


Fig.5: Sensor's responses towards (a) Linalool (b) Geraniol (c) Methyl salicylate (d) Trans-2-Hexenal

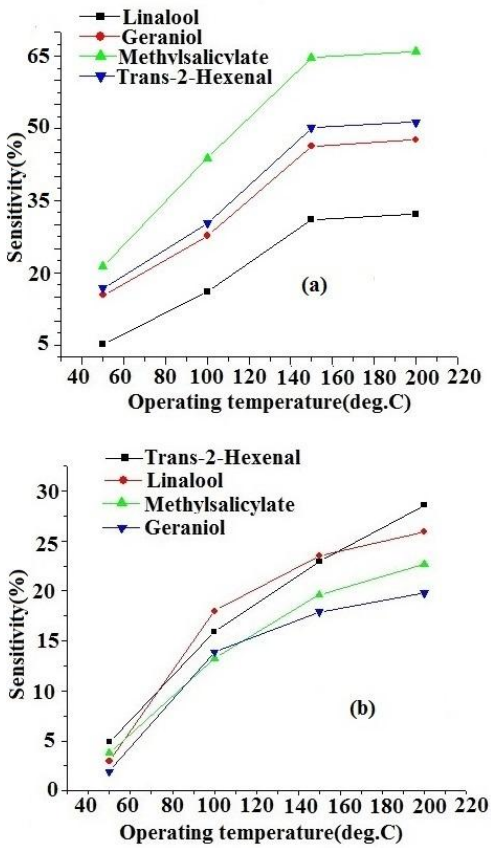


Fig.6: Sensitivity Vs Operating temperature (a) Ag doped SnO_2 (b) undoped SnO_2

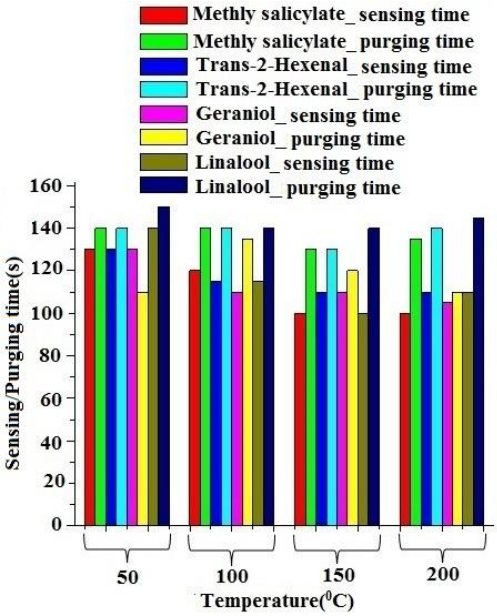


Fig.7: Sensing and purging time of the designed sensor at diverse operating temperatures.

V. CONCLUSION

In this paper, a study of Ag doped SnO_2 based gas sensor for sensing tea aroma compounds is presented. It is observed that the sensitivity of the Ag doped SnO_2 sensor is by far improved than that of the undoped SnO_2 sensor when tested with the vapour of the same compounds. The sensitivity enhances appreciably with the increase in operating temperature up to 150^0C. However, not much of raise in sensitivity is observed when operating temperature is increased from 150^0C to 200^0C. Thus the sensor can be made to operate at 150^0C to get a better response with optimum power consumption. At 150^0C, the Ag doped sensor shows the highest sensitivity towards methyl salicylate(64.69%). Among the tested gases at different operating temperatures, for the Ag doped sensor, methyl salicylate has the lowest sensing time of 100s both at 150^0C and 200^0C and the purging time is lowest(110s) for geraniol both at 150^0C and 200^0C. The XRD analysis shows proper formation of crystalline planes of both SnO_2 as well as of Ag and SEM analysis shows the formation of the agglomerated fibrous sensing layer. EDS analysis confirms the composition of the sensing layer. This work also shows that doping with a noble metal manipulates the sensitiveness of the SnO_2 sensing material towards different gases. The results open various scopes for future research where the sensors can be put in an array and exposed to tea samples directly. The responses from them can be then used in computational models based on artificial intelligence to correlate the measurements to obtain a decision on the quality of the tea sample.

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