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Drift analysis of a Pd loaded SnO_2 based linalool sensor

Priyanka Kakoty[a*], Manabendra Bhuyan [a] & Karen Das [b]

[a]Department of Electronics & Communication Engineering, Tezpur University, Tezpur 784028, Assam, India

[b]Department of Electronics and Communication Engineering, Assam Don Bosco University, Azara, Guwahati 781017, Assam, India

An approach has been made in this work to analyze sensitivity drift in a Pd decorated SnO_2 sensor developed for detection of linalool, a significant aroma compound in tea. Prior to the drift analysis, an attempt has been made to choose the optimum loading percentage of Pd in SnO_2 for linalool sensing. An inexpensive and simplistic hydrothermal method has been used to develop five different Pd decorated SnO_2 sensors (0.5 wt%, 2 wt%, 5 wt%, 6 wt% and 8 wt%) and compare their sensitivities when exposed to linalool vapour. The analysis has shown that 6 wt% exhibits better sensitivity (62.7%) towards Linalool at a relatively lower temperature (100 °C) as compared to all the other synthesized sensors. Henceforth, extensive experiments has been performed on the 6 wt% Pd decorated SnO_2 sensor for a period of one month to analyze its stability. Relative standard deviation and principal component analysis based drift analysis has been performed to understand its changing attributes under repeated measurements.

Keywords: Drift, Gas sensor, Linalool, Sensitivity

1 Introduction

Linalool is considered as one of the most important biochemical compounds that are responsible for the desirable sweet aroma in brewed, dry or extracted tea[1]. Linalool belongs to a group of volatile organic compounds (VOC) called terpenoids, whose presence highly enhances the quality of tea. Linalool is also known to possess the highest flavour dilution (FD) factor in black tea extract from the tea gardens of Darjeeling, India[2]. Therefore study on linalool is of utmost interest to estimate the quality of tea without the involvement of any human taster. SnO_2 loaded with palladium synthesized by the hydrothermal technique is known to exhibit excellent sensitivity towards linalool in tea[3]. When Pd additive is loaded, direct electronic interaction is known to take place between Pd and SnO_2 surface and the oxidation state of Pd changes according to the surrounding ambience[4]. Pd forms a stable oxide (PdO) in the air that induces a shift in its work function and this oxidized metal can be easily reduced back to its metal form when exposed to a reducing gas. PdO clusters dispersed on SnO_2 surface interact with the reducing gas, which is done by the adsorbed oxygen in case of undoped SnO_2. As the PdO is known to have higher electron affinity than adsorbed oxygen, loading Pd in SnO_2 can result in higher sensitivity of SnO_2 materials. Moreover, Nan Ma et al.[5] reported that loading Pd in SnO_2 also reduces the poisoning effect of water vapour in it. They stated that in the case of undoped SnO_{2a}, in a humid atmosphere, mainly O^- is adsorbed onto the surface which easily gets reduced to OH^- groups and hinders adsorption of O^{2-} on the surface. On the other hand, in case of Pd-loaded SnO_2, O^{2-} is adsorbed onto the surface and hence the oxygen adsorption is not affected by the humid atmosphere which leads to better sensitivity in that condition. In an earlier work[3], an attempt was made to explore whether Pd decorated SnO_2 films can be used for sensing aroma compounds available in tea. It was found that 5 wt% Pd decorated SnO_2 at an operating temperature of 150 °C, shows sensitivity to the vital tested aroma compounds in the following order: linalool>methyl salicylate>geraniol>trans-2-hexenal, where sensitivity towards linalool was found to be the highest (73.25%) as calculated using equation (1). However, in the quest of achieving the optimum loading percentage of Pd in SnO_2 for linalool sensing at comparatively lower working temperature, an attempt is made to develop few more Pd decorated sensors (0.5 wt%, 2 wt%, 6 wt% and 8 wt%) using the same method and compare their sensing performances. The preparation method and the measuring set-up used are as discussed in the earlier work[3]. All the sensors are developed with equal surface area so that hypothetically we can assume

*Corresponding author (E-mail: priyankak@tezu.ernet.in)

there is no variability in the exposed effective surface area of the sensors. The main aim of this work is to perform a drift analysis on the sensor for linalool sensing with the optimum palladium loading percentage.

2 Palladium Loading and its Characterization

In the earlier work, the 5 wt% Pd decorated SnO_2 sensor was found to saturate at 150 ppm linalool[3]. Therefore, all the developed sensors with various Pd loading are exposed to a constant concentration of linalool (150 ppm) at four different temperatures and their sensitivities are calculated using equation (1).

$$S = \frac{V_g - V_a}{V_a} \times 100\% \quad \ldots (1)$$

where, V_a is the output voltage in the air and V_g is the output voltage when exposed to a gas.

The sensitivities of the sensors show significant variation with change in the amount of Pd loading at four different operating temperatures. The sensitivity curves of the sensors (Fig. 1) shows that amongst all the developed sensors, 6 wt% Pd loaded SnO_2 gives paramount performance, whose sensitivity towards linalool is highest (62.7%) at comparatively lower operating temperature (100 °C). This may be attributed to the fact that at 6wt% an optimum ionization is achieved. And with the further increase in loading amount the crystalline structure attracts defects beyond a desirable level.

The physical characterization of the 6 wt% Pd loaded SnO_2 sensor is shown in Fig. 2. The X-ray diffraction (XRD) analysis (Fig. 2(a)) shows diffraction peaks that complement crystal planes of SnO_2 as per the tetragonal rutile structure (JCPDS 41-1445). The peaks due to Pd (JCPDS no. 5-681) could

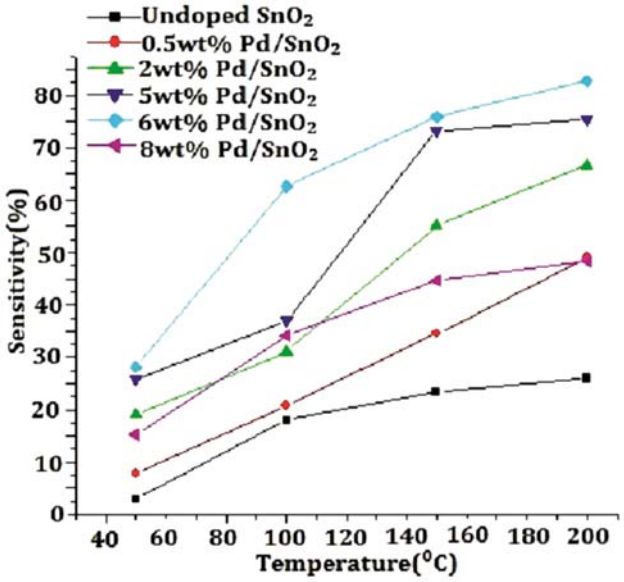

Fig. 1— Sensitivity curves of various sensors towards 150 ppm of linalool.

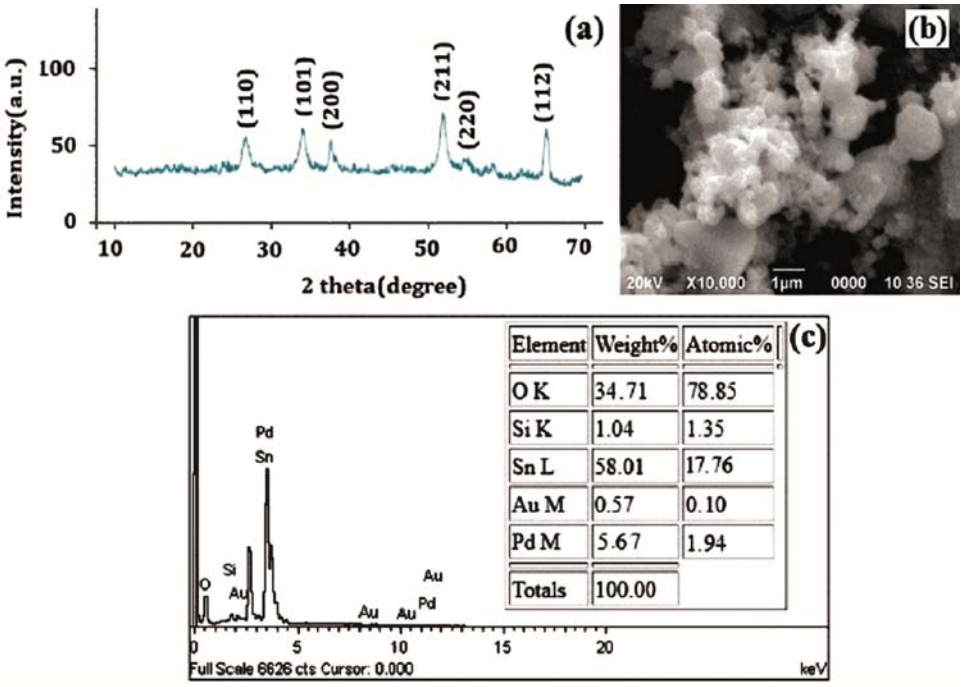

Fig. 2 — Physical characterization of the sensor (a) XRD pattern , (b) SEM image and (c) EDS spectrum.

not be separately detected either due to the lower relative intensity or due to its overlap with the crystal planes of SnO_2. The crystallite size of the material is calculated from the first major diffraction peak (110) using the Scherrer equation and is found to be 8.7 nm. The scanning electron microscope (SEM) image shown in Fig. 2(b) shows various round-shaped particles of different sizes, which are also agglomerated at some places resulting in macroparticles. The energy dispersive spectroscopy (EDS) spectrum shown in Fig. 2(c) confirms the elemental composition of the sensor, along with confirming the fact that no residual chloride ions are present in it.

In comparison to the physical characterization results of the 5 wt% Pd loaded SnO_2 presented in the previous work[3], it is seen that the results of the 6 wt% Pd loaded SnO_2 are apparently similar, but still there are few attributes which differentiates both the materials. The XRD peaks width is seen to increases with Pd loading and relative intensity gets reduced and thus the crystallite size gets reduced from 8.879 nm to 8.7 nm when Pd loading is increased from 5 wt% to 6 wt% respectively, which has probably aided in sensitivity improvement of the 6 wt% sensor. This result has verified the fact established by Chaonan Xu *et al.*[6] that gas sensitivity of SnO_2 sensors increases with decrease of crystallite size below 10 nm as space charge region becomes more dominant in each crystallite, thereby increasing the sensitivity to objective gases. This is perhaps the reason of sensitivity enhancement in the doped sensors as compared to pure SnO_2 whose crystallite size was 10.28 nm. However, the surface morphology depicted from the SEM images consists of similar shaped and sized particles. The EDS analysis confirms the difference in weight and atomic percentages in the elemental composition of the 5 wt% and 6 wt% Pd loaded SnO_2 sensors.

3 Major causes of Drift in MOS Gas Sensors

Although gas sensors are potentially inexpensive and a fast alternative to the analytical instruments and traditional human tasters, however the lack of stability over time many a time limit the adoption of artificial olfaction. The sensor drift, which has adverse effects on most of the sensors, consists of small and non-deterministic temporal deviations of the sensor response when it is exposed to the same analytes under identical conditions[7] which results in sensitivity degradation of the sensor over time and requires calibration over and over again. Different structural and morphological drifts are the major reasons for drift in a MOS gas sensor[8]. Chemical diffusion of oxygen due to stoichiometry changes generally causes severe drift effects. Change in oxygen vacancy concentration or redistribution of oxygen vacancies influences the space charge that results in a baseline drift of the sensor without linalool (Fig. 3). It is observed that the baseline voltage shows an increasing trend over time which means a decrease in the sensor resistance over time. The drift in the sensor resistance, in this case, could be mainly because of the impact of higher humid conditions (60 ± 5%) in Assam, India. Moreover, the sensor is experimented without any proper packaging because of which contamination of the sensing film may take place which may lead to its performance degradation after continuous and long term usage. A large number of heating and cooling cycles may also induce cracks on the sensing film which may result in a physical change that might lead to sensor drifts. A decreasing response can be attributed to the

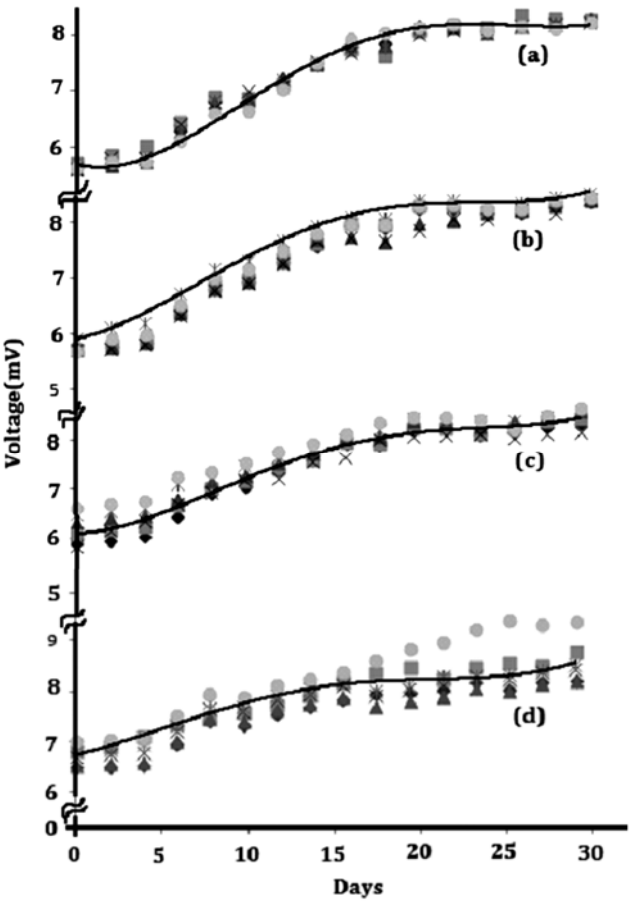

Fig. 3 — Baseline variation of the 6 wt% Pd decorated SnO_2 sensor for a period of one month without linalool at (a) 50 °C, (b) 100 °C , (c) 150 °C and (d) 200 °C .

amalgamation of grains due to their underlying poor degree of crystallinity. Sometimes, irreversible poisoning of sensor surface may occur due to the binding of certain particles to the sensing material leading to change in certain physiochemical properties.

4 Drift Analysis of the Sensor

A drift analysis is performed based on responses of 6 wt% Pd decorated SnO_2 sensor for various concentration of linalool at four different temperatures on every alternate day for a period of one month. The sensor response for the first day is shown in Fig. 4. It is seen that there is a substantial increase in sensor response from 20-150 ppm, beyond which, the increase in sensor response becomes insignificant. This may be attributed to the amount of gas molecules that can react with the adsorbed oxygen species on the surface sensing layer reaches a saturation value, beyond which there can be no surface adsorption of gas molecules.

The peak response voltages with variation of concentration as seen in Fig. 4 (a)-(d) are: 50 °C : 5.86 mV (20 ppm) and 7.22 mV for 200 ppm; 100 °C :6.097 mV (20 ppm) and 9.28 mV (200 ppm); 150 °C : 6.59 mV(20 ppm) and 1.77 mV (200 ppm); 200 °C : 8.57 mV (20 ppm) and 12.93 mV (200 ppm)

The calibration curve (Conductance versus concentration) of the sensor was plotted at four different temperatures for different linalool concentrations (20-200 ppm), assuming constant effective sensing area and is shown in Fig. 5.

After one month long experimentation, sensitivity of the sensor was calculated and plotted for every alternate

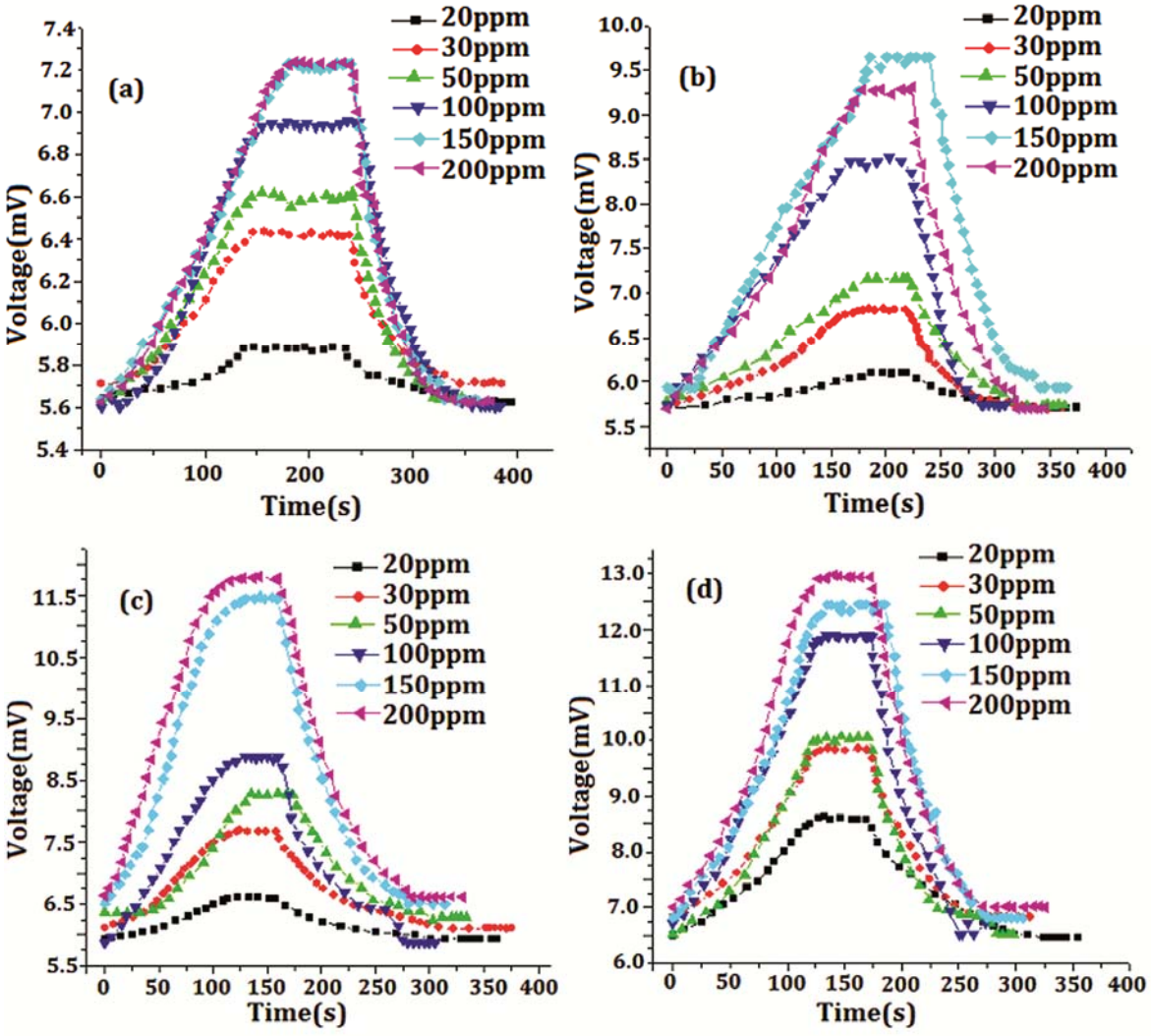

Fig. 4 — Response characteristics for linalool at different concentrations for 6 wt% Pd decorated SnO_2 sensor at (a) 50 °C , (b) 100 °C , (c) 150 °C and (d) 200 °C.

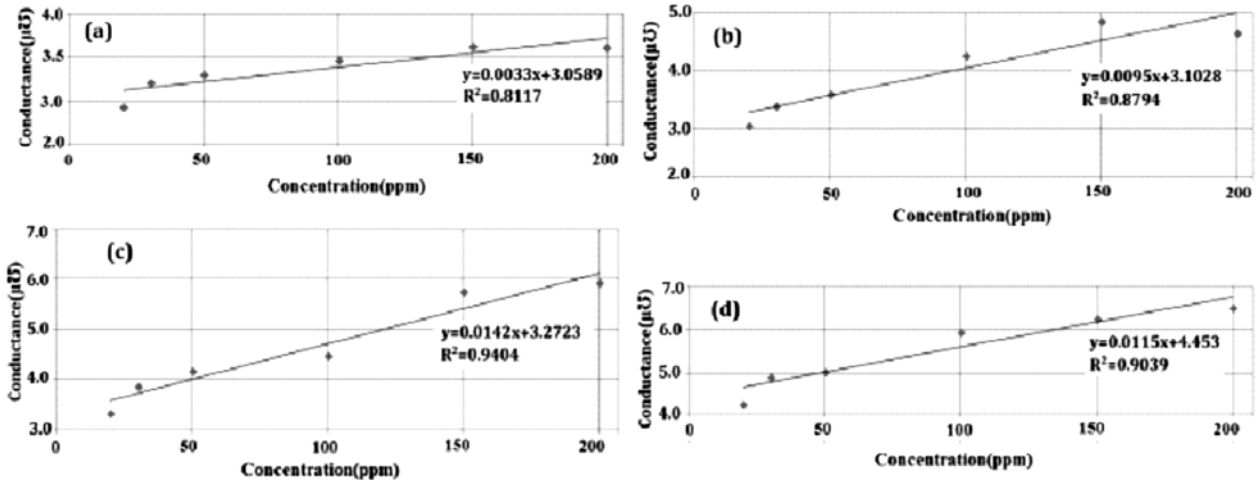

Fig. 5 — Calibration curve of the 6 wt% Pd decorated SnO_2 sensor for linalool at (a) 50 °C , (b) 100 °C , (c) 150 °C and (d) 200 °C

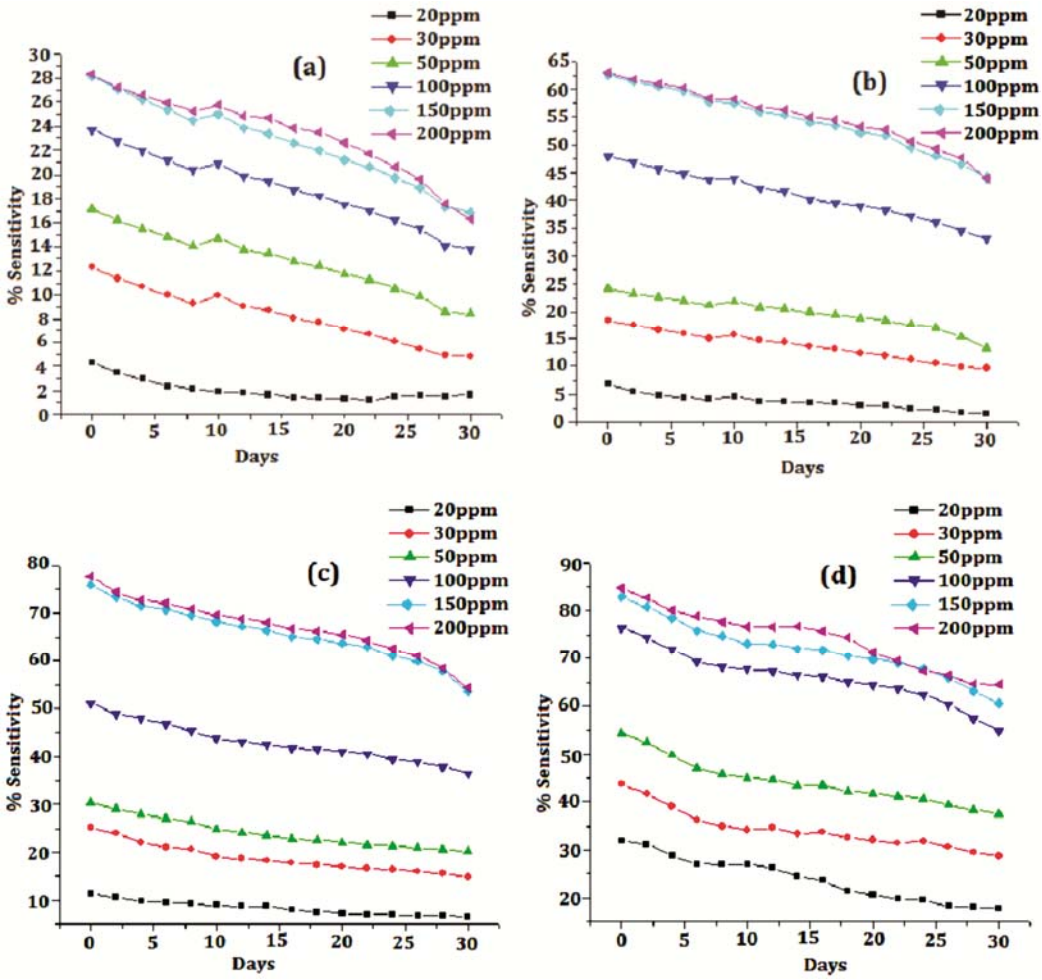

Fig. 6 — Sensitivity variation of the 6 wt% Pd decorated SnO_2 sensor for different concentrations of linalool for a period of one month at (a) 50 °C , (b) 100 °C , (c) 150 °C and (d) 200 °C.

days as shown in Fig. 6. In order to analyze the drift in sensitivity, two approaches are taken as discussed below:

It is found that the percentage relative standard deviation (%RSD) (Fig. 7) of change in sensitivity is high when experiments are performed at lower

operating temperatures and lower concentration of the target gas. The %RSD is seen to decrease with an increase in operating temperature and to a large extent with an increase in concentration. This may be due to the fact that any hindrance on the sensing layer caused by humidity is eliminated when operating temperature is raised. An acceptable range of %RSDs from 8.4% -- 10.8% is observed from 100 ppm onwards at an operating temperature of 100 °C and above. When the experiments are repeated at lower concentrations, even at higher temperature an undesirable %RSD of 42.9% is found. From this, an important conclusion can be obtained that the sensor cannot or should not be operated at lower concentrations (20-30 ppm) to avoid deplorable variation in sensitivity over time. This is also validates the data found in literature that aroma contributing volatiles in tea are found to be 0.01% of the total dry weight, i.e a concentration of 100 ppm [2]. This means, for quality monitoring of tea, a sensor capable of sensing tea aroma compound of minimum 100 ppm is acceptable.

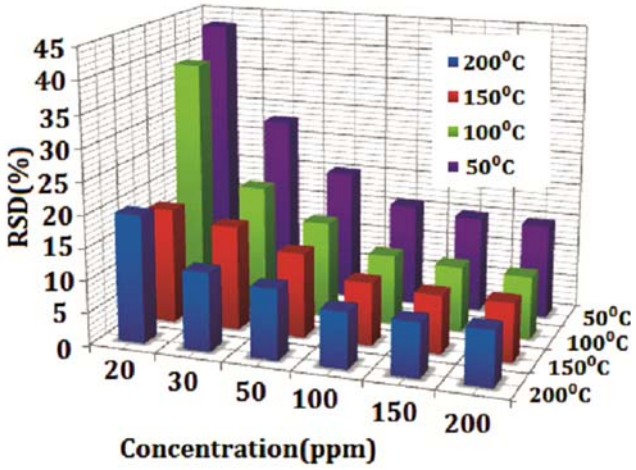

Fig. 7 — %RSD of the sensitivity of the 6 wt% Pd decorated SnO_2 sensor for different concentrations of linalool at different temperatures.

Drift in sensor response of the 6 wt% Pd decorated SnO_2 sensor is also analyzed using Principal component analysis (PCA). The difference in sensor voltage with linalool and the baseline voltage (V_g-V_a) at different concentrations and different temperatures over one month period is used as sensor data for PCA analysis. Fig. 8(a) shows the PCA plot of day 1 data and Fig. 8(b) shows the PCA plot of one-month long data and both the figures shows the formation of six clusters representing six different applied gas concentrations. It is seen that the Eucledian distances (Table 1) between both the PCA differ with a small value which is quite acceptable after one month for an unpackaged sensor. This indeed is an affirmative result that reinforces the fact that repetition over one month period does not deteriorate the sensor response attributes for a particular gas concentration. This is because the change in sensor resistance at a particular ppm over a period carries the multivariate nature of the sensors, hence the eigen values are well correlated in the PCA.

Thus, it is seen that when an unpackaged sensor prepared by a facile method sustains rigorous experimentations for a long period in a humid

Table1 — Eucledian distances of PCA clusters in the PCA plots.

	Distance from 20 ppm cluster to all other clusters				
	30 ppm	50 ppm	100 ppm	150 ppm	200 ppm
Day 1 PCA	3.81	5.21	5.856	7.996	9.096
One month PCA	1.679	2.446	4.858	6.861	7.266

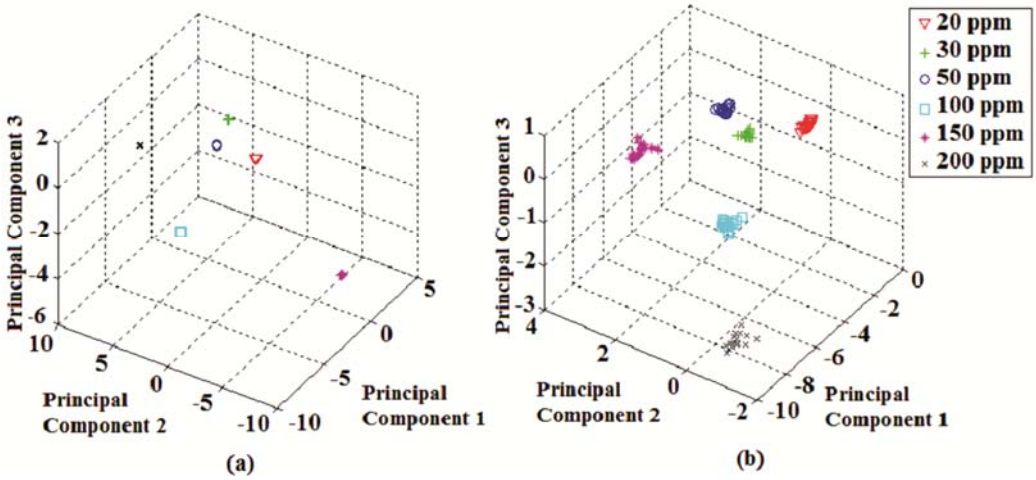

Fig. 8 — PCA plot of sensor data of the 6 wt% Pd decorated SnO_2 sensor for various linalool concentrations (a) day 1 and (b) one-month.

environment, it is expected to undergo certain drifts in its performance. Even though certain drifts in sensitivity are observed, from PCA analysis it can be inferred that sensor data attributes are quite intact as six distinct clusters are formed.

5 Conclusions

A performance comparison of undoped SnO_2, 0.5 wt%, 2 wt%, 5 wt%, 6 wt% and 8 wt % Pd decorated SnO_2 is done and 6 wt% is found to perform better comparatively in terms of sensitivity towards linalool at moderate temperature of 100 °C and above. The sensor was tested from 20-200 ppm from which 150 ppm was found as the saturation concentration for the sensor. The drift analysis over one month period shows an appreciable %RSD with a minimum of 8.4% to a maximum of 10.8% for linalool concentrations of 100 ppm and above at operating temperatures of 100 °C and above. %RSD is found to increase with a decrease in gas concentration as well as with operating temperature. The PCA analysis of one-month sensor data shows the formation of six defined clusters which reveal intactness of sensor response attributes over that period for a particular gas concentration after comparing with the PCA data of day 1. It can be expected that with proper packaging, the performance of the developed sensor would be even better.

This work brings into the limelight a sensor having a good sensitivity towards linalool at moderate temperature and its drift analysis over time. This work paves way for future research in the area of undertaking corrective measures for mitigating such drifts in sensors.

References

1 Bhuyan L P, Senapati K K, Saikia P & Hazarika M, *Two and a Bud*, 59 (2012) 112.
2 Sharma P, Ghosh A, Tudu B, Bhuyan L P, Tamuly P, Bhattacharyya N, Bandyopadhyay R & Chatterjee A, *Sens Actuators, B,* 190 (2014) 318.
3 Kakoty P, Bhuyan M & Das K, *IEEE Sens J*, 18 (2018) 4392.
4 Velmathi G, Mohan S & Henry R, *IETE Tech Rev*, 33 (2016) 122.
5 Ma N, Suematsu K, Yuasa M, Kida T & Shimanoe K, *ACS Appl. Mater. Interfaces*, 7 (2015) 5863.
6 Xu C, Tamaki J, Miura N, & Yamazoe N, *Chem Lett*, 19 (1990) 441.
7 Holmberg M, Davide F A, Di Natale, C, D'Amico A, Winquist F & Lundström I, *Sens Actuators B*, 42 (1997) 185.
8 Di Carlo S, & Falasconi M, Advances in Chemical Sensors, (Intech Open, New York), ISBN: 978-953-307-792-5, (2012), p. 305.