Chapter 4

Fabrication and Characterization of Gas Sensor based on grown SnS Nanoparticles

The recent improvements in science and industry lead to the release of toxic gases which cause pollution to the environments. The presence of some extremely toxic gases hazards the human life. Hence, the recognition of the toxic gases is very much urgent to check and control environment superiority [209-213].

A gas sensor is a device that can identify the existence of a particular gas in the atmosphere through the changing of its electrical resistance [214]. This gas sensing devices have been attracted vast attention in many fields of science and research areas such as environmental monitoring, pharmaceutical manufacturing, process control, waste-water treatment, security purposes, medical diagnostics etc [215-218]. The function of the sensors can be significantly improved when employing nanomaterials, the sensing elements. The higher surface to volume ratio produces additional active reaction locations. The performance of the sensors depends on various parameters such as crystal size, nature of crystallinity and working temperature [219-220]. Metal sulfide nanocrystals are relatively cheap and abundant in nature. Metal sulfide nanoparticles turn out an outstanding performance in the field of gas sensing areas and it is used in system monitoring and environmental security [221-222]. The environmental pollution is a more serious universal problem. Harmful gases mainly cause the pollution. To save people and environment from the dangerous gases, it is urgent to identify explosive, highly flammable and toxic gases [223]. There are some toxic gases such as sulfur dioxide [224], carbon monoxide [225], hydrogen sulphide [226], acetone [227], formaldehyde [228] and ethanol [229]. Ethanol is a versatile, common and potentially dangerous. Ethanol gas can affect the skin, body and other organs. It is known that the gas

sensing mechanism of metal sulfide semiconducting nanomaterial is the electron transfer from the surface of the materials when it is associated with the target gas. Due to their excellent sensitivity, fast response and fast recovery time, moderate stability and selectivity, metal sulfide nanoparticles are used for gas sensor [230]. Therefore to fabricate a good sensor with high stability and selectivity is an open challenge to the researchers. Many researchers are trying to improve the sensing performances in different ways of metal sulfide semiconductor by changing synthesis methodology, experimental conditions for instance reducing the dimension of crystal size, synthesizing porous materials, fabricating composite materials and so on.

SnS nanoparticles are grown by chemical route with the variation of growth time varied from 3 to 14h at room temperature. The grown nanoparticles are deposited on glass for the fabrication of gas sensor. The gas sensing properties of the sensors in ethanol are carried out for different growth time films. The sensing measurements were done at operating temperature ranging between 250 ^{0}C and 300 °C for SnS based sensor. Here we have chosen three operating temperature i.e. 250 °C, 275 °C and 300 °C. The gas sensing sensitivity was maximum for optimum growth time sample i.e. for the sample grown for 7 h at 300 °C. The percentage of sensitivity of 7 hours samples at 300 °C was about 61%. The chain like structure and good stochiometry of the SnS nanoparticles grown at 7 hours increases the sensitivity of ethanol gas sensing. The gas sensing properties of the samples have been studied in dry air as well as in humid conditions. The stability of the sensors has been also studied over 4 weeks and this indicates good stability of the sensors.

4.1. Experimental section

Tin sulfide (SnS) nanoparticles have been prepared by simple cost effective chemical reduction route with the variation of growth time (3h, 7h and 14 h). Tin chloride ($SnCl_2 \cdot 2H_2O$), sulfur powder (S), sodium borohydride ($NaBH_4$) and tetrahydrofuran (THF)

were used to grow SnS nanoparticles. The technique of sample preparation and its structural, optical properties is reported elsewhere [231].

4.1.1. Fabrication of Gas Sensor

To fabricate gas sensor, nanofilms of the different SnS nanoparticles have been grown from the dispersed SnS nanoparticles on glass. The cleaned glass substrates have been dipped into the dispersed SnS nanoparticles in toluene for 72 h. Uniformly nanofilms of SnS nanoparticles have been formed on glass substrate. For sensing measurements, a hand-made gas chamber was used to characterize electrically the SnS sensor by means of fluxing the gases through the micropipette. Firstly, silver electrodes were drawn on the sensor nanofilms. Then the sensors were annealed at their proper working temperature. A synthetic air was flow constantly over the sensors to reach the thermodynamic equilibrium of the SnS grain surfaces. Air and the specific gases from the labelled bottles were injected by fluxing technique through micropipette. The resistance of the sensors were measured thoroughly through a simple electronic circuit consisting of a power supply, a resistance, a Keithley electrometer and proper electronic interface data acquiring system. The sensing measurements were done at operating temperature ranging between 250 °C and 300 °C for SnS based sensor. Here we have chosen three operating temperature i.e. 250 °C, 275 °C and 300 °C. The gas sensing sensitivity is poor below the 250 °C. This result indicates that temperature below 250 °C is not enough to make active chemical reaction at the surface. Above 300 °C i.e. at higher temperature there is a tendency to make oxidize the SnS samples [232]. Hence higher temperature has been avoided during the experimental measurements. The resistance of the nanofilm sensors were measured during the injection of the gas in the chamber. The controlled gas concentrations were benzene (10 ppm), CO (10 ppm), CH_4 (10 ppm), H_2 (10 ppm) and ethanol (300 ppm). All these gas concentrations were taken on the

basis of human exposure limits. Figure 4.1 shows schematic diagram of gas sensor measurement of SnS nanoparticles.

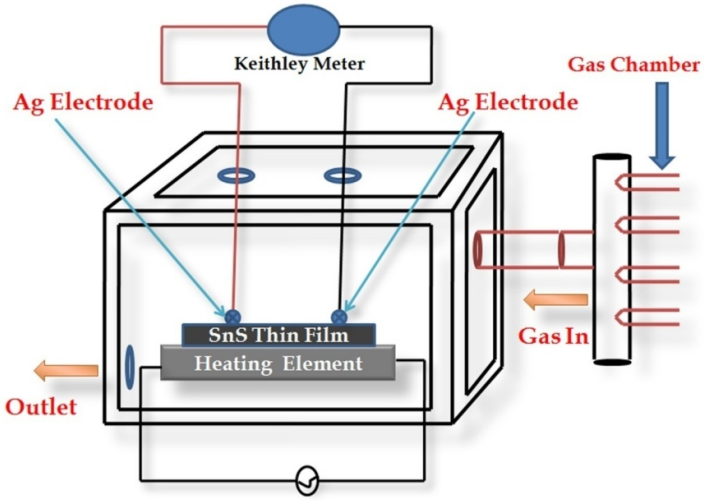

Fig. 4.1. Schematic diagram of gas sensor measurement of SnS nanoparticles

4.2. Results and discussion

4.2.1. Gas sensing properties

To study the gas sensing properties of SnS nanofilms it is necessary to explain the "3S rule" i.e., sensitivity, selectivity and stability. Here we have used five different gases (benzene, CO, CH_4, H_2 and ethanol) of different chemical groups. Among them SnS is more selective to ethanol gas i.e. it shows high selectivity and sensitivity to hydroxyl group. Best sensitivity was obtained for all sensors at 300 °C. In this temperature the sensors are more sensitive to select the specific chemical groups (Fig. 4.2). At first gas sensing sensitivity was studied under dry air condition using ethanol with SnS samples which are grown in different times. The gas sensing behaviour of the SnS sensors were also studied in wet air conditions. As humidity is a major parameter in the environment, it can affect the sensing sensitivity of the sensors. Water bubble was injected into the handmade gas chamber by fluxing with the help of micropipette. It was seen that gas sensing sensitivity decreased for each of the SnS

sensors. The decrease in the sensing resistance with the exposure time for 3 h, 7 h and 14 h SnS sensors was recorded.

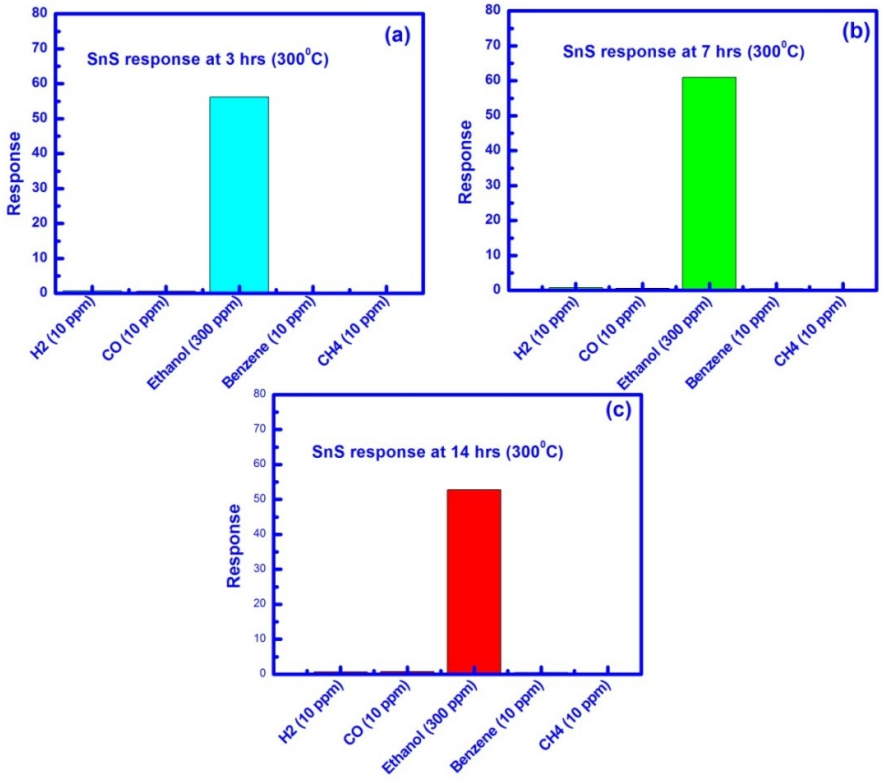

Fig. 4.2. Selectivity of (a) 3 h SnS, (b) 7 h SnS, (c) 14 h SnS

The percentage of sensitivity of 3 h, 7 h and 14 h SnS sensors at 300 °C in humid condition were 8%, 13% and 6% respectively. The relative humidity was maintained with HIH-4000 humidity sensor. The relative humidity of the gas chamber was approximately RH = 25%. The decrease in sensing resistance is due to the interaction between chemical (SnS) substances and OH− group on the SnS nanofilms. The presence of water vapour can reduce the sensitivity but does not affects on the selectivity in the dry air condition. The sensitivity and selectivity mainly depends on particle size, shape, and morphology and stochiometric ratio. Hence particle size, shape, and morphology and stochiometry play an important role in the selectivity and sensitivity. Due to the higher selectivity, good response in dry air as well as humid conditions, SnS sensors can be used for detection of alcoholic compounds.

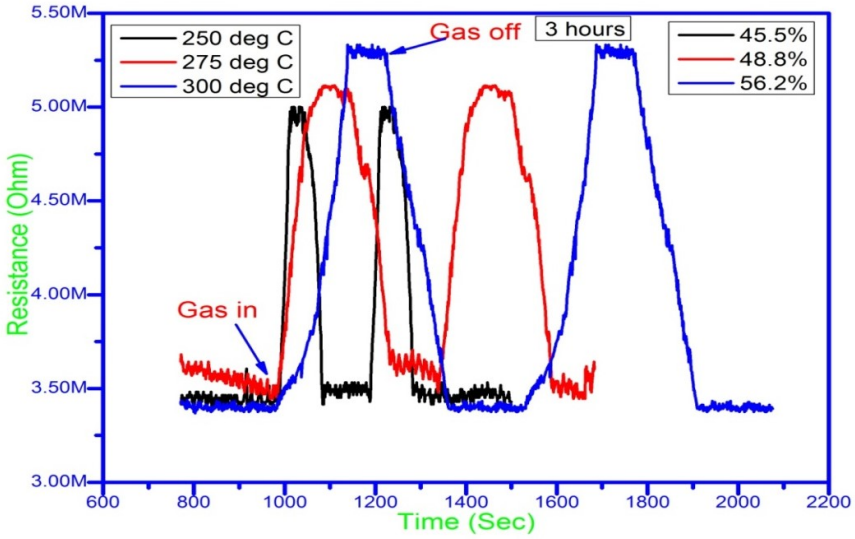

Fig. 4.3. Variation of resistance with time in dry air condition for 3 h SnS

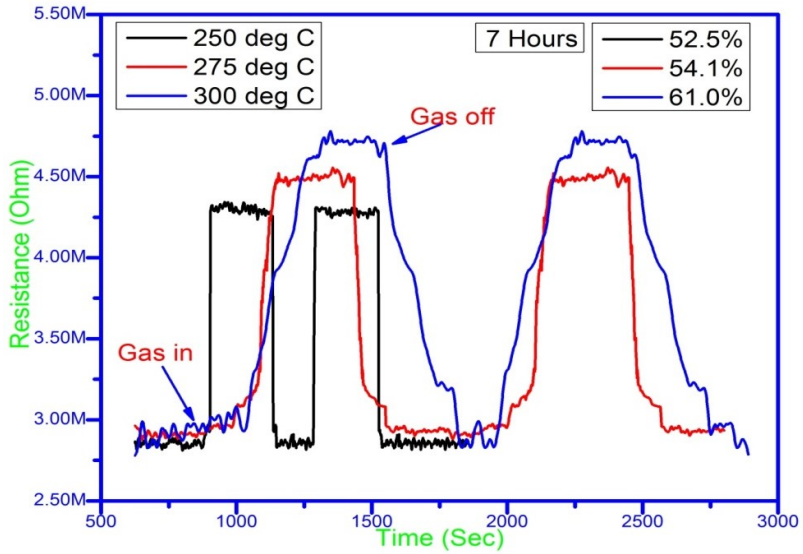

Fig. 4.4. Variation of resistance with time in dry air condition for 7 h SnS

In the present work we have studied gas sensing properties of SnS in ethanol at dry air conditions as well as in humid conditions. In case of SnS nanomaterials the resistance increases in presence of reducing gases in dry air conditions. So it can be considered as p-type semiconducting material. The variations of sensing resistance and exposure time in different temperature in dry air conditions are shown in Figs. 4.3, 4.4 and 4.5 respectively for 3 h, 7 h and 14 h samples.

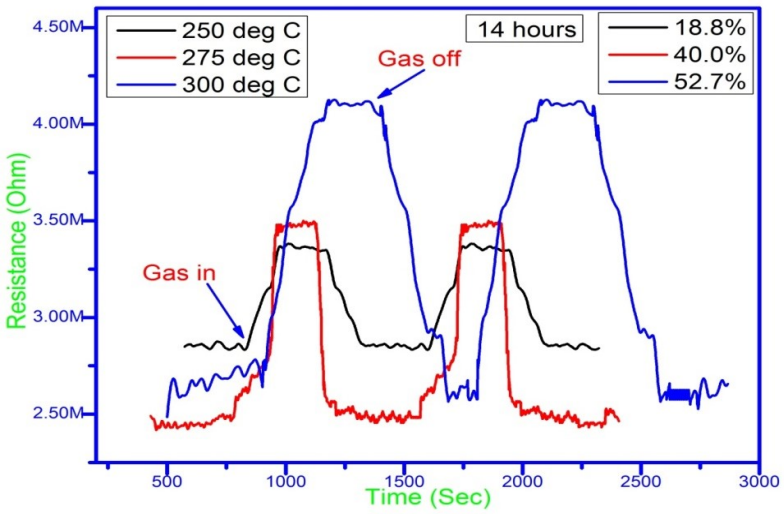

Fig. 4.5. Variation of resistance with time in dry air condition for 14 h SnS

Figure 4.6 gives the variation of sensing resistance of each sensors with time at 300 °C temperature in humid conditions (RH = 23%).

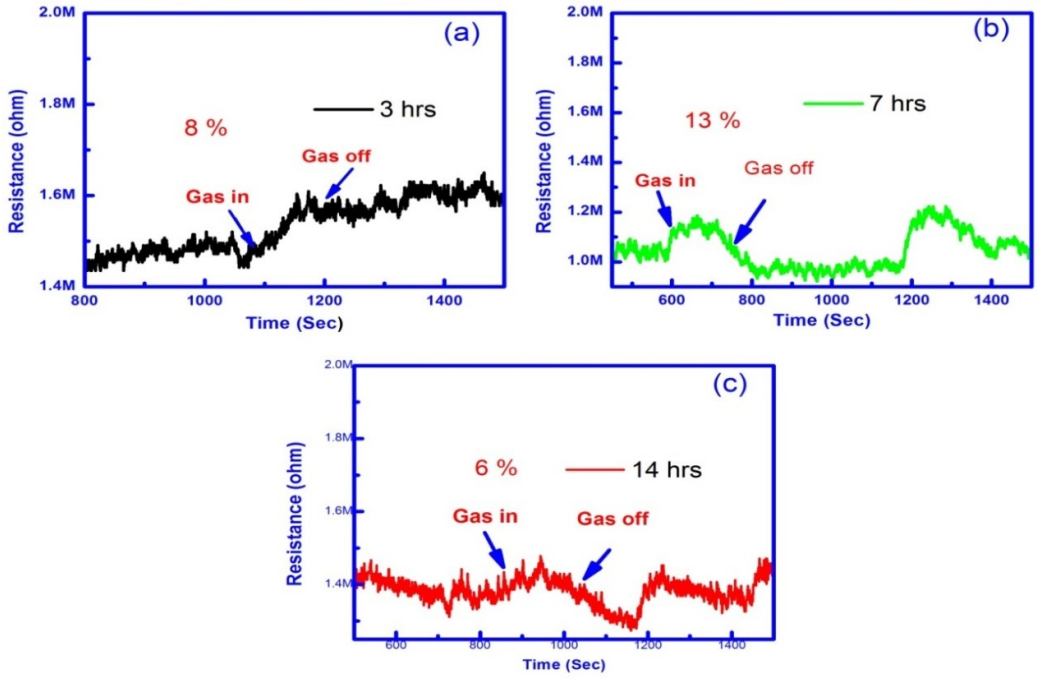

Fig. 4.6. Sensitivity curve in humid condition of (a) 3 h SnS (b) 7 h SnS (c) 14 h SnS

A decrease of sensing resistance has been observed in humid conditions with respect to dry air conditions. The sensitivity is greater for sample grown for 7 h. Sensitivity depends on the

particle size. This is depicted in Fig. 4.7 (a). The sensitivity increases with increase of sensing temperature for each sample and are shown in Fig. 4.7 (b). The response time (air to ethanol) and recovery time (ethanol to air) of SnS nanostructured sensor from 250 °C to 300 °C is shown in table 4.1. The response and recovery time of all samples increase with increase in temperature. The response and recovery time is maximum at 300 °C for all samples. From table 4.1, it is observed that response time (29 s) as well as recovery time (21 s) is lowest at 250 °C for the sample grown for 7 h duration.

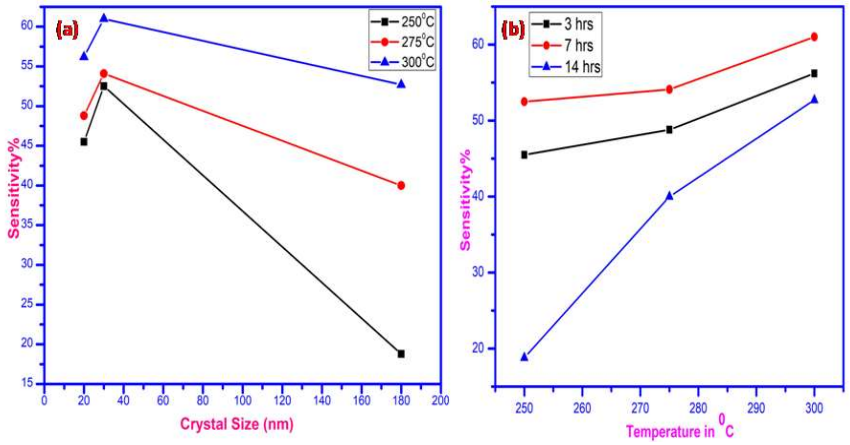

Fig. 4.7. (a) Sensitivity as a function of crystal size of SnS NPs (b) relationship between sensitivity and operating temperature of SnS NPs.

The response and recovery times has been calculated from Figs. 4.3, 4.4 and 4.5 for different samples. The gas sensor sensitivity (S) can be measured by the following equations:

$$S = \left(\frac{R_g}{R_a} - 1\right) \times 100\% \qquad \text{for } R_g > R_a$$

$$S = \left(\frac{R_a}{R_g} - 1\right) \times 100\% \qquad \text{for } R_a > R_g$$

Where R_g and R_a are the saturated resistances in gas and air respectively. We see that the sensitivity in dry air conditions becomes maximum for 7 hours SnS sample at 300 ^{0}C. This may be due to the chain like nanostructure associated with this SnS nanocrystals. Also from the EDS analysis it evident that stochiometry is maintained well for sample grown at 7 hours.

With increase of particle size, sensitivity decreases. This is due to the proportionality relation between sensitivity and the aspect (surface to volume ratio) ratio of nanoparticles. The shape and size of nanoparticles affect sensitivity and it is depicted in tabular form as shown in table 4.2. Sensitivity of 3 hrs sample is less than the 7 hrs sample. This is probably due to shape of the nanoparticles as well as the stochiometry. The particles are uniform for 7 hrs sample and chain like pattern is observed in TEM image. AFM picture indicates that roughness is moderate for this sample. Also stochiometry is good for such sample. Hence sensing ability is more for 7 hrs sample compared to the other samples grown for 3 hrs and 14 hours.

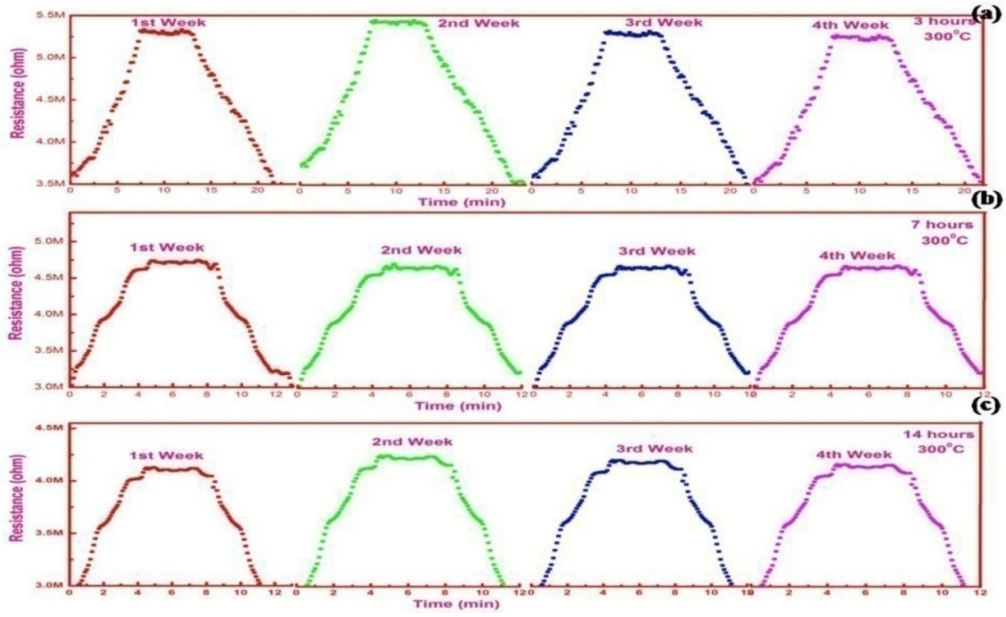

Fig. 4.8. Stability over 4 weeks of (a) 3 h SnS (b) 7 h SnS (c) 14 h SnS

Figure 4.8 shows the stability graphs of SnS sensors over time, a period of four weeks. To improve the stability of the SnS sensor we have measured the variation of resistance with time over four weeks repeatedly. To get better sensitivity we have used operating temperature only at 300 ^{0}C for each sample at dry air conditions. From the stability graphs we see that the sensitivity is more or less constant over four weeks with very fulfilling results.

4.2.2. Gas sensing mechanism

The hole concentrations and the coefficient of reaction rate increases exponentially with increase in operating temperature. It is well known that, the sensing response is directly proportional to the reaction rate coefficient and inversely proportional to the electron concentrations [148]. SnS is basically a p-type semiconducting materials. When SnS nanofilms are placed into air, they adsorb O_2 molecules from air. According to Wolkenstein's model which states that the adsorbed O_2 molecules are partly ionized into O^-, O_2^- and O^{2-} ions by capturing electron from surface of the semiconducting materials at different temperatures.

$$O_2\,(gas) + e^- \rightarrow 2\,(O^-)_{ads}$$

$$O_2\,(gas) + e^- \rightarrow (O_2^-)_{ads}$$

$$O_2\,(gas) + e^- \rightarrow (O^{2-})_{ads}$$

Due to capturing of the electrons from the valence band of the SnS nanofilm surfaces, there is decrease in electron concentrations producing a net positive accumulation region by holes. Hence the whole surface of the SnS sensors are covered by the negative charges layer (O^-, O_2^- and O^{2-}). Therefore the sensor response i.e the sensing resistance of the SnS sensors decreases and fixed to a constant value when saturation is established. Now the SnS sensors are exposed to ethanol gas, the possible reactions with the captured oxygen are explained as follows:

$$CH_3CH_2OH + O_2^- \rightarrow CH_3COOH + H_2O + e^-$$

$$CH_3CH_2OH + O^- \rightarrow CH_3CHO + H_2O + e^-$$

When the ethanol gas is fluxed to the gas chamber, their molecules are trapped by the sensors with adsorbed O_2 layer (O^-, O_2^-). Hence, one H can lose from CH_3CH_2 group. This lose H combine with OH group as well as adsorbed oxygen, which results in the formation of water (H_2O) molecule. This water (H_2O) molecule desorbs releasing a single electron (e^-) into that material. As a result ethanol turns into ethanoic acid (CH_3COOH) and acetaldehyde

(CH_3CHO). Hence, the adsorption of ethanol gas on the surface of SnS sensors causes electron–hole (e^- - h^+) pair annihilation. So, there are decreases in hole (h^+) density as well as consequently decreases in the surface negative charge which increases in the overall sensing resistance of SnS sensors.

Table: 4.1

Response and recovery time of SnS at different temperatures in presence of ethanol

Sample	SnS film temperature	Response time in sec (Air to ethanol)	Recovery time in sec (Ethanol to air)
3 hour-SnS	250 ^{0}C	30	46
	275 ^{0}C	104	105
	300 ^{0}C	164	143
7 hour-SnS	250 ^{0}C	29	21
	275 ^{0}C	170	131
	300 ^{0}C	287	277
14 hour- SnS	250 ^{0}C	152	150
	275 ^{0}C	196	193
	300 ^{0}C	288	282

Table: 4.2

Percentage of sensitivity for all samples in different temperature

Sample	Pattern	Size	Sensitivity in dry air condition		
			250 ℃	275 ℃	300℃
SnS-3 hour	Particle	~20 nm	45.5%	48.8%	56.2%
SnS- 7 hour	Particle	~30 nm	52.5%	54.1%	61.0%
SnS- 14 hour	Rod	~180 nm	18.8%	40.0%	52.7%

4.3. Conclusion

The grown nanoparticles are deposited on glass for the fabrication of gas sensor. The film roughness increases with increase of size of particles. The gas sensing sensitivity is maximum for sample grown for 7 hour at 300 ^{0}C. The shape of the nanoparticle for such sample is chainlike and may play role to increase the sensitivity. Also the stochiometry of SnS is well maintained for the sample grown for 7 hours. Thus stochiometry, shape and roughness also take an important role in sensing the gas. It is evident that response time and recovery time is lowest at 250 ^{0}C for the sample grown for 7 hour duration. So it is most efficient in gas sensing compared to other samples. Hence ethanol gas is sensed efficiently by the sample grown for 7 hours by chemical method. The gas sensing properties has been studied in dry air as well as humid conditions. The stability of the sensors has been also studied over four weeks and this indicates good stability. Hence the '3S' rules i.e sensitivity, selectivity and stability mainly depends on particle size, shape, morphology and chemical compositions.