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GAS SENSING STUDY OF CuO MODIFIED SnO2-ZnO(10-90) COMPOSITE SENSOR TOWARDS H2S

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ABSTRACT

The SnO2 and ZnO is synthesized by co-precipitation method using microwave oven. The XRD, SEM and EDAX of both oxides are carried for structural and morphological study and for confirmation of the sample. For constructing the thick film of the mixture, the two oxides are mixed together by taking 10% of SnO2 and 90% of ZnO. FE-SEM and EDAX of the composite is completed for morphological study and compositional analysis. The V-I characteristics, conductivity and gas sensing properties of composite is studied.

Keywords: *SnO2-ZnO (10-90) composite thick film, CuO modification, H2S sensing.*

I. INTRODUCTION

21st century is the century of tremendous development in Science and Technology. This development has made the human life easy and comfortable. However, in the voracity of progress, the man has not care about the protection of environment. Burning of toxic hydrogen sulfide gas with atomic oxygen, molecular oxygen or ozone gives rise to Sulfur dioxide [1]. Gases containing sulfur is created during the combustions of petroleum and coal, [2]. The sulfur contaminated surrounding can result in harmful infection to respiratory track and lung cancer [2,3]. H_2S is used in large amounts by various chemical industries and research laboratories. The threshold for H_2S detection by human nose is very low as 0.02 ppm. ; A person in the surrounding of H_2S no longer discerns its characteristic smell before the dangerous threshold values of 50-100 ppm is reached. The occupational exposure limit to H_2S is 10ppm (for 8h). Therefore, it is very important to detect H_2S gas when present at few ppm levels and possibly at sub-ppm levels in the surrounding air. In various report it is observed that, materials like ZnO, SnO2, Fe2O3, Ga2O3, etc. [4–19] can be used to detect inflammable and toxic gases. The gas sensitivity of the materials can be improved by using some additives and modifying the surface of the metal oxide film [20–22]. Sensitivity and selectivity of material can be improved by linking the catalysts like Pt, Pd, Ag, Ru and Cu [21,22] to the base material. CuO is proved to be wonderful promoter for enhancing the catalytic activity and gas sensing properties of SnO2 or ZnO for H2S detection [4–8]. In the air ambient oxygen molecules in the air is adsorbed by the sensor surface which trapped the free electron in the conduction band leading to increase in resistance of sensor. Upon exposure of semiconductor gas sensors to the reducing gas like NH3, H2S or H2, surface oxygen reacts with the targeted gas and release the free electrons to the conduction band leading to decrease in resistance of sensor [23–26] ,. The hetero-junction effect synergistic effect or catalytic effect can be used to explain sensing behavior of the surface modified or composite sensor [27–34]. In heterojunction type sensor potential barrier is high in ambient air and it reduces upon exposure of sensor surface to targeted reducing gas. It does not require adsorption and desorption of oxygen for the detection of H2S gas. The H2S gas sensing properties of material like SnO2–CuO [4–9], CuO–SnO2–ZnO [14], SnO2–Pd [19], modified BaTiO3 [35], SnO2–Al2O3 [36], SnO2– CuO-SnO2 [37] and ZnSb2O6 [38] are studied in the respective report. In present article SnO2-ZnO composite thick films are fabricated using 10 % SnO2 and 90 % ZnO. The surface of composite thick films are decorated with CuO by dipping the films in solution of CuCl2 in deionized water for 2 minute and minute.

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II. METHODS & MATERIAL

Preparation of thick films:
Thick films of synthesized nanocrystalline (SnO2– ZnO) composite were prepared by using screen printing technique. In typical process, thixotropic paste was formulated by mixing the 10% SnO2 and 90 ZnO powder with ethyl cellulose (temporary binder) in mixture of organic solvents such as Butyl cellulose, Butyl carbitol acetate and turpeneol. The ratio of mixture of SnO2 and ZnO to ethyl cellulose was 90:10. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The thixotropic paste was screen printed on a glass substrate in desired pattern. The films prepared were fired at 500 ^{0}C. Prepared thick films called as nanocrystalline (SnO2–ZnO)(10-90) composite thick film sensor.

Thickness measurement:
Thickness of thick films were measured by using digital micrometer. Thick films of uniform thickness 36 μm were used for further characterization.

Surface modification of SnO2–ZnO composite thick films by CuO:
Surface of fabricated (SnO2–ZnO) nanocomposite thick films were decorated by dipping them into a 0.01M aqueous solution of copper chloride (CuCl2·2H2O) of Merk India ltd for different intervals of time (2 min, 4 min). After dipping, thick films were dried in air. Dried thick films were fired at 500^{0}C for 6 hrs in air. The CuCl2 dispersed on the film surface was oxidized in firing process and sensor elements with different mass % of Cu on the surface of (SnO2–ZnO) nanocomposite thick films were obtained. 2minit and 4 minit activated films are termed as CuO102 and CuO104 sensor respectively. In the article, the basic system is SnO2-ZnO composite. The surface of basic composite system having 10 % SnO2 and 90% ZnO is modified by CuO. 10 in 102 of CuO102 represent the weight percent of SnO2 in (10% - 90%) sensor. Naturally the wt. percentage of ZnO will be 90% and last digit 2 in 102 represent the dipping time. CuO104 means the surface of basic system is decorated with CuO by 4 minit dipping time.

III. MATERIALS CHARACTERIZATION

FE- SEM analysis

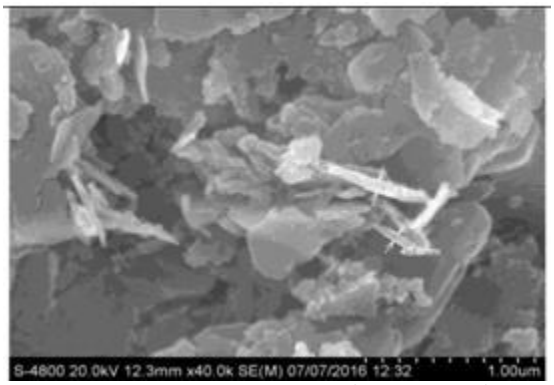

Figure1a, FE-SEM micrograph of 10-90 thick film

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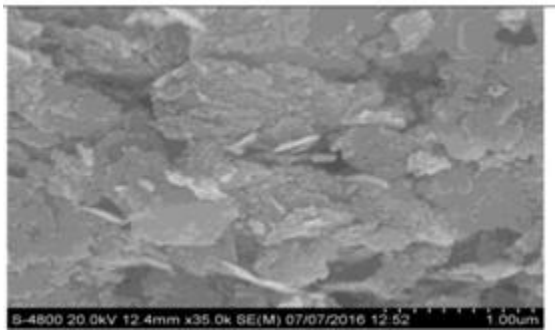

Figure1b, FE-SEM micrograph of CuO102 thick film

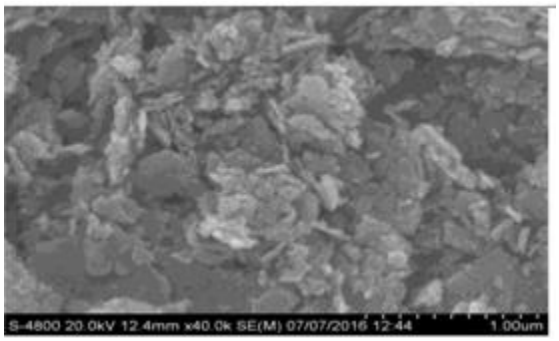

Figure1c, FE-SEM micrograph of CuO104 thick film
Figure1(a-c) FE-SEM micrograph of different thick films

Field emission scanning electron microscopy FE-SEM was employed to characterize the surface morphology. FE-SEM micrograph of SnO2–ZnO (10-90), CuO102, CuO104, composite thick films are carried out with the help of S4800 Hitachi Japan field emission scanning electron microscope linked with spectrometer, University Institute of Chemical Technology, North Maharashtra University Jalgaon.

Fig.1 depicts the FE-SEM micrograph of different SnO2–ZnO (10-90), CuO102, CuO104 composite sample at 1 µm magnification. As seen in Fig.1 CuO modified composite thick films consist of randomly distributed ZnO along with very few small size spherical particle of SnO2. Fine particles of CuO are also present in surface modified film. Such tube structure of ZnO and small size SnO2 grains provides large surface area for adsorption of ambient oxygen, which enhances the possibility of higher sensitivity. As in Fig. of FE-SEM micrograph of unmodified thick films, the ZnO rods have size range from 46 nm to 66 nm. SnO2 particle ranges from 16 nm to 35 nm. SnO2 and ZnO particles are rather agglomerated and deformed.

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EDAX Spectra:

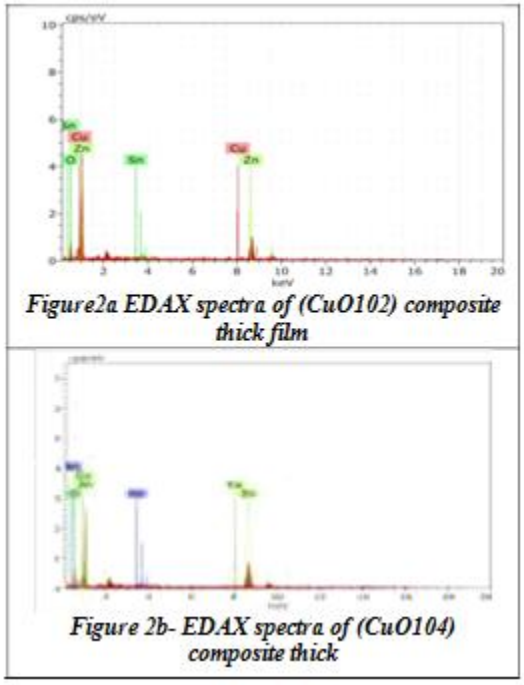

Figure 2 EDAX spectra of material

Elemental analysis of all (SnO2–ZnO) composite thick films are carried out by S4800, Hitachi Japan field emission scanning electron microscope linked with spectrometer, University Institute of Chemical Technology, North Maharashtra University Jalgaon. The EDAX spectra depicted the presence of Sn, Zn, and O in undecorated and Sn, Zn,Cu and O in CuO activated (SnO2–ZnO) composite thick films as expected, no other impurity elements were present in the (SnO2–ZnO) composite thick films.

Elemental composition of composite thick film:

Table 1Composition of (10%-90%) composite thick film

Element	Atomic number	Mass %	At. Wt. %
O	8	14.76	42.36
Zn	30	78.29	54.96
Sn	50	6.95	2.69
Total		100	100

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Table 2- Elemental composition of (CuO102) composite thick film

Element	Atomic number	Mass %	At. Wt. %
O	8	22.16	54.07
Cu	29	1.69	1.04
Zn	30	74.02	44.19
Sn	50	2.12	0.70
		100	100

Table 3- Elemental composition of (CuO104) composite thick film

Elements	Atomic number	Mass %	At. Wt. %
O	8	16.14	44.37
Cu	29	2.94	2.04
Zn	30	78.20	52.59
Sn	50	2.72	1.01
Total		100	100

From elemental composition, it was found that the (SnO2–ZnO) composite thick films are non-stoichiometric in ratio. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess zinc or tin ions in the crystal**.** There will be two electrons that remain trapped in the solid material, thus leading to non-stoichiometricity in the solid. This leads to the formation of the n-type semiconductor [39]. Table 1,2 and 3 displayed quantitative elemental analysis of undecorated and CuO modified (SnO2–ZnO) composite thick films**.**

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IV. RESULT & DISCUSSION

Electrical characterization:
(V-I) characteristics

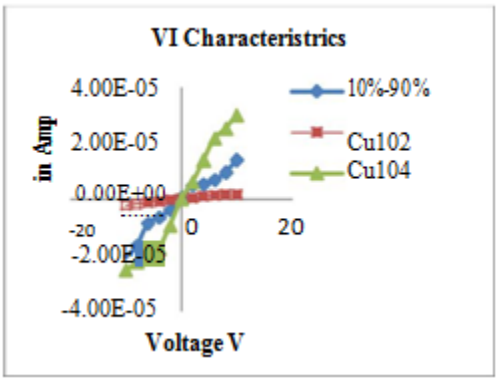

Figure3, V-I characteristics of thick films

Fig. represents the V-I characteristics of undecorated CuO decorated (SnO2 – ZnO) nanocomposite thick films at temperature 350^0 C. The characteristics are studied with the help of Keithley 6487 picoammeter cum voltage source. Current was measured with forward bias voltage from 0 to 10 V with the step of 2V .The measurement is repeated with negative voltage. The VI characteristics of samples shows that, the silver contacts fabricated on the film are ohmic in nature [40].

Electrical conductivity:

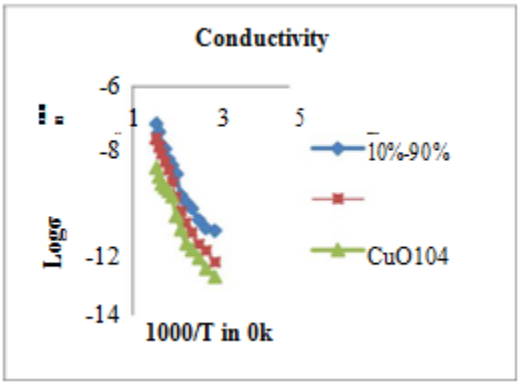

Figure4-Variation of log σ with 1000/T of 10-90, CuO102, CuO104 composite thick films

The electrical conductivity is studied with the help of Keithley 6487 picoammeter cum voltage source. The variation of electrical conductivity log(σ) with reciprocal of temperature of 10-90 composite, CuO102, CuO104 are shown in Fig.4. The nature of conductivity shows the negative temperature coefficient of resistance ie. Semiconducting nature of undecorated and CuO decorated (SnO2–ZnO) nano composite thick films [41]. The highest conductivity of 10-90 thick film can be attributed to lowest number of heterocontacts and lowest conductivity of CuO104 thick film is due to the highest number of heterocontacs present in the sensor. As the temperature increases, more electrons will be thermally excited to the conduction band which leads to increase in conductivity with temperature.

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Gas Sensing Studies:

The gas sensitivity can be defined as s = Ig/ Ia , where Ia is the current in presence of ambient air and Ig is the current in presence of gas under test. The undecorated and CuO102, CuO104 composite thick films were tested in presence of reducing gas H2S at fixed concentration of 600 ppm. at different operating temperature 30-350 ^{0}C in equal step of 50 ^{0}C except 30^0 C reading by using static gas sensing system. The thick films are also tested for 60 ppm gas concentration only at optimum temperature.

Table4-Sensitivity and respective temperature

Sensor	Corresponding Temperature	Highest sensitivity
10-90	100^0 C	37.7
CuO102	150^0 C	72
CuO104	150 ^{0} C	358

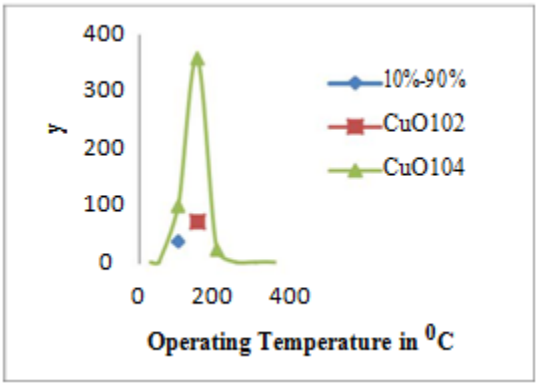

Figure5: Sensitivity vs. operating temperature

Fig5 describes the variation of gas response with operating temperature at 600 ppm of H2S gas for unmodified and CuO modified (SnO2-ZnO) composite thick films sensors towards H2S gas. From each graph it is clear that for all (SnO2-ZnO) composite thick film sensor, gas sensitivity towards H2S increases with operating temperature reaches maximum corresponding value at suitable (optimum) temperature and decreases with further increase in temperature [42-48]. The shape resulted from the competition between slow kinetics at low temperatures and enhanced desorption at high temperatures [42].The CuO104 composite sensor shows higher sensitivity (358) than sensitivity of unmodified (37.7) and 2 minute activated thick films (72).

Heterocontacts present in CuO104 sensors are contact between n-SnO2 and n-ZnO, contact between n-SnO2 and p-CuO, contact between n-ZnO and p-CuO. The highest sensitivity of CuO104 sensor can be attributed to formation of heterojunction between different components of composite [49-54] and their disruption on exposure to target gas**.** Upon exposure to H2S the CuO will transform to more conducting metallic CuS which reduces the potential barrier and produced more current [53]. Again numbers of these heterocontacts will definitely more in CuO104 in comparison with rest of two composite sensor. More the heterocontact disrupted, more will be the free electron available for producing the current. Thus the current or sensitivity increases. More surface area will be available in ZnO dominating senor because of its tube structure and porous surface which increased the active sites on surface, thus higher sensitivity is received [55-56]. Synergy between different components of composite is favorable for augmentation in sensitivity [57-58]. Sensitivity of nano crystal depends not only on their composition, but also on their structure, phase, shape, size, and size distribution. Nonuniformity in sizes and shapes of entire three

components is also favourable for high score sensitivity of respective sensors [59-61]**.** At higher temperature, due to desorption of oxygen molecules from the surface more conduction electrons get available for producing higher current in air ambient, thus the change in current after exposure to testing gas is less, which reduces the sensitivity. The species $O2^{--}$ would have available largely on the CuO104 sensor surface at 150 ^{0}C and H2S gas would have been reduced CuO quickly to CuS and in greater extent at 150^{0}C temperature to give higher sensitivity. Further hetero-contact enhancement effect might be responsible for higher sensitivity of CuO104. Hence the response of CuO104 was higher. Relatively lesser number of hetero–contacts in (10-90) and CuO102 thick film than CuO104 attributed to lower response relative to CuO104. At 150^0 C less conducting CuO transfer to more conducting CuS metallic conductor which produce more current. Relatively higher percentage of Cu in CuO104 sensor produced higher number of CuS which enhance the current. All these result can be attributed to synergistic effect, heterocontact effect. From Cu mass percent, it is pointed out that, the sensitivity of all three sensor is determined by number of hetero contacts and mass percent of Cu in al three sensor.

Higher sensitivity of CuO104 sensor can be explain with help of following chemical reaction –

$$CuO + H2S \rightarrow CuS + H2O$$

It is obvious from above reaction that CuO react with H2S and CuS is formed. Nature of CuS is metallic. Metallic nature of CuS will destroy the n-p-n junction and n-metalic-n hetero junctions will form and potential barrier reduced markedly. Considerable destruction of potential barrier promotes the electrical conduction.

On removal of H2S the sensor will come back in original form in ambient condition of air, CuS react with the oxygen as,

$$2CuS + 3O2 \rightarrow 2CuO + 2SO2$$

Thus CuO is reformed in above reaction. Hence potential barrier increases, which results in low electrical conduction. Beyond 150^{0}C temperature the sensitivity of CuO modified composite sensor reduces sharply. Lattice structure of CuS changes at higher temperature and CuS decomposes to Cu2S . The Cu2S is high resistive ionic conductor; due to this the sensor shows poor sensitivity above 150^{0}C.

Concentration vs sensitivity curve in CuO104 sensor depicted that the response got saturated above 600 ppm of H2S concentration. CuO104 sensor was sensitive to 5 ppm of H2S gas.

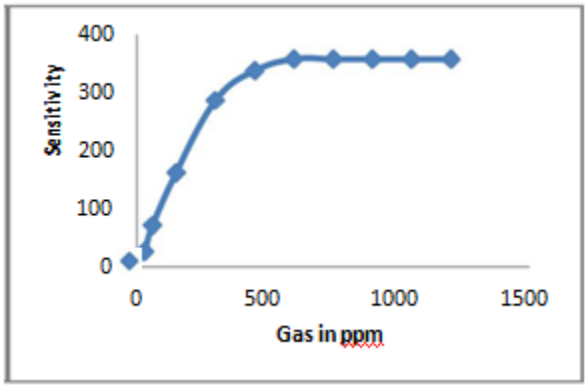

Figure6- H2S concentration vs. sensitivity of CuO104 thick film

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Response and recovery time of CuO104 thick film:

H2S response of CuO104 composite sensor with time: The response and recovery time of CuO104 composite sensor against H2S is displayed in fig.7. The response and recovery time of CuO104 sensor was 163 sec and 173 sec respectively.

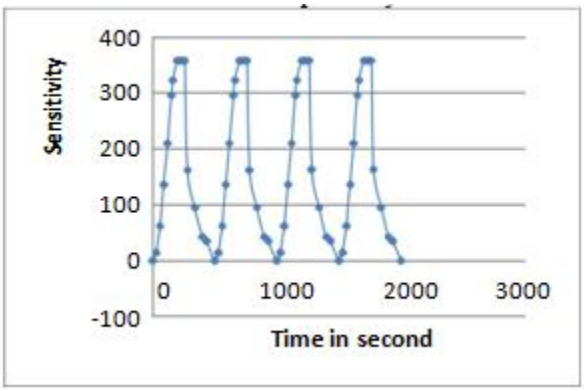

Figure7-response and recovery time of CuO104 thick film

Selectivity of CuO104 thick film:

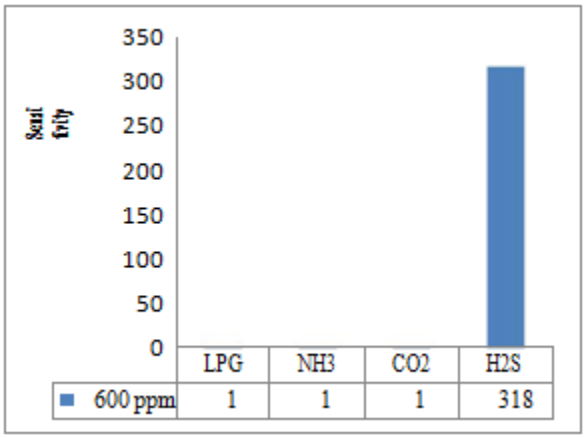

Figure9-Selectivity of CuO104 thick film

CuO104 is selective to H2S gas only among mixture of H2S, CO2, NH3 and LPG

V. CONCLUSION

From the work carried out here, it can conclude that, the SnO2 and ZnO can be synthesized within ten minute by using microwave oven. H2S sensitivity can be improved in composite thick film consisting of SnO2 and ZnO. It can further conclude that, the H2S sensitivity can be improved by decorating the surface of SnO2-ZnO composite by CuO.

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