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Hydrogen sulfide sensor based on cupric oxide thin films

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ABSTRACT

In this work, thin films of copper oxide (CuO) doped with different concentration of samarium oxide (Sm₂O₃) have been prepared using spray pyrolysis technique with optimum temperature of 325 °C. Structural, optical and gas sensor behaviors of CuO:Sm₂O₃ nano films for Hydrogen sulfide (H₂S) gas were studied. XRD analysis of high dopant concentration, more than 5%, revealed a mixed phase of monoclinic and cubic symmetry of CuO and SmO structure respectively, with two most preferred orientations along (11-1) and (111) planes. Optical properties reveal high transparency in the range of visible region. Energy gap varied from 2.2 eV to 2.28 eV by increasing dopant concentration. Sensing results determined that, the best doping ratio with Sm₂O₃ was 3% to achieve fast response sensor.

1. Introduction

Many researches were focused on air pollutant gases, such as H₂, CO, NO₂, CH₄, NH₃, C₃H₈, and H₂S, that contribute to the harm of human health, climate change and global warming [1]. The semiconductor gas sensors are being used on a large scale because of the low cost, easily manufacturing and high sensitivity as compared with the other sensor types like, optical, biochemical acoustic, and other gas-sensing devices [2]. The main reason for choosing semiconductor metal oxides as a gas sensor that it appears to change the electrical conductivity because of the reactions between gas molecules and the surface of semiconducting metal oxide, which make the Fermi level shifting either upward or downward within the band-gap [3]. However, the sensing device can not screening or gas measuring molecules of gas, but converting the signals into change in chemical or physical properties, e.g.:frequency, conductivity, temperature, pressure, color, or capacitance [1]. There are different methods used by researchers in preparation thin films of copper oxide. For example, Rzaij [4] have prepared nano films of CuO on silicon substrates by PLD (pulsed laser deposition) method with different energies (200–600)mJ of laser pulses.

Rydosz et al. [5] nano films of CuO doping with Si, Sb, Au, Ag, Pd, Pt, and Cr have been prepared using MST (magnetron sputtering technique) on ceramic substrates. Chapelle et al. [6] have been using a radiofrequency sputtering to prepare nano composite of CuO–Cu_xFe_{3–x}O₄. The effect of annealing on optical and structural properties of CuO thin films deposited on glass substrate using sol-gel method have studied by Dhaouadi et al. [7]. CuO is one of a metal oxide, which possesses an important advantages in many researches, in recent years to detect toxic and harmful gases such as O₃ [8], C₂H₅OH [9], H₂ [10] and CO [11]. The sensitivity of gas on the surface can be as a part of billion (ppb). Due to large surface area, it is highly desirable to use these materials in the field of sensing applications, so as to accommodate the largest possible number of molecules of the substance to be a response with gas on the surface of the material and thus will increase the ability to respond [12].

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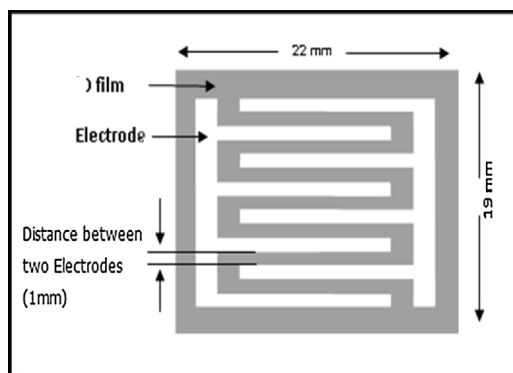


Fig. 1. Mask used for Gas Sensing.

In our present work, CuO thin films prepared by low cost spray pyrolysis technique. These samples are examined by X-ray diffraction (XRD). Transmittance, absorption coefficient and optical energy gap are recorded using ultraviolet-visible spectrophotometer (UV-vis). Furthermore, H₂S gas sensing properties of CuO were studied.

2. Experimental procedure

Undoped Copper oxide (CuO) and doped with (1%, 3%, 5% and 7%) of samarium oxide (Sm₂O₃) thin films using spray pyrolysis (SP) technique on glass and p-type Si (111) substrates. Aqueous solutions of 0.05 M CuCl₂ with purity 99.99% provided by BDH chemical Ltd pool England, were used as Cu source. 0.05 M Sm₂O₃ with a purity of 99.98% supplied by Fluka Chemicals, were used as a Sm doping agent. The solution mixed with a magnetic mixer with hot plate and heated at 60 °C, so that the reaction is stimulated towards completion. Volumetric solutions were prepared depending on the system (CuO)_{1-x}:(Sm₂O₃)_x, where (X = 0, 1%, 3%, 5% and 7%). After many experimental trials, the films were grown at an optimum substrate temperature of 325 °C. Film thickness was obtained by depth profile probe (TF probe) model SR300 (Angstrom Sun Technologies Inc., USA), which were 100 ± 3 nm. X-ray diffraction (XRD) patterns of these films were determined, using a (Cu-Kα) radiation with Wavelength = 1.5406 Å, Voltage = 40 kV, Current = 30 mA, Scanning angle: (20–60°) and Scanning Speed = 5 (°/min). Optical transmission data were recorded using (SP-8001) spectrophotometer over (Meterrech) with the range of (200–1100) nm. The gas test system can be described as an open cylinder made of stainless steel with a diameter of 19 cm and a height of 7.5 cm. The cover of cylinder has two entrances, one for entering the fresh air (to cleaning chamber testing) and the other for entering the gas (to exposing it to the symbols). Aluminum metal used to fabricate the mask that used for sensor measurements, as shown in Figs. 1 and 2 shows the electrical circuit which used for sensing test.

3. Steps of gas sensor testing

After open the cover of test chamber we placed the sample on the heater with checking all necessary electrical connections, then closed the cover of the test chamber. A rotary pump was used to evacuate the chamber of gas sensor with 1 mbar approximately. Switch on heater reach to the required temperature. Applied 6 V between both sides of electrodes as a bias voltage. To control gas flow we used needle valves to reach 25 ppm. Resistance was changed for different doping ratio (1%, 3%, 5% and 7%) at different operating temperature (RT, 100 °C and 150 °C) registered by a digital multi-meter attached to a computer.

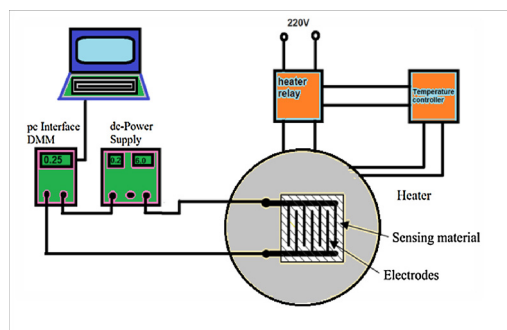


Fig. 2. Schematic diagram of gas sensing and the electrical circuit setup.

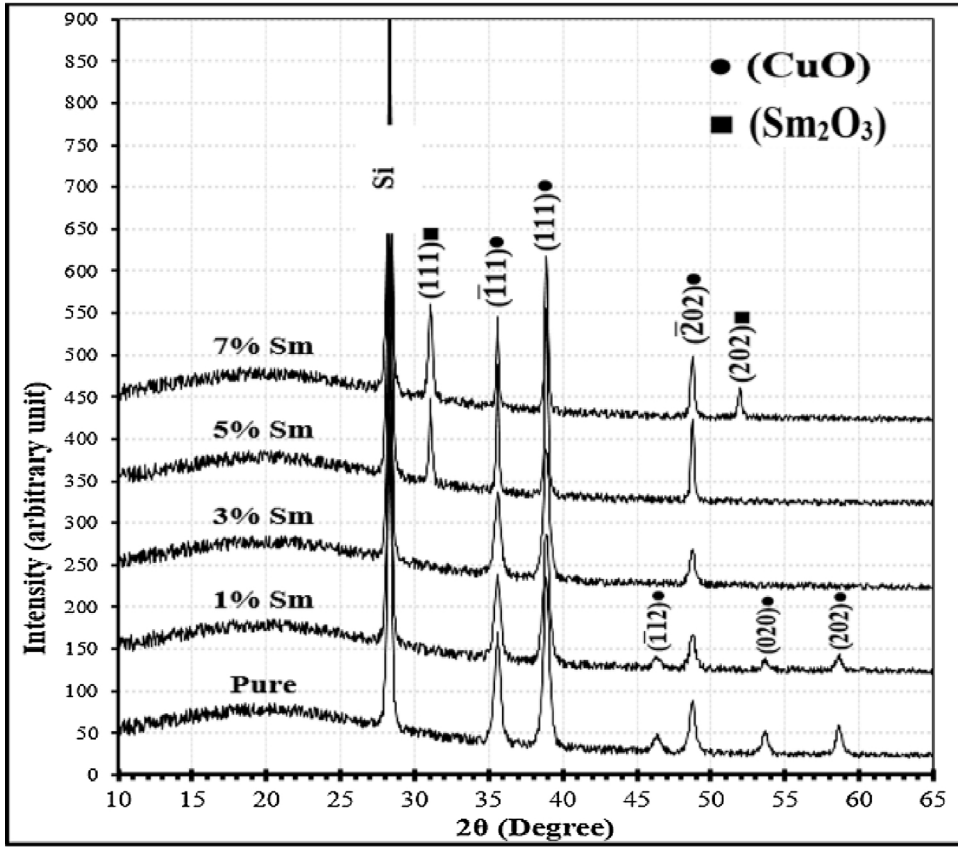


Fig. 3. XRD patterns of undoped CuO thin films and doped with Sm₂O₃.

4. Results and discussion

4.1. Structural properties

X-ray diffraction patterns of undoped CuO thin films and doped with 0, 1%, 3%, 5% and 7% concentration of Sm₂O₃ on Silicon (111) substrates were shown in Fig. 3. From this figure, it could be seen that CuO thin films exhibit polycrystalline structure with a monoclinic symmetry and a = 4.6809 Å, b = 3.4176 Å, c = 5.1220 Å and β = 99.784° as lattice parameters and match well with standard data (JCPDS 96-410-5686) with two most preferred orientations along (i11) and (111) planes. XRD patterns indicate sharp peak and high intensity at 2θ = 28° which is returned to crystalline substrate (Si) with (111) plane. FWHM of diffraction peaks suggested nanocrystalline nature of the particles depending on the calculation of average crystallite size using Debye Scherer's formula [13]:

$$D = \frac{k\lambda}{\beta \cos(\theta)} \tag{1}$$

Where k: is the shape factor (≈0.89), β: is the full width at half maximum (FWHM) in radian, λ: is the wavelength of X-ray and θ is the angle of Bragg's which represents the incident angle. A new peaks along (111) and (202) planes appeared when Sm₂O₃ concentration increased to 5% and 7%, which belongs to Sm₂O₃ structure with a cubic crystal structure, according to standard data (JCPDS 96-900-8718). There was no shifting in angle of diffraction peaks, which denoted the stability of CuO thin films with the preparation conditions used. Table 1 illustrates the FWHM and the Average grain size for undoped and Sm₂O₃ doped CuO thin films.

4.2. Optical properties

Fig. 4 shows the optical transmittance of undoped CuO and doped with 1%, 3%, 5%, and 7% of Sm₂O₃ films vs wavelength in the range of (300–1100) nm, which were sprayed on the glass substrate and kept at T_s = 325 °C

The transmittance was calculated from the relation [14]:

$$T = 10^{\bar{A}} \tag{2}$$

Where (̄A) is the logarithm to base 10 of the transmittance

Table 1
Structural parameter for undoped and Sm₂O₃ doped CuO thin films.

materials	2θ (Deg.)	FWHM (Deg.)	G.S (nm)	Phase
Pure CuO	28.30	0.3000	27.3	Si
	35.60	0.4722	17.7	CuO
	38.89	0.4770	17.7	CuO
	46.34	0.4817	17.9	CuO
	48.75	0.4760	18.3	CuO
	53.64	0.4790	18.6	CuO
	58.63	0.4780	19.1	CuO
CuO doped by 1% Sm ₂ O ₃	28.30	0.3000	27.3	Si
	35.60	0.4630	18.0	CuO
	38.89	0.4680	18.0	CuO
	46.34	0.4240	20.4	CuO
	48.75	0.4580	19.1	CuO
	53.64	0.4610	19.3	CuO
	58.63	0.4710	19.4	CuO
CuO doped by 3% Sm ₂ O ₃	28.30	0.3000	27.3	Si
	35.60	0.4680	17.8	CuO
	38.89	0.4730	17.8	CuO
	48.75	0.4620	18.9	CuO
CuO doped by 5% Sm ₂ O ₃	28.30	0.3000	27.3	Si
	35.60	0.1860	44.9	CuO
	38.89	0.2360	35.7	CuO
	48.75	0.2410	36.2	CuO
	31.07	0.2410	34.2	Sm ₂ O ₃
CuO doped by 7% Sm ₂ O ₃	28.30	0.3000	27.3	Si
	35.60	0.1860	44.9	CuO
	38.89	0.2360	35.7	CuO
	48.75	0.3050	28.6	CuO
	31.07	0.3050	27.0	Sm ₂ O ₃
	51.96	0.2740	32.3	Sm ₂ O ₃

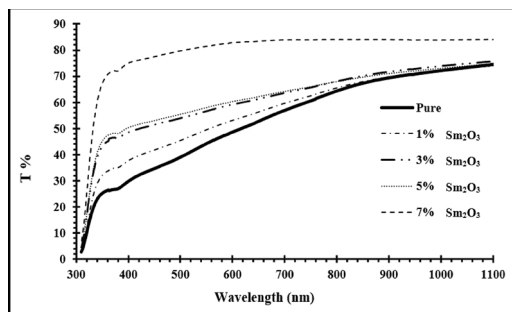


Fig. 4. Transmittance spectra of undoped CuO and doped with different concentration of Sm₂O₃ thin films.

Generally, the transmittance was increased in the visible and near (IR) wavelength regions for all samples as the doping concentration of Sm₂O₃ increased. Noticeable jump with a sharp increase in optical transmittance of 7% Sm₂O₃ doping in wavelength of ~325 nm (more than 80% in the visible region), which can be attributed to the presence of Sm₂O₃ phases in the thin films, and/or formation of nano-structured films due to Sm₂O₃ doping [15]. These results are in agreement with (Sucheta et al.) [16]. The increase of transmittance with Sm₂O₃ doping, made these films can be used in window gap field for solar cells Because of the effective region of this application are in the range of visible spectrum [17].

4.3. Absorption coefficient (α)

Optical properties were studied by determining the absorption spectrum of prepared CuO thin films such as, type of electronic transitions and the optical energy gap. The variation of absorption spectra as a function of wavelength for prepared thin films with different dopant concentration of Sm₂O₃ are shown in Fig. 5. The absorption coefficient was calculated using the relation [14]:

$$\alpha = 2.303 \frac{A}{t} \tag{3}$$

Where (A) and (t) are absorbance and thickness of films respectively.

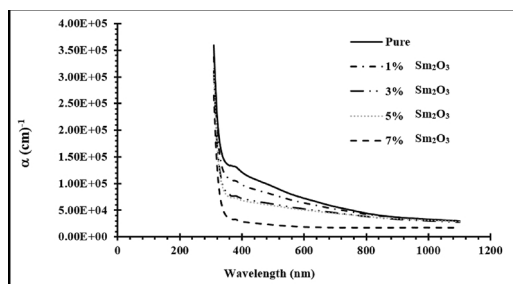


Fig. 5. absorption spectra as a function to the wavelength of (CuO) thin films with different dopant concentration of Sm₂O₃.

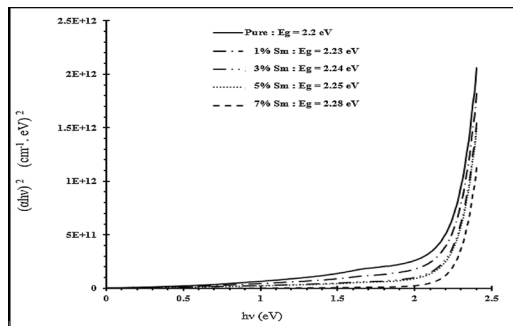


Fig. 6. E_g as a function to the photon energy of (CuO) thin films with different dopant concentration of Sm₂O₃.

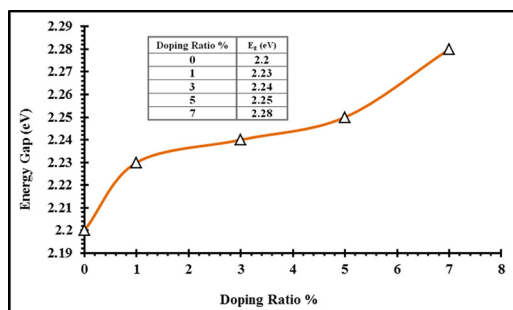


Fig. 7. Variation of E_g with different dopant concentration of Sm₂O₃.

It reveals a high absorbance in the range of ultraviolet spectrum while in visible/near infrared spectrum was low. It was observed that there was a sharp decrease in the absorption coefficient near the fundamental absorption edge in the wavelength of ~ 325 nm. The absorption coefficient (α) values were larger than $1 \times 10^4 \text{ cm}^{-1}$ which revealed that the type of electron transition is allowed direct transition [18]. The absorption coefficient can be used as absorbent coatings to the sun as a selective radioactive filters on the windows of buildings to control radiation [19].

4.4. Optical energy gap (E_g)

The difference in energy between conduction and valence band, (E_g), also can be estimated using optical measurement, which describe thermoelectric and electronic properties of materials [20]. The optical energy gap (E_g) was calculated depending on Tauc formula as follows [21]:

$$(\alpha h\nu)^2 = B(h\nu - E_g) \tag{4}$$

h : Planck constant, ν : frequency of incident photon, α : absorption coefficient, $h\nu$: energy of incident photon, B : constant and E_g optical energy. The value of E_g can be determined by extrapolating the straight-line of the plot $(\alpha h\nu)^2$ as a function of $(h\nu)$ for zero photon energy. Fig. 6 shows the plot of $(\alpha h\nu)^2$ vs. the photon energy. The optical energy gap for undoped CuO films is about (2.2) eV. However, the values of band gap are in agreement with [22] and [23]. The difference in the reported values of energy gap may be attributed to the conditions and technique of preparation. It can be observed that E_g is increasing slightly from 2.2 eV to 2.28 eV as the doping with Sm₂O₃ increased, as shown in the Fig. 7. This is can be attributed to defects in semiconductors such as a disorder or impurity which affect the band tails near band edge by creating localized electrical fields [24]. The results of optical energy gap

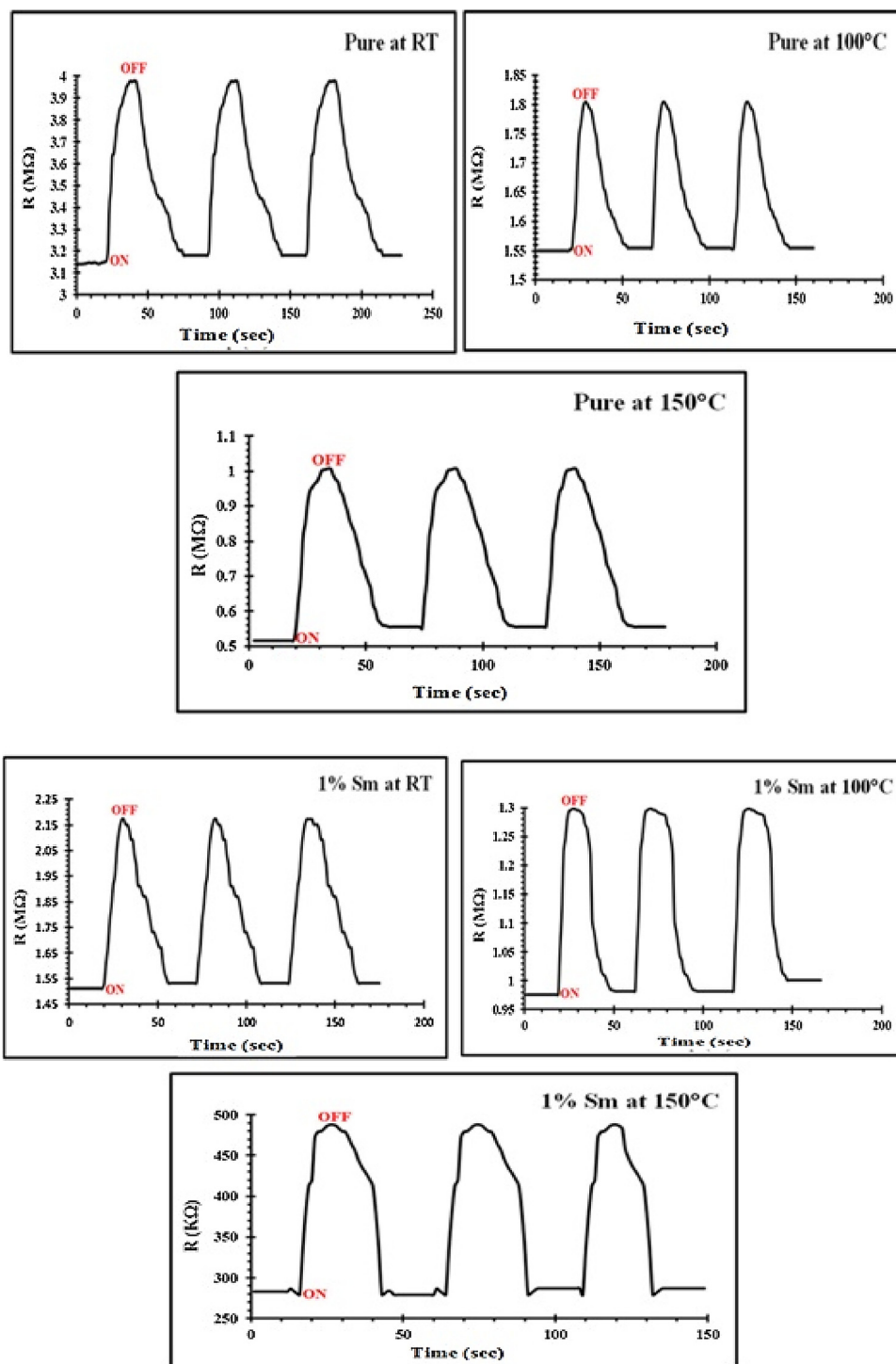


Fig. 8. Variation of resistance as a function to the time at different operating temperature with different concentration of Sm_2O_3 .

indicate that all the films have localized states, which result from the density of defects at the grain boundaries and donor levels, so it can be said that E_g can be controlled through the control of the nanostructure size and ratios of impurities

4.5. Gas sensor

Generally, When a device has the ability to detect changing in chemical and/or physical properties under gas exposure then it can

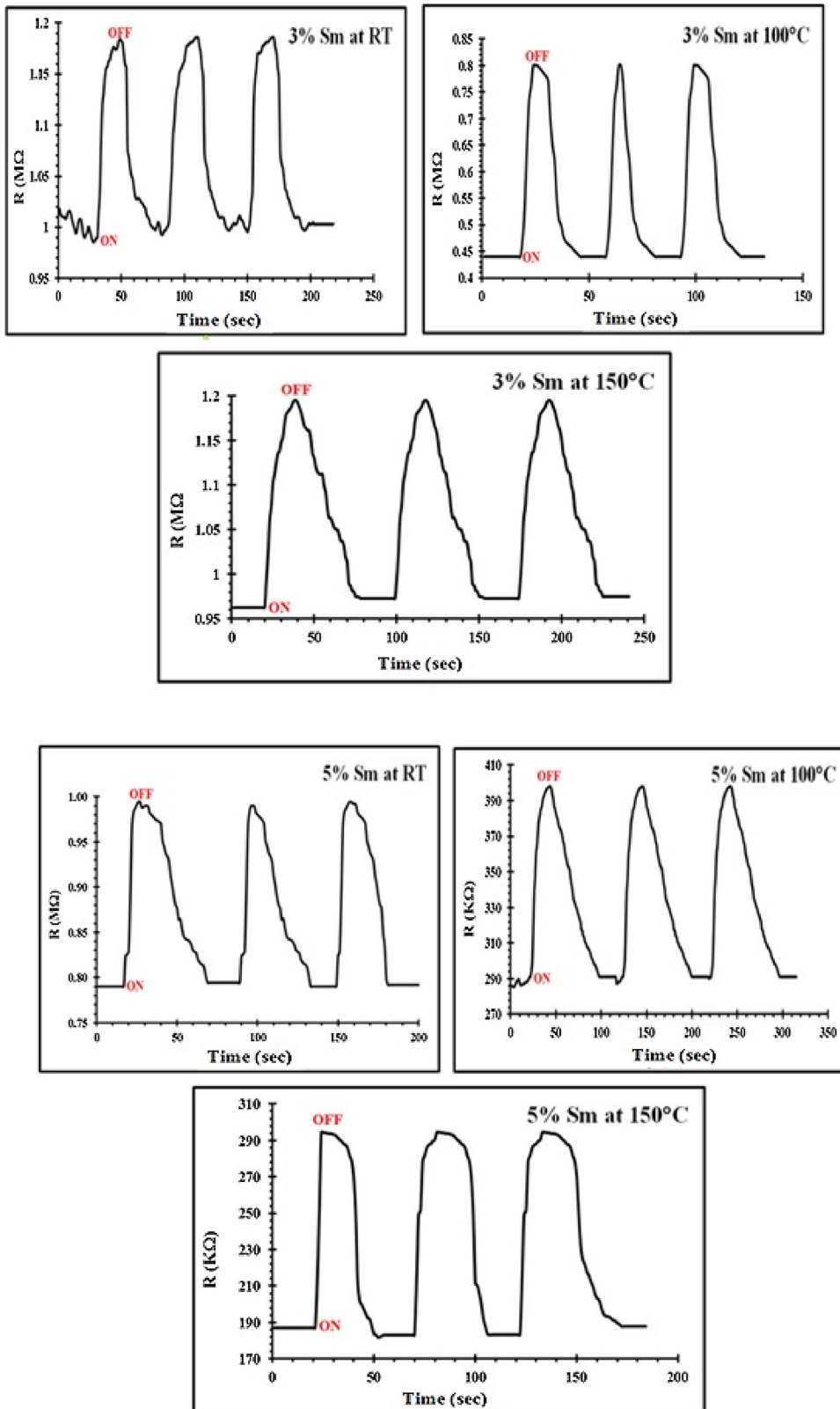


Fig. 8. (continued)

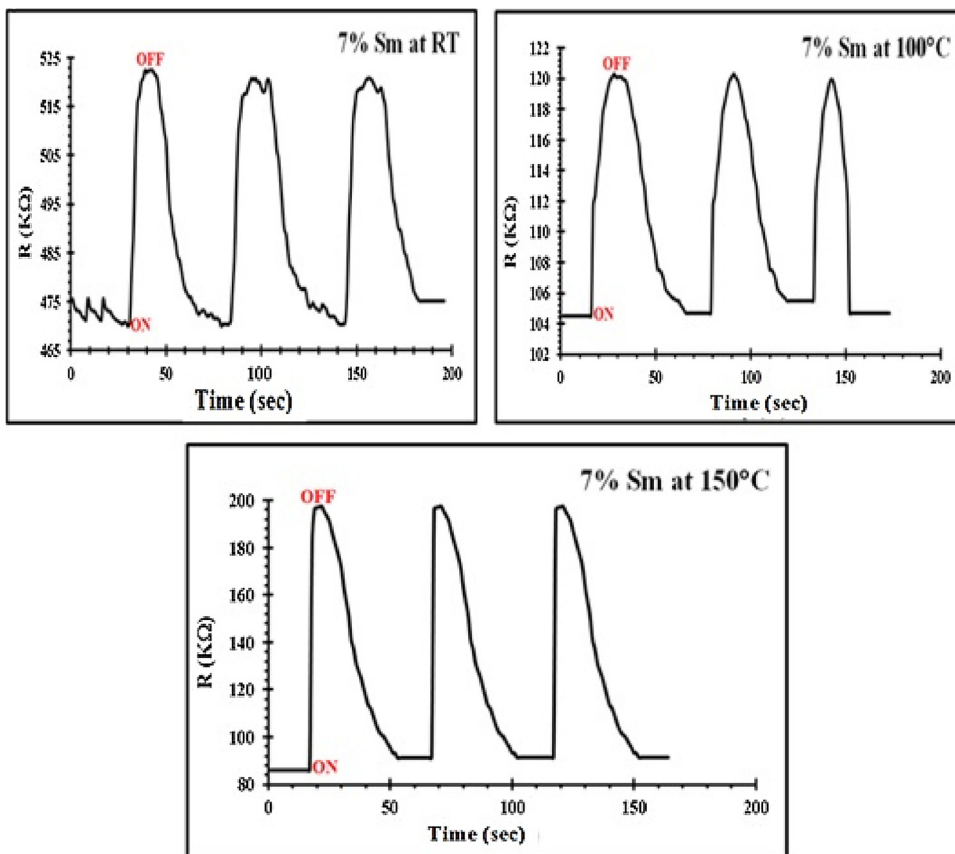


Fig. 8. (continued)

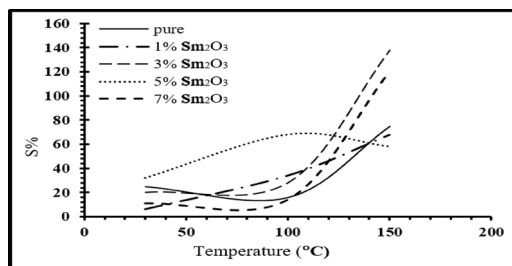


Fig. 9. Sensitivity as a function to the temperature for undoped CuO and doped with different concentration of Sm_2O_3 thin films.

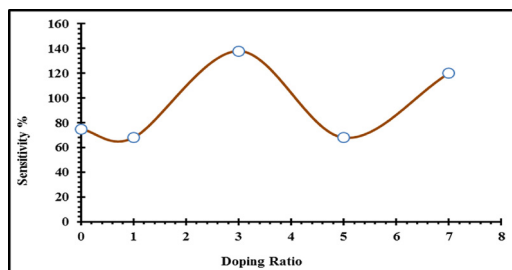


Fig. 10. Sensitivity to H_2S gas as a function of Sm_2O_3 doping ratio.

be used as a significant response for gas sensor applications [1]. The mechanism sensing of CuO thin films attributed to ionosorption over material surface for gas species which refers to relocate charge between surface molecules and gas leading to change in electrical conductance [25].

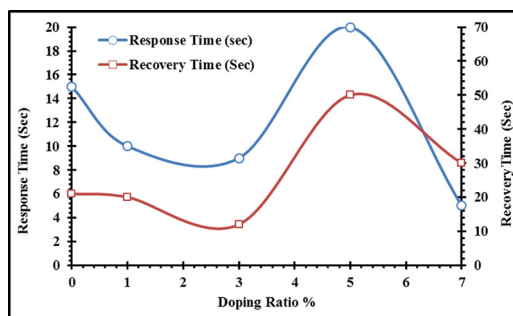


Fig. 11. response and the recovery time with different Sm₂O₃ doping ratio at optimum operating temperature.

Table 2

Sensitivity%, response time and recovery time of un-doped CuO and doped with different ratio of Sm₂O₃.

Sample	Sensitivity%			Response time (Sec)			Recovery time (Sec)		
	30 °C	100 °C	150 °C	30 °C	100 °C	150 °C	30 °C	100 °C	150 °C
pure	25	16	75	18	11	15	30	22	21
1%	6	34	68	12	12	10	23	21	20
3%	20	28	138	18	21	9	13	36	12
5%	32	68	58	10	20	8	40	50	20
7%	11	14	120	10	14	5	26	33	30

Variation of resistance versus time at different operating temperature for undoped CuO and doped with different concentration of Sm₂O₃ shown in Fig. 8 which illustrate increasing in values of resistance with Gas ON, (exposed films to H₂S gas), while there was back downward in resistance values with Gas OFF, (at the closure of the gas). This behavior can be explained as follows: an ionic reaction between H₂S gas molecules and adsorption oxygen on the surface leads to extract electrons from the semiconductor causes a decrease in conductivity of the CuO, meaning increasing in resistance [21].

Sensitivity are the main factors in practical applications for gas sensors where higher sensitivity allows these sensors to detect the lower concentrate of gas molecules on the symbol surface. Sensitivity (S%) can be defined as the changing in the resistance when the sensor symbol exposed to gas with a certain concentration. At different temperatures S% was calculated according to the relation:

$$S = \left| \frac{(R_g - R_a)}{R_a} \right| \times 100\% \tag{5}$$

Where, S: sensitivity, R_a and R_g: electrical resistance in air and in existence of gas, respectively.

Fig. 9 shows S% versus operating temperature of undoped CuO thin films and doped with different ratios of Sm₂O₃ deposited on Si substrate.

The operating temperature of gas sensor defined as the temperature when the resistance of sensor approximates to a constant value. The reason for this change in resistance is the reactant gases on the surface of the sensor [26,2]. The test of gas sensitivity performed at RT, 100 °C and 150 °C with 25 ppm concentration of H₂S and 3V as bias voltage. Result obviously shows increases in sensitivity with operating temperature increase for all prepared films, as shown in Fig. 10. Which imputed to more rate of reaction on surface of target gas, except 5% Sm₂O₃ doping ratio, the sensitivity was a decreased at 150 °C operating temperature, which may be attributed to the surface was unable to complete gas oxidation so intense or maybe the gas was burned before it reaches to the surface at this temperature [27].

The maximum sensitivity for H₂S gas observed for the film that doped with 3% Sm₂O₃ (about 138%) at operating temperature of 150 °C, as shown in Fig. 10. Maximum values of sensitivity are seen at the optimal temperature at this point where the energy of activation may be sufficient to complete required chemical reaction, which may be also return to the good surface roughness, larger ratio of oxidation and optimum number for the disparity in surface area.

the variation of recovery and response time according to operating temperature for pure CuO and doping with different Sm₂O₃ ratios thin films shown in Fig. 11. It reveals that the film doped with 3% Sm₂O₃ sample exhibit a fast speed to response (9 s) and (12 s) as time to recover this mean that 3% Sm doping was the best ratio to get a fast sensor response, as shown in Table 2.

The quick sensor response to H₂S gas may be refers to faster gas oxidation [27]. Besides that, Samarium ions take energy level below conduction band and it became as an activator, so electrons easily move to the conduction band, and increased oxygen adsorption on the surface of sensor and extracts electrons of conduction band from the region of near surface forming a depleted surface layer from the electron. Therefore the number of active adsorption sites will increased and get a fast response sensor [28].

5. Conclusions

Undoped CuO and doped with different concentration of Sm_2O_3 have successfully grown using chemical spray pyrolysis technique. XRD measurements show a monoclinic structure of CuO. It reveals that most peaks of diagram returns to cupric oxide with (010) plane as dominant of crystal structure and a few peaks for samarium oxide appears at doping ratio above 5%. Optical properties reveal low absorbance in the range of visible and near infrared spectrum region while is high in the region of ultraviolet spectrum. Gas sensing measurement of H_2S gas revealed that the sample of CuO doped with 3% Sm_2O_3 exhibits a fast response of (9 s) and recovery time (12 s) with sensitivity of 138% at operating temperature 150 °C.

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