

CuO- ACTIVATED ZnO THICK FILMS FOR H₂S GAS SENSOR AT LOWER TEMPERATURE

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Abstract

the zno nanostructures have been synthesized and studied as the sensing element for the detection of h₂s gas. the zno nanostructures were synthesized by sol-gel method followed by sonication. by using screen printing method, thick films of synthesized zno nanostructure were deposited on glass substrate. surface of this films were activated by cuo for gas sensing properties, low concentration h₂s gas at different temperature. zno nanostructure synthesized by this method can be used as a promising material for semiconductor gas sensor to detect gas like h₂s at room temperature with high sensitivity and selectivity.

Keywords: zno nanostructure; thick films; surface activation; h₂s sensor.

Introduction

the last century has seen increased industrial growth worldwide. a side effect of this development is an exponential increase in pollution of earth, air and water, especially in densely populated areas. while land pollution is locally restricted and great efforts have been made during the last decades to improve the quality of rivers and larger bodies of water, air pollution is not so easily reduced. the hazardous gas detection spans from environmental monitoring, automotive applications, air conditioning in airplanes, space crafts and houses, explosive detection of sensors networks, and so forth.

nowadays, there is a great interest in implementing sensing devices in order to improve environmental and safety control of gases. the most used gas sensor devices can be divided in three big groups depending on the technology applied in their development: solid state, spectroscopic and optic. while spectroscopic and optic systems are very expensive for domestic use and sometimes difficult to implement in reduced spaces as car engines, the so called solid state sensors present great advantages due to their fast sensing response, simple implementation and low prices [1-3]. these solid state gas sensors are based on the change of the physical and chemical properties of their sensing materials when exposed to different gas atmospheres.

numerous materials have been reported to be usable as metal-oxide chemical sensors including both single-component (e.g., zno, sno₂, wo₃, tio₂, and fe₂o₃) and multi component oxides (bifeo₃, mgal₂o₄ and sr_{1-y}ca_yfeo_{3-x}). the metal-oxide semiconductors like zno or sno₂ react with atmospheres like oxygen, carbon monoxide and carbon dioxide which has been known for years and investigated intensively. conductometric metal-oxide-semiconductor thin or thick films are the most promising devices among solid state chemical sensors, due to their small dimensions, low cost, low power consumption, on-line operation, and high compatibility with microelectronic processing.

zno is also a promising material for the realization of electronic and optoelectronic devices due to its specific chemical, electrical, surface, and microstructural properties. zno is a

wide band gap semiconductor, having high exciton binding energy of 60mev which allows excitonic transitions at room temperature. it has attracted intensive research efforts for its unique properties and versatile applications in antireflection coatings, transparent electrodes in solar cells, ultraviolet (uv) light emitters, diode lasers, piezoelectric devices, spin electronics, surface acoustic wave propagator [4], photonic applications [5], and gas sensing [6]. for gas sensing, zno is good candidate to replace the toxic and expensive materials like sno₂ generally used for gas sensing applications [7]. the zno is particularly useful to gas sensors because of its typical properties such as resistivity, high electrochemical stability, absence of toxicity, and abundant availability in nature [8]. this is primarily due to the high mobility of conduction electrons in the material and good chemical and thermal stability under operating conditions. zno-based gas sensors have been fabricated using powders, pellets, thick and thin films, and so forth. thick or thin films are found to be suitable for such sensors, since the gas sensing properties of metal oxides are related to the material surface and the species are adsorbed and react with the surface [6,9], leading to change in the resistance of sensor element [10].

the mechanism for gas detection in these conductometric materials is based, in large part, on reactions that occur at the sensor surface, resulting in a change in the concentration of adsorbed oxygen. variation in conductivity is due to the adsorption of atmospheric oxygen on the oxide surface that extracts electrons from the semiconducting material leading to change in carrier density and conductivity.

although the number of materials used to implement this kind of devices is huge, this work was centered in studying material using zno based sensing materials. the main purpose of this work is to study and develop new materials for gas sensing elements starting from the knowledge in thick film production using screen-printing technique. the efforts were made to prepare co-activated zno nanostructure thick films and studied morphological, structural and sensing properties at room temperature.

Materials And Methods

Chemicals:

all the chemicals used in this study were of gr grade purchase from sd-fine, india (purity 99%). the chemicals are used without any further purification. zinc nitrate hexahydrate [zn (no₃)₂·6h₂o] sodium hydroxide [naoh] and deionized water was used during reaction.

Synthesis of Zno Nanostructure:

all chemicals were of analytical grade and used as purchased without further purification. in present work, 4.461 g zinc nitrate hexahydrate [zn (no₃)₂·6h₂o] was dissolved in 100 ml distilled water and 2.0 g of sodium hydroxide [naoh] was dissolved in 100 ml distilled water. the zinc nitrate solution was added drop wise to the naoh solution to form white solution. then, white solution was subsequently kept at 75 °c for 12 hr. after 12 hr, allow it to cool to room temperature naturally and the resultant white solution were collected in a beaker. the obtained white solution were sonicated (ultrasonic wave treatment) for interval of time say 30 min with pulse rate 4 s and power 0.7 a. the resulting white precipitates were collected by centrifugation, washed with distilled water and ethanol several times and then dried at 80°c in vacuum oven for 2hr. so the moisture will removed from the final product and we will get dry product. then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of zno was calcinated at temperature 800°c for 6 hrs in the auto controlled muffle furnace (*gayatri scientific, mumbai, india.*) so that the impurities from product will be completely removed and get a final product of zno nanoparticles. obtain zno nanostructure particles product were used for further study.

Preparation Of Thick Films:

thick films of synthesized nanostructure zno were prepared by using screen printing technique. in present process, thixotropic paste was formulated by mixing the synthesized zno powder with ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol. the ratio of zno to ethyl cellulose was kept at

95:05. the ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. the thixotropic pastes were screen printed on a glass substrate in desired patterns. the films prepared were fired at 500°C for 12 hr. prepared thick films were called as pure zno thick films. this method adopted from elsewhere [11].

Cuo Modified Zno Thick Films:

surface of pure zno thick film were modified by dipping them into a 0.01 m aqueous solution of cupric chloride (99%, ar grade, merck) for different intervals of time (2 and 4 min). after dipping, thick films were dried under ir lamp for 60 minutes. dried thick films were calcinated at 600°C for 60 min in air ambient. the cupric chloride dispersed on the film surface was oxidized in calcination process, and sensor elements with different mass% of cuo on the surface of zno thick film were obtained. these surface activated films are termed as cuo modified zno thick films

Result And Discussion

Materials Characterization:

Thickness Measurement:

thickness of all zno thick films were measured by using technique “marutek film thickness measurement system” with the help of provided equipment. the thick-nesses of all films were observed in the range from 31 to 35 µm. thick films of approximately uniform thicknesses were used for further characterization.

Uv-Visible Absorption Spectrum:

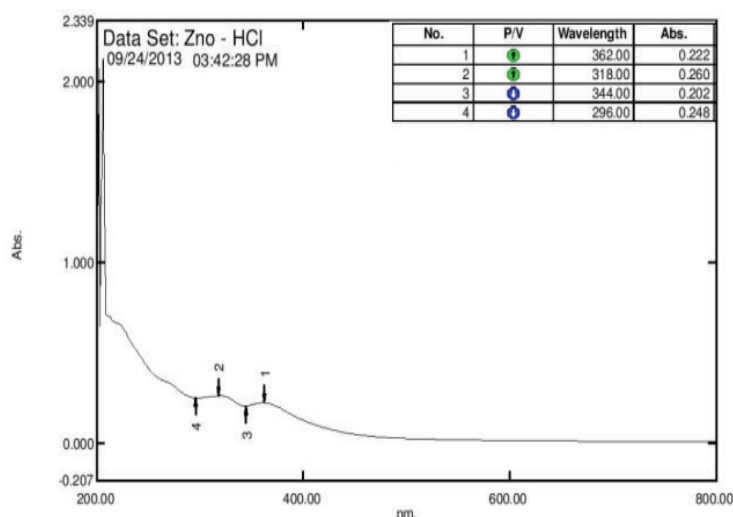


figure 1: uv-visible absorption spectrum of pure zno

uv-visible absorption spectroscopy is widely used tool for checking the optical properties of nanosized particles. figure 1 shows the uv-visible absorption spectrum of zno nanoparticles calcinated at temperature 800°C for 6 hrs. from the spectrum four peaks are observed at 362nm, 318nm, 344nm and 296nm, out of this at 318 nm wavelength has been found maximum absorption, if we calculate band gap for this wavelength it is 3.30ev, which is very close to the band gap of zno 1s–1s electron transition (3.37ev) [12].

X-Ray Diffraction Studies:

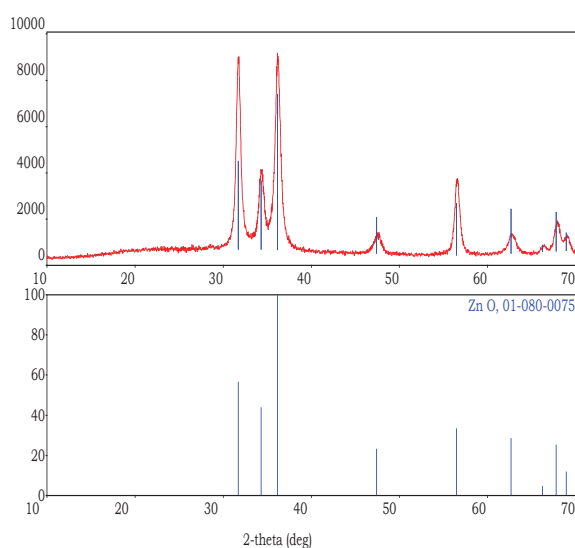


figure 2: x- ray diffraction pattern of pure zinc oxide (zno)

the crystallographic structure of the synthesized zno nanostructure was characterized by powder x-ray diffraction (philips x-ray diffractometer) with cu- α source and 2θ range of 10° - 70° . fig 2 shows the xrd pattern of the zno nanostructure. the recorded xrd pattern confirmed that synthesized zno are highly crystalline in nature. the corresponding x-ray diffraction peak for (100), (002), (101), (102) (110), (103) and (112) planes confirm the formation of hexagonal wurtzite structure of zno (jcpds card no.-01-080-0075). the domain size of the crystal can be estimated from the full width at half maximum (fwhm) of the peaks by means of the scherrer formula,

$$D = \frac{k\lambda}{\beta \sin\theta}$$

Where λ is the wavelength of incident beam (1.5406 \AA), β is the fwhm of the peak in radians, θ is the diffraction angle and k is scherrer constant. the average particle size was calculated from (101) peak zno is found to be 78 nm.

using x'pert high score plus software it is confirm that synthesized zinc oxide powder contains zn and o elements only, not any impurity and another element.

Transmission Electron Microscope:

figure 3 shows transmission electron microscope image of zno nanostructure synthesized by sol-gel method. it is clearly seen from the tem image that zno particles display sphere-like form basically, which indicates the growth of the nanostructures along a certain direction. the particle size determined from tem varies between 70 nm to 78 nm. the value is in reasonable agreement with calculated from xrd peaks.

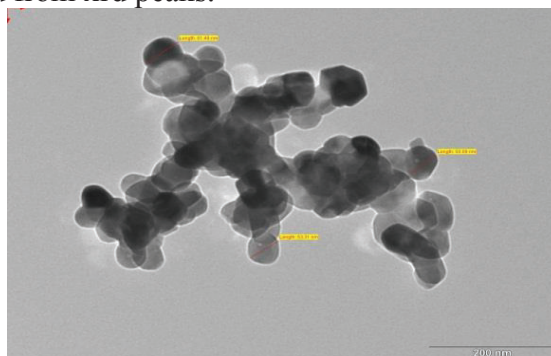


figure 3 (a)

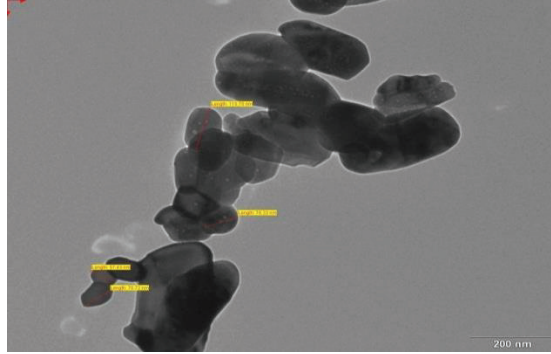
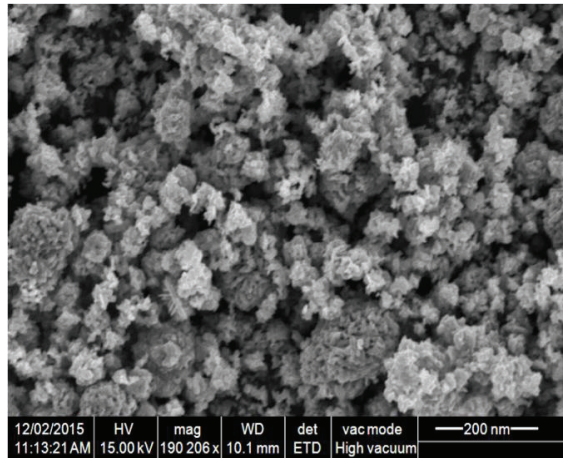


figure 3 (b)

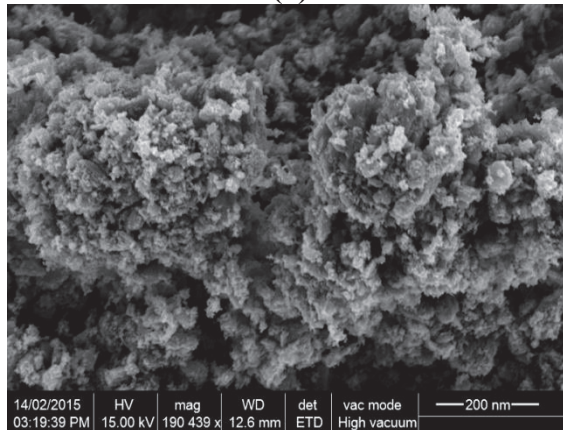
figure 3 (a, b): transmission electron microscope images of pure zinc oxide (ZnO)

Scanning Electron Micrograph:

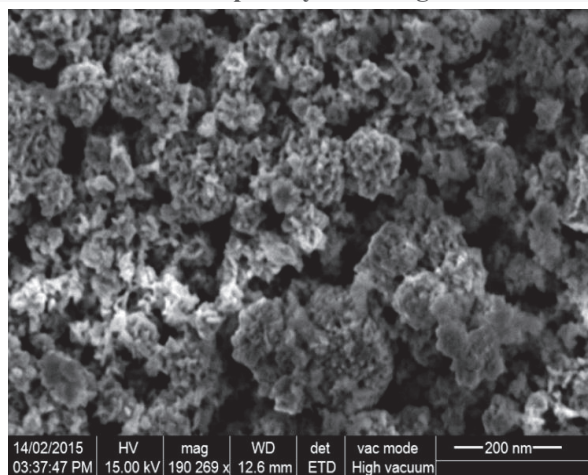
figure 4 shows typical FE-SEM images of the pure and CuO modified ZnO thick film prepared by screen printing technique. The figure depicts the FE-SEM images of unmodified (pure) and three CuO-activated ZnO films (dipped for 2 min and 6 min). The pure ZnO film (fig 4a) consists of randomly distributed grains with smaller size and shape distribution. Figure 4b depicts the microstructure of CuO-activated film consisting of some larger particles distributed around smaller grains. Figure 4c indicates a larger number of larger grains would be of CuO as compared to grains in figure 4b. These nanospheres could be attributed to CuO. Due to such a deposition of nanosphere, the surface-to-volume ratio of the ZnO thick film may be increased. Figure 4(b-c) represents that, as the dipping time increases, the amount of CuO nanosphere on the surface of ZnO thick films increases.



(a)



(b)



(c)

figure 4 micrograph of (a) pure (b) cuo –activated (dipped for 2 min) and (c) cuo – activated (dipped for 4 min) zno samples.

Electrical Properties: I–V Characteristics:

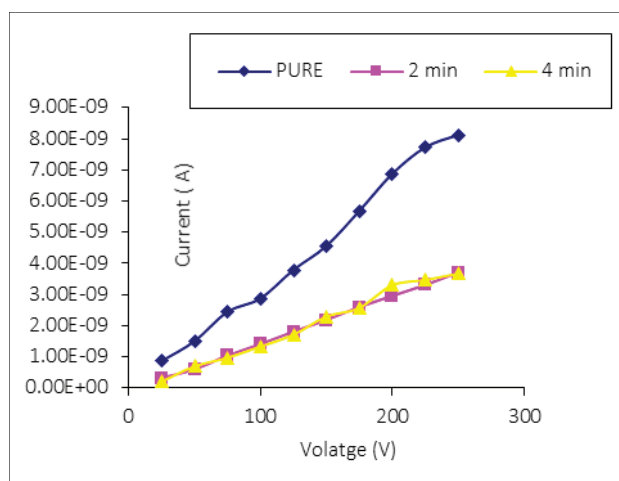


figure 5: i-v characteristics of pure zno and cuo modified zno thick films

figure 5 depicts the i–v characteristics of the pure and cuo-activated zno films at room temperature. the symmetrical nature of i–v characteristics shows that silver contacts on the film are ohmic in nature [13-14].

Thermoelectric Power (Tep) Measurements:

the p-type semiconductivity of thick films of cuo and n type semiconductivity of thick films of zno were confirmed by measuring thermoelectromotive force of the thick film samples.

Sensing Performance Of Pure Zno Thick Films:

Effect Of Dipping Time:

the response of cuo-activated films to 600 ppm h₂s as a function of the dipping time is shown in figure 6. the sample with a dipping time of 4 min of cupric oxide was observed to be the most sensitive at room temperature. the higher response of this sample as compared to other cuo- activated samples may be due to the optimum number of cuo grains dispersed on the surface. if the amount of cuo is smaller than the optimum, then the number of cuo misfits would be insufficient to cover the surface uniformly and the interaction of target gas would be weak giving smaller response. when the amount of cuo dispersed on the surface is larger than the optimum, cuo would mask the zno base material, resisting h₂s gas to reach to the cuo–zno

surface. due to this, the resistance of the sensor could not change considerably, giving comparatively smaller response [14-15].

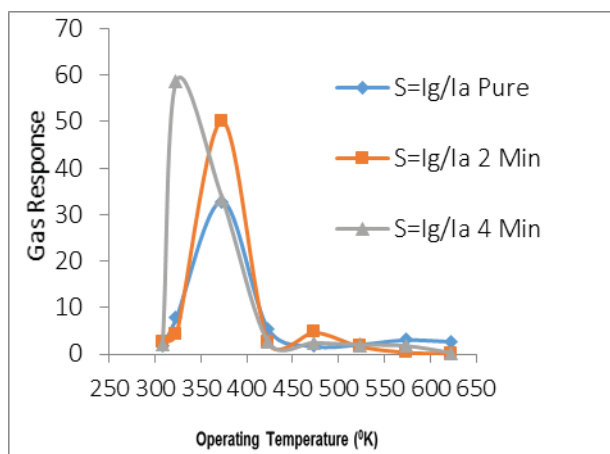


figure 6 variation of operating temperature with dipping time.

Selectivity Of Sensor:

selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of different gases [16]. it is observed that the zno thick film sensor gives maximum response to h₂s (600 ppm) at 50⁰c. the sensor showed highest selectivity for h₂s against all other tested gases: lpg and h₂s.

Response Time And Recovery Time:

the response/ recovery time is an important parameter used for characterizing a sensor. it is defined as the time required to reach 90 % of the final change in current, when the gas is turned on /off respectively [17], [18]. the response was quick (25 s) while the recovery was fast (75 s). the quick response may be due to faster oxidation of gas.

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References

- [1] meixner h., gerblinger j., and fleischer m., (1995),thin film gas sensors based on semiconducting metal oxides, sensors and actuators b, 23,119-125.
- [2] takeuchi.t.,(1988),oxygen sensor, sensors and actuators b, 14,109-124.
- [3] woetsman j.t. and logothetis e.m., (1995),controlling automotive emissions, the industrial physicist 20-24.
- [4] gorla c. r., emanetoglu n. w., et al., (1999),structural, optical, and surface acoustic wave properties of epitaxial zno films grown on (0112) sapphire by metal organic chemical vapor deposition, journal of applied physics, vol. 85, no. 5, 2595–2602.
- [5] wang x. d., summers c. j., and wang. z. l., (2004), large-scale hexagonal-patterned growth of aligned zno nanorods for nano optoelectronics and nanosensor arrays, nano letters, vol. 4, no.3, 423–426.
- [6] patil s. b. andsingh a. k, (2010), solution grown nanocrystalline zno thin films for uv emission and lpg sensing, journal of materials science, vol. 45, no. 19, 5204– 5210.
- [7] shinde v. r., gujar t. p., and lokhande c. d., (2007),lpg sensing properties of zno films prepared by spray pyrolysis method: effect of molarity of precursor solution, sensors and actuatorsb, vol. 120, no. 2, 551–559.
- [8] ismail b., abaab m., and rezig b.,(2001),structural and electrical properties of zno films prepared by screen printing technique, thin solid films, vol. 383, no. 1-2, 92–94.
- [9] liu x. q., tao s. w., and shen y. s., (1997), preparation and characterization of nanocrystalline α by sol-gel process, sensors and actuators b, vol. 40, no. 2-3,161–165.

- [10] chatterjee a. p., mitra p, and mukhopadhyay a. k.,(1999),chemically deposited zinc oxide thin film gas sensor, journal of materials science, vol. 34, no. 17, 4225– 4231.
- [11] kalyamwar v. s, raghuwanshi f.c., (2013), zinc oxide nanostructure thick films as h₂s gas sensors at room temperature, journal of sensor technology, vol. 3, 31-35.
- [12] hsieh p.t., chen y.c., kao k.s., lee m.s., cheng c.c.,(2007),journal of the european ceramic society, vol. 27, 13-15, 3815-3818.
- [13] jain g. h., wagh m.s.,(2007),sensors and actuators b12, 233-239.
- [14] patil d.r., patil l.a., patil p.p, (20007), cr₂o₃ activated zno thick film resistors for ammonia gas sensing operable at room temperature, ,sensors and actuators b126, 368-374.
- [15] kalyamwar v. s, raghuwanshi f.c., (2013), tio₂ modified zno thick film resistors as ammonia gas sensors, advanced materials letters, vol. 4(12), 895-898.
- [16] shinde s.d., patil g.e. and g. h. jain, (2012), synthesis of zno nanorods by spray pyrolysis for h₂s gas sensor, journal of alloys and compounds, vol. 528, 109-114,.
- [17] patil.g.e., kajale d.d., gaikwadv.b., pawar n.k.,(2012),properties and gas sensing mechanism study of cto thin films as ethanol sensor, sensors & transducers journal, vol. 137, issue 2, 47-58.
- [18] patil, p. g., kajale, d. d., patil, v. p., patil, g. e., & jain, g. h., (2012),synthesis of nanostructured zno for gas sensing, sensors & transducers journal,vol.5(3), .673–684.

