Ammonia gas sensing property of nanocrystalline Cu₂S thin films

¹M S Shinde, ²D R Patil & ¹R S Patil*

¹Department of Physics, PSGVPM's Arts, Science & Commerce College Shahada, Dist Nandurbar

²Bulk and Nano-Materials Research Lab, Rani Laxmibai College, Parola, Dist. Jalgaon

E-mail: mahen3569@rediffmail.com, rspatil_shahada@yahoo.co.in

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Nanocrystalline semiconducting thin films of copper sulphide (Cu_2S) were deposited by novel chemical route using aqueous solution of 0.1 M copper chloride, 0.05 M thiourea, complexing agent 10% aqueous ammonia (NH_3) and hydrazine hydrate. The characterization and gas sensitivity of as deposited Cu_2S thin film sensor have been investigated. The as deposited Cu_2S thin films were observed to be very sensitive for NH_3 gas at room temperature. Upon exposure of NH_3 gas the Cu_2S sensors lead to decrease in resistance which is attributed due to inter-conversion of Cu(I) and Cu(II) charge states. The response to ammonia gas by Cu_2S thin film is detected at 200 to 500 ppm concentration in air. The maximum sensitivity (19.78%) for ammonia gas by Cu_2S sensor was found at 500 ppm gas concentrations on the gas sensing performance of the Cu_2S sensor have been studied and discussed

Keywords: Thin films; Copper sulphide, Sensitivity, Response times, Ammonia gas sensor

1 Introduction

Sensor is an 'electronic nose' provides an interface between the electronic equipment and the physical world, typically by converting non-electrical physical or chemical quantities into electrical signals. Gas sensing principle is associated with a surface phenomenon so it brings high value for nanocrystalline thin film technology. Nanocrystalline thin films have great novelty because of their huge surface-to-volume ratio and high porosity. Due to this high ratio and porosity, a large number of analyte molecules can be adsorbed by nanostructures and within nanostructures in a short time. This leads to both high sensitivity and short response time for sensors. The Gas sensors based on resistance changes of selected materials have been successfully used for simple gas monitoring functions. In particular, the semiconducting metal chalcogenide thin film based sensors has gained great interest because of its application in the field of environmental monitoring devices.

Copper sulphide (Cu₂S) belongs to I-VI group compound of semiconducting material. The Cu₂S thin films have wide range of well perspective applications such as photovoltaic cells¹, tubular solar collectors², automobile glazing³, solar control coatings⁴, dye-sensitized solar cells^{5,6}, photodetectors⁷, electroconductive electrode⁸, microwave shielding coatings⁹, super conductors¹⁰, potential nanometerscale switch¹¹ gas sensors. Previously some of the researchers work out with copper sulphide as gas sensor such as Galdikasa *et al*¹². reported the use of Cu_xS thick films for detection of traces of ethanol, acetone and ammonia. Setkus *et al*¹³. studied properties of CuS thin film based structures and its effect on the sensitivity to ammonia gas at room temperatures. Sagade *et al*¹⁴⁻¹⁶. have been developed room-temperature-functioning ammonia gas sensor and study the effect of irradiation to improve the sensitivity of Cu_xS thin film sensor. Recently, Yu *et al*¹⁷. made a study over gas sensing properties of CuS hallow spheres.

In the present study, resistance based nonstructural Cu_2S thin film sensors have been prepared by novel chemical route. The changes in conductance of the films were monitored on exposure to NH_3 gas at room temperature. These sensors were observed to show stable response and recovery times with the highest sensitivity (19.78%) for NH_3 gas ever recorded.

2 Experimental Details

The deposition was carried out by using Corning glass slides (25 mm \times 75 mm \times 1 mm) as substrate which was initially boiled in concentrated chromic acid for 30 min rinsed in acetone, deionised water and finally ultrasonically cleaned. All analytical grade (A.R) reagents were used as it is without further purification for the deposition of Cu₂S thin films.

Aqueous solution of 0.1 M copper chloride, 0.05 M thiourea, complexing agent 10% aqueous ammonia and hydrazine hydrate were used. Initially 10 ml of $CuCl_2$ solution and 8.5 ml ammonia and 1.5 ml hydrazine hydrate were placed in 100 ml beaker, after stirring for several minutes solution becomes purple and homogeneous under continuous stirring, 5 ml thiourea solution was introduced then pretreated substrate was vertically immersed into the prepared bath at room temperature. Preparative parameters are optimized for best quality Cu_2S film.

2.1 Characterization set-up for gas sensor

The gas sensing performance of the thin film sensors was examined using the 'static gas sensing system'. The gas sensing assembly comprising temperature controller, chromel-alumel thermocouple, electric heating plate, gas chamber, digital temperature indicator etc.

The heater was used to heat the sample under test up to desired operating temperature. The two-probe dc measurement technique was used to measure the electrical resistance in the presence of various gases and air atmosphere. For electrical measurements, silver paste contacts of 1 mm were applied at the edges of the Cu₂S films separated by 1 cm, as top electrodes whose ohmic nature was tested within ± 10 V. The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON-OFF time intervals. The Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe.

3 Characterization Techniques

The structural characterization of the films was carried out using Philips (PW-3710) X-ray diffractometer with CuK α radiation ($\alpha = 1.5404$ Å) in 2 θ range 20°-80°. The surface morphological study of Cu₂S films was carried out by scanning electron microscopy using a Model JOEL, JSM 6360 A. The optical absorption spectra of the films were recorded on Systronic spectrophotometer in the wavelength range 350-850 nm.

4 Results and Discussion

4.1 Structural studies

Figure 1 shows the X-ray diffraction pattern of as-deposited Cu_2S thin film on to the amorphous glass substrate. The film shows the nanocrystalline nature with broad hump due to amorphous glass substrate.

The short intense peaks at $2\theta = 27.42$ (d = 3.2496 Å), $2\theta = 31.76$ (d = 2.8143 Å) and $2\theta = 45.50$ (d = 1.9900 Å) corresponding to the (1 1 1), (2 0 0) and (2 2 0) planes of Cu₂S of with cubic crystal phase. The crystallite size was estimated by using the well-known Scherrer's formula:

$$D = 0.9\lambda/\beta\cos\theta... \tag{1}$$

where, $\lambda = 1.5406$ Å for CuK α , β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg's angle. The sample of as-deposited Cu₂S thin film resulted in an average crystallite size of 30-40 nm.

4.2 Surface morphological studies

Scanning electron microscopy (SEM) is a versatile technique for studying microstructure of thin films. The Cu_2S thin film with 450 nm thickness was used to study the surface morphology using a scanning electron microscopy.

Figure 2 shows a scanning electron microscope of Cu_2S thin film at X 100,000 magnification, the scale bar length is 100 nm. The microstructure of the Cu_2S thin film on glass substrate shows uniform surface morphology with particle size 30-40 nm. From Fig. 2, it can be inferred that the particles with well-defined shape could not be detected. Instead, these films showed particles with spongy looking texture due to agglomeration of nano-fibers of Cu_2S material.

4.3 Optical properties

The optical properties of Cu₂S thin films are determined from absorbance measurement in the range 350-850 nm. The plot of $(\alpha h \nu)^2$ versus $h\nu$ for



Fig. 1 — X-ray diffraction pattern of as-deposited Cu_2S on glass substrate at room temperature



Fig. 2 — Surface morphology of as-deposited Cu_2S on glass substrate at room temperature by scanning electron microscopy studies



Fig. 3 — Variation of $(\alpha h\nu)^2$ verses $h\nu$ of as-deposited Cu₂S thin film

as-deposited Cu₂S thin film is shown in Fig. 3. The linear nature of the graph indicates the existence of direct allowed transitions. The value of the optical band gap has been determined from the value of the intercept of the straight line at $a (\alpha h \upsilon)^2 = 0$. The as-deposited Cu₂S thin film shows the optical band gap 2.34 eV, which is in good agreement with the band gap values reported by other researchers^{18,19}

4.4 Sensor performance for ammonia (NH₃) gas

Sensitivity, selectivity and rate of response are the important performance related characteristics of sensors. The sensitivity 'S' is defined by:

$$S = (R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$$

where R_{air} is the resistance in air and R_{gas} is resistance in gas at saturation value. Nanocrystalline Cu₂S thin films have been investigated for their use as ammonia (NH₃) gas sensors operating at room temperature. The sensors were operated at 100 to 500 ppm concentration to analyze the effect of gas concentration. When ammonia (NH₃) gas was injected



Fig. 4 — Response and recovery curves of Cu_2S nanocrystalline film towards increasing concentration of ammonia gas at room temperature



Fig. 5 — Conductance response time curve towards 500 ppm concentration of ammonia gas

into the gas sensing chamber, Cu_2S thin film starts to show response signals from 200 ppm to higher concentrations as shown in Fig. 4.

It is seen that the conductance of Cu_2S thin film decreases in response to increasing concentration of ammonia (NH₃) gas. Fig. 5 shows the conductance response time towards a detectable ammonia (NH₃) gas concentration at 500ppm particularly. From Fig. 6, the change in sensitivity has a linear correlation with ammonia concentration²⁰.

In our experiment, we have been observed that the response time of Cu_2S gas sensor was 60 s and the recovery time was about 90 s. This result is consistent with that obtained by Sagade *et al.* by another method¹⁵. It is well known that the fundamental sensing mechanism of semiconductor based gas sensors relies on a change in electrical conductivities due to conversion of Cu (I) to Cu (II) as reported by Sagade *et al*¹⁶. Crystalline copper sulphide has a complex layer structure. In this layer, some of copper atoms are trigonally coordinated Cu(II) and remaining are tetrahedrally coordinated Cu(I). This Cu(II) and Cu(I) charge states have very important role in



Fig. 6 — Variation of sensitivity of nanocrystalline Cu₂S thin film with concentration of ammonia gas

sensitivity of reducing gases. Particularly in Cu_2S , the amount Cu(I) is large compared to Cu(II). When molecules of reducing gas lands on the Cu_2S surface the charge states Cu(II) and Cu(I) exchanges electron lone pair. This leads the conversion of charge state Cu(II) into Cu(I) and thus the gas sensor phenomenon is detected. Sensitivity of Cu_2S thin film for oxidizing and reducing gases depends on exchange of electron lone pair.

5 Conclusions

We have fabricated resistance based nanostructural Cu_2S thin film sensors by novel chemical route. The changes in conductance of the films were monitored on exposure to NH₃ gas at room temperature. The nanocrystalline Cu_2S thin film sensors showed good sensitivity (19.78%) and quick response (~60 s) and recovery times (~90 s) for room temperature detection of ammonia (NH₃) gas indicating that these thin films may be well applied in sensor devices.

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