Gas Sensitivity of Cu_2S Thin Films by CBD Route

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Abstract

Nanocrystalline semiconducting copper sulphide (Cu_2S) thin films were deposited on glass substrate by relatively simple, quick and cost effective chemical route. The characterization of as deposited thin films was carried out for the structural, compositional, surface morphological, optical and gas sensing properties using X-ray diffraction (XRD), E-DAX, Scanning electron microscopy (SEM), AFM, UV-VIS Spectra and Gas sensing static unit. Conductance responses of the nanocrystalline Cu_2S thin films were measured by exposing as deposited film to different gases like carbon dioxide (CO_2), Ethanol(C_2H_5OH), Ammonia (NH_3), Hydrogen sulphide (H_2S) and Chlorine (Cl_2). It was found that the sensors exhibited various sensing responses to these gases at different operating temperature. Furthermore, the sensor exhibited a fast response and a good recovery times. The results demonstrated that nanocrystalline Cu_2S thin film can be used as a new type of gas sensing material which has a high sensitivity and good selectivity to Ammonia (NH_3) gas at 400 ppm.

Keywords: Nanocrystalline Cu_2S, Gas sensing, Sensitivity, Selectivity, Recovery times.

Introduction

A gas sensor is a electronic interface which sense the presence of various gases within an area, usually as part of a safety system. Gas sensors are important in environmental monitoring, home safety and chemical controlling. Many different semiconducting metal oxides [1-4] and sulphides [5,6] in bulk, thick film, and thin film form have been studied as a candidate sensor element for gas sensing. 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 sensing mechanism consists in the change of electrical resistivity resulting from chemical reaction between gas molecules and the metal sulphide surface and hence the surface morphology has an essential role on the sensitivity of solid-state sensors.

Copper Sulphide (Cu_2S) belongs to I-IV group compound of semiconducting material. Its band gap varies between 1.2 to 2.5 eV. The Cu_2S thin films have wide range of well perspective applications such as photovoltaic cells[7], tubular solar collectors[8], automobile glazing[9], solar control coatings[10], dye-sensitized solar cells [11.12], photodetectors[13], electroconductive electrode[14], microwave shielding coatings[15], super conductors[16], potential nanometer-scale switch[17].

Previously some of the researchers work out with copper sulphide as gas sensor such as Galdikasa et. al. [18] reported the use of Cu_xS thick films for detection of traces of ethanol ,acetone and ammonia. A.Setkus et.al [19] studied properties of CuS thin film based structures and its influence on the Sensitivity to ammonia gas at room temperatures. Sagade et. al. [20-22] 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 X.L. Yu et. al. [23] made a study over gas sensing properties of CuS hallow spheres.

The main objective of the present investigation is to fabricate and study the gas sensing property of Nanocrystalline Cu_2S thin film sensor, having higher sensitivity along with optimization of selectivity, operable at lower operating temperature and short response and recovery times. In present investigation nanocrystalline copper sulphide (Cu_2S) thin film sensor were fabricated by using chemical bath deposition method to study its gas sensitivity. The gas-sensing properties of Cu_2S thin films to different reducing gases, namely Ammonia (NH_3), carbon dioxide (CO_2), Ethanol (C_2H_5OH), Hydrogen sulphide (H_2S) and Chlorine (Cl_2) were studied.

Experimental Details

The deposition was carried out by using Corning glass slides (25mm X75mm X 1mm) as substrate which were 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 Cu_2S thin films. Aqueous solution of 0.1M Copper chloride, 0.1M thiourea, complexing agent 10% aqueous ammonia and hydrazine hydrate were used. Initially 10ml 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 were vertically immersed into the prepared bath at room temperature. Preparative parameters are optimized for best quality Cu_2S nanocrystalline thin film.

Characterization Techniques

The thickness of the thin films was measured by a surfcom 480°A profilometer. The structural characterization of the films was carried out using Philips (PW-3710) X-ray diffractometer with CuKα radiation (α= 1.5404°A) in 2θ range from 20^0-80^0. The surface morphological study of Cu_2S films was carried out by scanning electron microscopy using a Model JOEL, JSM 6360 A. Energy dispersive X-ray analysis (EDAX) were recorded on Energy dispersive X-ray spectrometer attached to the SEM model.

The surface morphology of the thin films was recorded using atomic force microscopy by Quesant Instrument Corporation, Q-Scope 250.The optical absorption spectra of the figure were recorded on Systronic spectrophotometer in the wavelength range of 350-850 nm.

Result And Discussion

Structural Studies

Fig. 3 shows the X-ray diffraction pattern of as-deposited Cu_2S thin film on to the amorphous glass substrate.

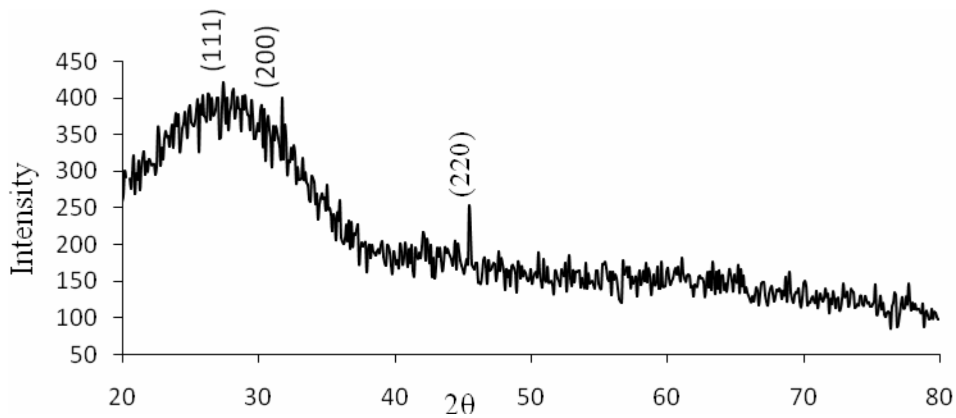

Fig. 3: The X-ray diffraction pattern of as-deposited Cu_2S on glass substrate at room temperature

The film exhibit the nanocrystalline nature with broad hump due to amorphous glass substrate. The short intense peaks at $2\theta = 27.42$ (d = 3.2496Å), $2\theta = 31.76$ (d=2.8143) and $2\theta = 45.5$ (d = 1.9900Å) corresponding to the (111) (200) and (220) planes respectively Cu_2S of with cubic crystal structure. The crystallite size was estimated by using the well-known Scherrer's formula as,

$$D = 0.9\lambda/\beta\cos\theta \qquad \textbf{(1)}$$

where λ = 1.5406 Å for CuKα, 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 Cu_2S thin film resulted in an average crystallite size of 40-50 nm.

The EDAX technique is used to determine quantitative composition of Cu_2S films deposited on glass substrate .The composition ratio was 2:1of atomic mass percent for Cu and S respectively as shown in fig.4. From the compositional analysis we found that deposited copper sulphide thin film was copper rich.

Surface Morphological Studies

Scanning electron microscopy (SEM) is a versatile technique for studying microstructure of thin films. The Cu_2S thin film with 200 nm thickness was used to study the surface morphology using a scanning electron microscopy. **Fig. 5** shows a scanning electron microscope of Cu_2S thin film at X

100,000 magnification the scale bar length is 100nm the average grain size of Cu_2S thin films was estimated using Cotrells methods [24].

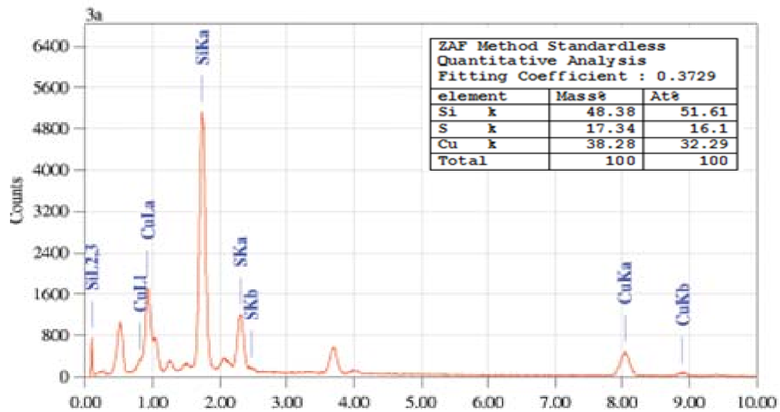

Fig.4: The energy dispersive X-ray analysis of as-deposited Cu_2S film on glass substrate at room temperature, showing the inclusion of Copper and Sulphar in Cu_2S film.

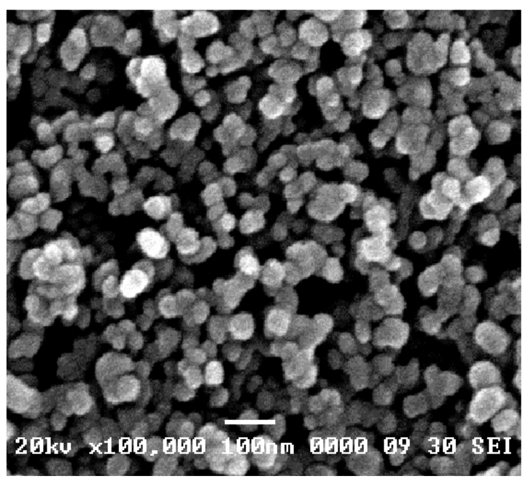

Fig. 5: The surface morphology of as-deposited Cu_2S on glass substrate at room temperature by scanning electron microscopy studies.

The as-deposited film shows nanometer size spherical grains (40-50 nm). Somewhere bigger size grains are formed due to agglomeration of small size nanoparticles . The film surface looks smooth and uniform. It was observed that the film was uniform golden brownish colored and well substrate covered.

Fig. 6 (a)and (b)show the three-dimensional and two-dimensional atomic force microscopy (AFM) images for Cu2S thin films deposited on glass substrate

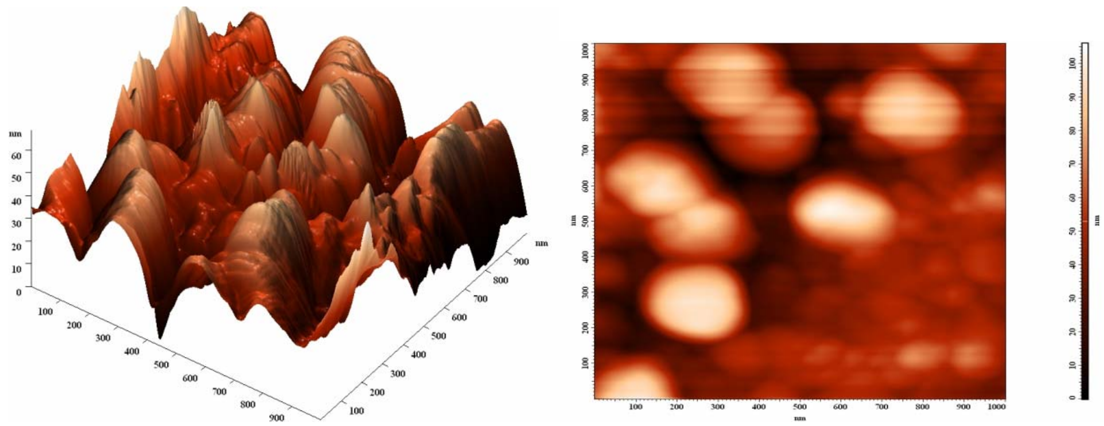

Fig. 6 (a) and Fig. 6(b) show the three-dimensional and two-dimensional atomic force microscopy (AFM) images for Cu_2S thin films deposited on glass substrate.

All the AFM images were measured for an area of 1000 nm x 1000 nm. The atomic force microscopy images of the films prepared on glass substrate indicate spherical shaped grains. The substrate surface is well covered with grains that are uniformly and regularly distributed over the surface which indicating more nucleation sites has formed. The average sizes of smaller grains are observed to be 40 to 50 to nm. The surface is relatively uniform and somewhere the spherical part get agglomerated to form a large grain features with the Average surface roughness and thickness is 48.30 and 65 nm respectively.

Optical Properties

The optical properties of Cu_2S thin films are determined from absorbance measurement in the range 350-900nm **Fig.7** shows the absorbance spectra of Cu_2S thin films.

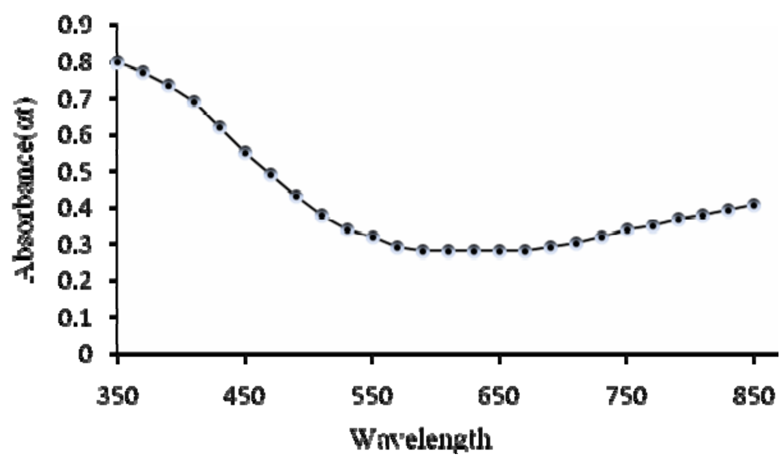

Fig. 7: The absorbance spectra of as-deposited Cu_2S on glass substrate.

Absorbance coefficient α associated the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using relation [25]

$$\alpha = 2.3026\ A/t \qquad (2)$$

The absorption coefficient α was analyzed using the following expression for near age optical absorption of semiconductors [26]

$$(\alpha h\upsilon) = K\ (h\upsilon - E_g)^{n/2} \qquad (3)$$

Where k is Boltzmann's constant, E_g is separation between valance and conduction bands and n is constant that is equal to 1 for direct band gap semiconductor. The band gap were determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus hυ graph shown in **fig. 8**

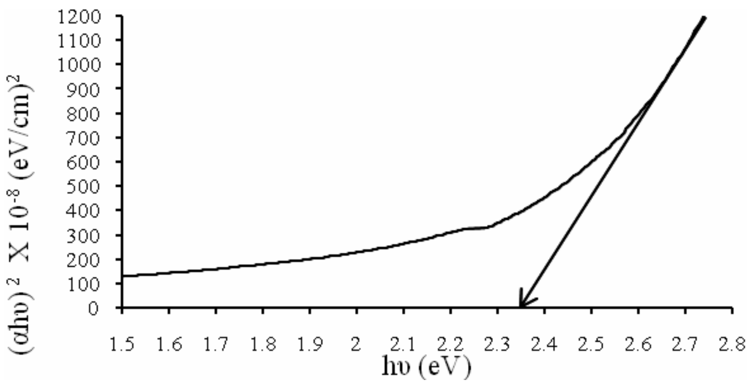

Fig. 8: Variation of $(\alpha h\upsilon)^2$ verses hυ of as-deposited Cu_2S thin film on glass substrate at room temperature.

The observed band gap values of the films was 2.34 eV This is good agreement with the reported values [27,28].

Sensing Performance

Measurement of Gas response, Selectivity, Response and Recovery Time

Sensitivity (S) or Gas response is defined, as the ratio of change in conductance of the sensor on exposure of the target gas to the original conductance in air medium. The relation for S is as:

$$S = (Gg - Ga) / Ga,$$

where Ga is the conductance of sensor in air medium and Gg is the conductance of sensor in gaseous medium.

Selectivity or specificity is defined, as the ability of a sensor to respond to certain gas in the presence of more gases. Selectivity of one gas over other is defined as, the ratio of the maximum Response of other gas to the maximum response of the target gas at optimum temperature.

$$\text{Selectivity} = S_{\text{target gas}} / S_{\text{gas}}$$

The Response time is defined , as the time taken for the sensor to attain 90 % of the maximum change in conductance on exposure to the target gas and The time taken by the sensor to get back 90 % of the original conductance is the recovery time

Fig. 9 depicts the variation gas responses as function of operating temperature of nanocrystalline Cu_2S thin films for different gases with 400 ppm concentration.

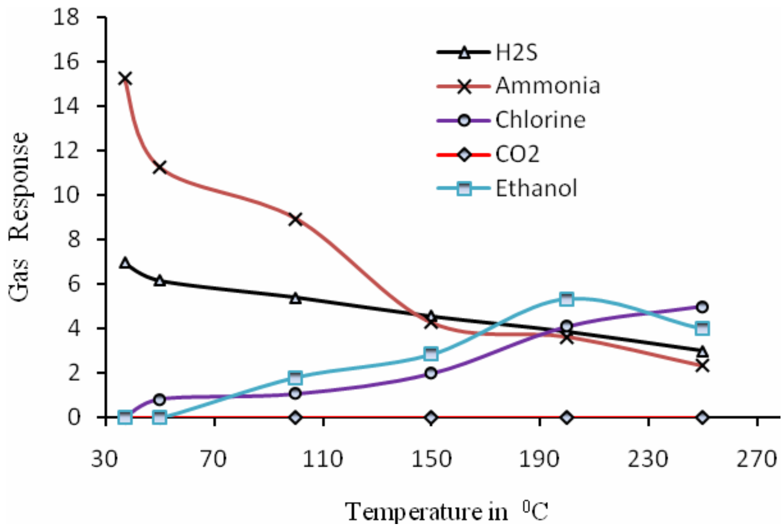

Fig. 9: Variation of gas response as function of operating temperature.

From fig.10 it is observed that nanocrystalline Cu_2S thin film sensor shows high sensitivity at room temperature for ammonia and H_2S gas. The sensitivity for NH_4 and H_2S was observed to decrease with increase in temperature but in case of ethanol and chlorine the behavior of thin film sensor is quite different .

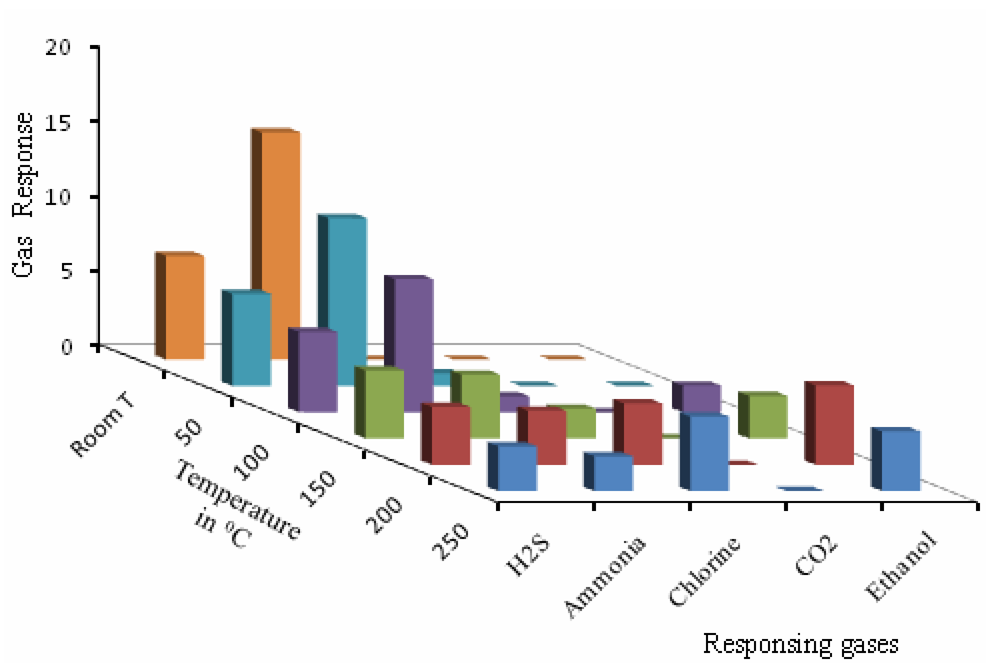

Fig. 10: Variation of gas response with operating temperature for Cu_2S thin film gas sensor for different gases.

For ethanol it is observed that gas response was starts from 100^0C and remains up to 250^0C . Cu_2S sensor shows highest sensitivity at 200^0C for ethanol and at 250^0C for chlorine but didn't show any sensitivity for CO_2 gas.

Selectivity for NH_3 Against Various Gases

The gas response of nanocrystalline Cu_2S thin film sensor was tested for NH_3, H_2S, C_2H_5OH and Cl_2, CO_2.

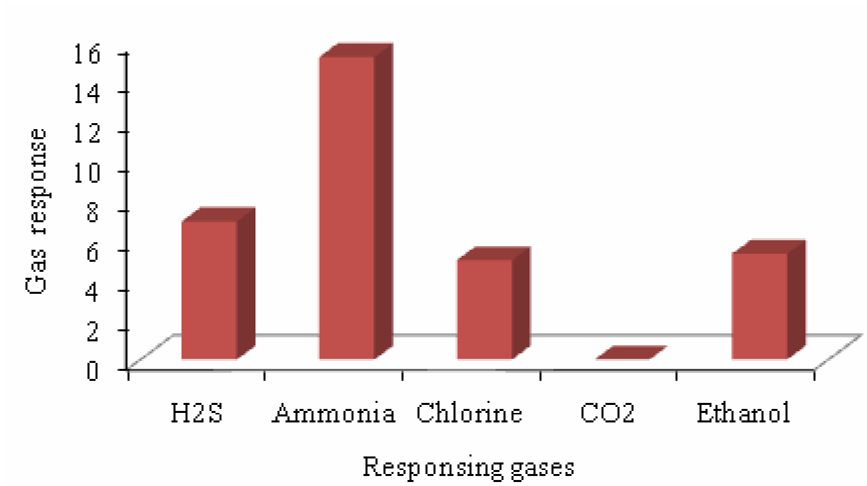

Fig. 11 Selectivity of Cu_2S thin films for various gases at 400 ppm gas concentration .

It is observed from **Fig. 11** that the nanocrystalline Cu_2S sensor gives maximum response to NH_3 gas at room temperature. The nanocrystalline Cu_2S thin film sensor showed highest selectivity for NH_3 among all other tested gases.

Response and Recovery Time

The response of nanocrystalline Cu_2S thin film sensor was found to be quick (~ 30 s) to 400 ppm of NH3 while the recovery was fast (~ 90 s). The fast response may be due to inter-conversion of Cu(II) into Cu(I) The negligible quantity of the surface reaction product and its high volatility explains its fast response and quick recovery to its initial chemical status.

Discussion

In p type of semiconductors when any reducing gases comes in contact with the film surface its resistivity get increases and for oxidizing gases its conductivity increases . Generally in metal oxide semiconductors sensing property is solely due to adsorption and desorption of oxygen species over thin film surface. But in copper sulphide thin films the gas sensing activity collectively is due to two different effects 1) Adsorption and desorption of oxygen 2) Inter-conversion of Cu(II) to Cu(I) charge states.

As discussed by X.L.Yu et. al [23] when reducing gases comes in contact with O^- or O^{2-} which is adsorb on film surface . It leads to the decrease of the carrier (holes) density in the surface charge layer and thus the gas sensor phenomenon is detected .But this effect is less dominant as compared to the effect of inter-conversion of Cu(II) to Cu(I) charge states as discussed by Sagade et. al [20].Crystalline Copper sulphide has a complex layer structure. In this layer $(1/3)^{rd}$ copper atoms are trigonally coordinated Cu(II), $(2/3)^{rd}$ Copper atoms are tetrahedrally coordinated Cu(I) and $(2/3)^{rd}$ sulphar atoms are as S_2^{2-} i.e. collectively this can be expressed as $Cu^{I}_4Cu^{II}_2–(S_2)_2S_2$. This Cu(II) and Cu(I) charge states have very important role in 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 reducing gas is depends on exchange of electron lone pair.

Here we observed that Cu_2S thin film sensor shows increase in resistivity for reducing gases like NH_3, H_2S, C_2H_5OH ,and increase in conductivity for oxidizing gas Cl_2 i.e. surface chemistry of nanocrystalline Cu_2S thin film sensor is suitable for gas sensing of various gases.

Conclusions

The nanocrystalline Cu_2S thin films were synthesized by A simple chemical bath deposition method and its gas sensing properties were investigated .The following statements can be made from the present investigation:

i) A simple chemical bath deposition method was used to fabricate nanocrystalline Cu_2S thin films gas sensor and this fabricated sensor was characterize by XRD,SEM, EDAX,UV-VIS spectra and AFM .
ii) Nanocrystalline Cu_2S thin films gas sensor showed highest response to ammonia at room Temperature.
iii) The sensor showed rapid response and recovery time.
iv) This sensor showed response for NH_3, H_2S, C_2H_5OH and Cl_2 .
v) The sensor has good selectivity to NH_3 against H_2S, C_2H_5OH, CO_2 and Cl_2 .

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