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Comparative Study of Gas Sensing Properties of Nanostructured Cu_2S Thin Films Deposited by CBD and MCBD Route

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ABSTRACT: Nanocrystalline semiconducting Cu_2S films have been prepared onto corning glass substrates using chemical bath deposition (CBD) and modified chemical bath deposition (M-CBD) methods. In chemical bath deposition (CBD), preparative parameters such as concentration, deposition time, complexing agent and pH of the bath are optimized, while in modified chemical bath deposition (M-CBD) preparative parameters such as concentration, immersion cycles, immersion time and rinsing time were optimized. The comparative gas sensing property study of CBD and MCBD deposited Nanocrystalline Cu_2S have carried out. These as deposited Nanocrystalline semiconducting Cu_2S films work as sensor and gave optimum responses to different gases at different operating temperatures. The surface misfits operating temperature can affect the microstructure and gas sensing performance of the sensor. The resistance responses of the nanocrystalline Cu_2S thin films were measured by exposing as deposited film to different gases namely ammonia (NH_3), carbon dioxide (CO_2), ethanol (C_2H_5OH), hydrogen sulphide (H_2S), liquid petroleum gas (LPG), hydrogen (H_2) and chlorine (Cl_2). It was found that the sensors exhibited various sensing responses to these gases at different operating temperature. The results demonstrated that CBD deposited nanocrystalline Cu_2S thin film have more gas sensing response than MCBD Cu_2S thin films and Cu_2S can be used as a new type of gas sensing material which has a high sensitivity and good selectivity..

Keywords: Nanostructure; CBD; MCBD; Cu_2S; gas sensing; sensitivity.

INTRODUCTION: Nanoscale materials are offering a variety of novel features. New physical and chemical properties are expected to occur in such systems, arising from the nanoscale material. In short, the properties of the material in nanocrystalline form are quite different and often superior to those of conventional coarse grained polycrystalline materials with grain sizes down to 100 nm. nanostructures bridge the gap between the behavior of an isolated atom bulk counterpart where interatomic interaction becomes dominance.

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 gas sensor, supercapacitor, and potential nanometer-scale switch.etc. The nanoparticals are synthesized by various deposition methods such as spray pyrolysis [1], reactive magnetron sputtering [2], atomic layer deposition (ALD) [3], activated reactive evaporation [4], electrochemical methods [5], chemical vapour deposition (CVD) [6], chemical bath deposition(CBD) [7-8], modified chemical bath deposition(M-CBD) [9], successive ionic layer adsorption and reaction(SILAR) [10], microwave assisted chemical bath deposition (MA-CBD) [11] have been used for the deposition of copper sulphide thin films.

MATERIALS AND METHODS:

Nanocrystalline Cu_2S thin film formation by CBD and MCBD: In the present work, nanocrystalline Cu_2S films have been prepared onto corning glass substrates using analytical grade chemicals (loba chemicals) were used as supplied without any further purification. Chemical bath deposition (CBD) and modified chemical bath deposition (M-CBD) methods and their comparative gas sensing property study have carried out. In chemical bath deposition (CBD), preparative parameters such as concentration, deposition time, complexing agent and pH of the bath are optimized [12], while in modified chemical bath deposition (M-CBD) preparative parameters such as concentration, immersion cycles, immersion time and rinsing

time were optimized which is explained in earlier manuscript[13].

Characterization:

Structural studies: The X-ray diffraction pattern of as-deposited CBD and MCBD deposited Cu_2S thin films onto the amorphous glass substrate is shown in fig.1. The film exhibit the nanocrystalline nature with broad hump due to amorphous glass substrate. The short intense peaks at 2θ = 27.42 (d = 3.2496Å), 2θ = 31.76 (d=2.8143) and 2θ = 45.5 (d = 1.9900Å) corresponding to the (1 1 1), (2 0 0) and (2 2 0) planes respectively. The XRD pattern shows that Cu_2S films having cubic crystal structure. The crystallite size was estimated by using the well-known Scherrer's formula as,

$$D = 0.9\lambda/\beta\cos\theta \qquad \ldots\ldots\ldots\ldots (1)$$

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.

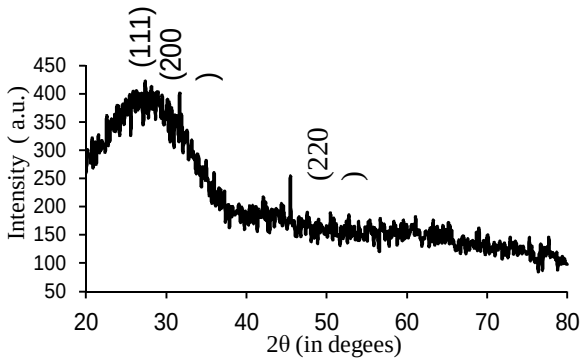

Figure 1: The X-ray diffraction pattern of as-deposited Cu_2S on glass substrate.

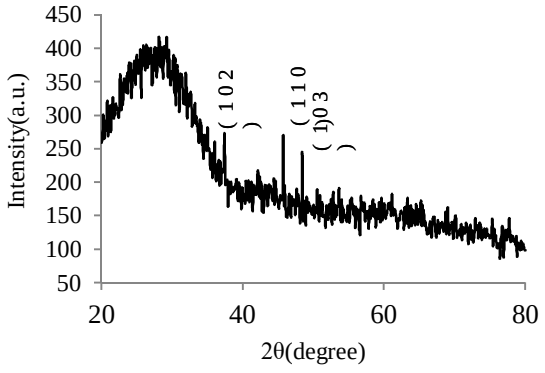

Figure 2: The X-ray diffraction pattern of as-deposited Cu_2S on glass substrate at room temperature.

The sample of as-deposited Cu_2S thin film resulted in an average crystallite size of 30-40 nm. While Fig. 2 shows the X-ray diffraction pattern of as-deposited Cu_2S thin film on to the amorphous glass substrate. The short intense peaks at 2θ = 37.423 (d = 2.4010Å), 2θ = 45.774 (d=1.9805 Å) and 2θ = 48.484 (d = 1.8759 Å) corresponding to the (1 0 2) , (1 1 0) and (1 0 3) planes of Cu_2S with hexagonal crystal phase angle. The sample of as-deposited Cu_2S thin film resulted in an average crystallite size of 20-30 nm.

Gas sensing properties of nanocrystalline Cu_2S thin films: From fig. 3 it is observed that nanocrystalline Cu_2S thin film sensor shows high sensitivity at room temperature for ammonia and H_2S gas but no response to H_2 and CO_2. The sensitivity for NH_4, H_2S, and LPG was observed to decrease with increase in temperature but in case of ethanol and chlorine the behavior of thin film sensor is quite different. For ethanol it was observed that gas response was started from 100^{0}C and remains up to 250^{0}C. Cu_2S sensor showed highest sensitivity at 200^{0}C for ethanol and at 250^{0}C for chlorine.

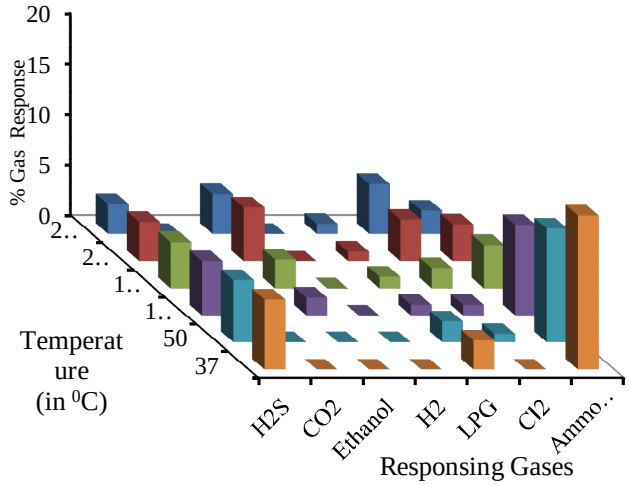

Figure 3: Variation of gas response with operating temperature for CBD deposited Cu_2S thin film gas sensor for different gases.

From fig. 4 it is observed that nanocrystalline MCBD Cu_2S thin film sensor shows high sensitivity at room temperature for ammonia and H_2S gas but no response to H_2 and CO_2.

The highest responses of MCBD deposited nanocrystalline Cu_2S thin film to ammonia (NH_3), ethanol (C_2H_5OH), hydrogen sulphide (H_2S), liquid petroleum gas (LPG) and chlorine (Cl_2) were found to be 14.28%, 4.84%, 6.19%, 2.38% and 4.50% respectively. The sensitivity for NH_4, H_2S, and LPG was observed to decrease with increase in temperature but in case of ethanol and chlorine the behavior of thin film sensor is quite different. For ethanol it is ob-

served that gas response was starts from 100 ^{0}C and remains up to 250 ^{0}C. Cu_2S sensor shows highest sensitivity at 200 ^{0}C for ethanol and at 250 ^{0}C for chlorine.

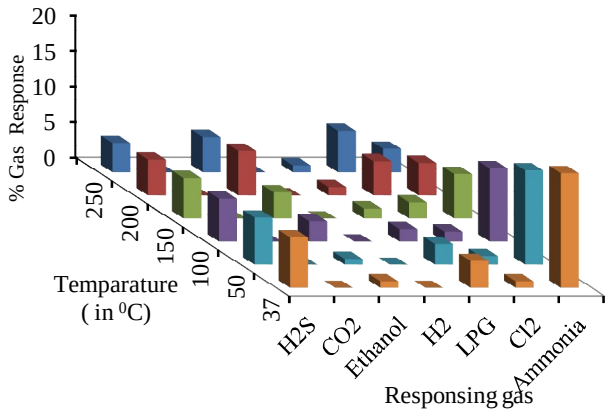

Figure 4: Variation of gas response with operating temperature for MCBD deposited Cu_2S thin film gas sensor for different gases.

RESULTS AND DISCUSSION: All the results are summarized and From all the studies it is concluded that nanocrystalline Cu_2S films prepared by CBD and MCBD methods exhibited good sensitivity towards different gases as discussed earlier[14]. For each method, the grain size was controlled through the preparative parameters of these methods. Among these two methods, the Cu_2S films prepared by CBD method exhibited the more sensitivity. In CBD technique the cationic solution, anionic solution and complexing agents were mixed together for film formation, hence at the time of film formation the grains were grow automatically to form certain morphology and structure. On the other hand in MCBD method, the cationic solution and anionic solution were placed separated at the time of film formation hence the grains were forcefully made to bind to substrate. Therefore, there is no orientation or perfect morphology in MCBD. Thus the way of interaction of MCBD deposited Cu_2S films with gas molecules may be different and this may be the reason for lower sensitivity of these films towards different sensing gases.

CONCLUSION: Thus with Comparative study we can conclude that, though the MCBD method is the most cost effective, the sensing performance of these films was the lowest. On the other hand, CBD method having drawback of loss of material, exhibited excellent morphology. From gas sensing response studies, it is seen that CBD deposited Cu_2S thin films have more gas sensing response than MCBD. This difference in sensitivity is due to variation of grain size and surface morphology of deposited Cu_2S thin films.

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