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Highly selective H_2S gas sensor based on Cu-doped ZnO nanocrystalline films deposited by RF magnetron sputtering of powder target

K.G. Girija [a, *], K. Somasundaram [a, 1], Anita Topkar [b], R.K. Vatsa [a]

[a] Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Electronics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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ABSTRACT

Cu – doped ZnO (CZO) films were synthesized by RF magnetron sputtering of composite target prepared with powders of ZnO and copper. Crystalline nature, morphology and chemical/electronic composition of the films were investigated by X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). XRD showed hexagonal wurtzite structure with strong c-axis orientation for both doped and undoped films. AFM study revealed uniform deposition of nanocrystallites and XPS confirmed the Cu incorporation into ZnO lattice. Further the H_2S sensing properties of the CZO films were investigated at different operating temperatures and gas concentrations. While all the doped films were highly selective to H_2S, 2% CZO film showed highest sensitivity at an operating temperature of 250 °C.

1. Introduction

Zinc oxide is an interesting II–VI compound semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV. It is a unique material that exhibits both semiconducting and piezoelectric properties and has a wide range of applications such as surface acoustic wave (SAW) devices, transparent conducting oxide electrodes, solar cells, blue/UV light emitting devices, gas sensors, etc. [1]. In recent years, ZnO has become a potential gas sensor material owing to its easy synthesis procedure, good electrical properties and in particular its compatibility with Si leading to MEMS (Micro Electro-Mechanical Systems) -based chemical sensors [2].

The morphology-controlled synthesis of ZnO nanostructures for gas sensing has been extensively studied, since reactions at grain boundaries and complete depletion of carriers in the nanograins can strongly modify the material transport properties. The morphology of ZnO can vary from nanoparticles, nanowires, nanorods, nanoflowers, nanoneedles to nanobeads by choosing appropriate synthesis methods and preparation conditions [3–8]. Among these ZnO morphologies, nanocrystalline thin films exhibit better sensitivity and reproducibility for gas sensing applications, in comparison with other types of ZnO sensors [9,10]. Most of the nano structures are placed randomly on the substrate while thin film deposition has better control and uniformity of the nanoparticles. Moreover thin films are more compatible with the micro fabrication technology and batch production.

RF magnetron sputtering is one of the most popular and preferred growth techniques for thin films due to its low cost, low operating temperature, good reproducibility and compatibility with surface micromachining technologies. Magnetron sputtering enables deposition of uniform ZnO films on various substrates during or after fabrication of MEMS structures for device applications. Since most of the deposited ZnO thin films have large number of point defects (such as oxygen vacancy, zinc interstitial, zinc vacancy, oxygen interstitial etc) they are inherently n-type semiconductors [11]. Doping with a suitable impurity is a well known method in order to tune the structural and electrical properties of sensing materials. Nanto et al. [12] demonstrated that doping of ZnO films resulted in significant change in resistance, higher gas sensitivity and lower operating temperature. The most commonly used metallic dopants in ZnO based systems are Al, Co, Cu, Ga, Ni, Sn, etc. [13–16]. Due to its similar electronic shell structure, Cu has

* Corresponding author.
E-mail address: kgirija@barc.gov.in (K.G. Girija).
[1] Department of Physics, Nallamuthu Gounder Mahalingam College, Pollachi, Tamil Nadu 642001, India.

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many physical and chemical properties similar to those of Zn [17]. Substitution of copper into the ZnO lattice has been shown to improve the gas sensitivity among other properties [18]. Herein we report that while pure ZnO films showed no response, we observed highly selective response to hydrogen sulfide (H_2S) in RF sputtered CZO thin films.

Hydrogen Sulfide is a toxic and flammable gas, usually generated in sewages, swamps, mines etc. It is also used in laboratories, industries and in heavy water plants as a process gas for producing heavy water (D_2O). Hydrogen sulfide reacts strongly with living tissues and attacks the central nervous system. According to the Occupational Safety & Health Administration (OSHA, USA), the acceptable concentration limit for exposure to H_2S is 20 ppm for an 8-h period. Thus it is imperative that the gas must be detected at ppm levels in air by selective and sensitive sensors, especially when it is encountered in the presence of other gases in a wide variety of industrial and environmental situations. There are few reports available on the gas sensing properties of CZO thin films [19–22], however H_2S sensing with sputtered CZO film has not been explored so far. In this context, we use powders of ZnO and Cu to produce CZO films by RF magnetron sputtering and assess their potential as highly sensitive and selective H_2S gas sensor.

2. Materials and methods

2.1. Thin film deposition by RF sputtering

Sputtering targets were prepared in-house by mixing powders of ZnO and Cu. For this purpose, Cu powder was synthesized by dissolving 1:1 M ratio of commercially available Zn powder (99%, May and Baker Ltd.) and $CuSO_4 \cdot 5H_2O$ (Sigma Aldrich, AR) in 20 ml distilled water and stirring for 30 min. The residual Cu powder was washed with water for two or three times and dried at 80 °C for one hour. Stoichiometric quantities of commercial ZnO powder (99%, May and Baker Ltd.) and synthesized Cu powder were mixed and ground for few hours. Sputter target was prepared by spreading the ground powder evenly in a copper holder of 2″ diameter, having a trench of ~1.5 mm depth and pressing manually with a solid piece of stainless steel to make it compact. No further processes were involved in the target preparation. Thus the preparation of sputter target was simple and economical, in addition to the flexibility of changing the composition for various Cu doping concentration.

Thin films of $Zn_{1-x}O$: Cu_x were grown on glass substrates using a RF magnetron sputtering system (HindHigh Vac make) in sputter up configuration at a fixed target-to-substrate separation of ~45 mm. Before loading into the sputtering chamber, the glass substrates were ultrasonically cleaned with methanol, acetone and isopropanol in sequence and rinsed with distilled water and dried. The sputtering chamber was evacuated to ~1.5×10^{-5} mbar prior to the introduction of the Ar–O_2 gas mixture. The flow rates of Ar and O_2 were controlled by mass flow controllers (MKS) at 30 and 20 sccm respectively. The working pressure, RF power and deposition time were optimized and fixed at 2×10^{-2} mbar, 100 W and 2 h respectively. Substrate holder was rotated (~10 rpm) to enable uniform film deposition. Although no external substrate heating was provided during the deposition process, the substrate temperature rose up to a maximum of 50 °C due to self-heating in plasma. No post annealing was carried out on the films.

2.2. Characterization of thin films

Crystalline structure and surface topography of the as deposited films were characterized by X-ray diffraction (Philips X-ray diffractometer model PW 1071) and Atomic Force Microscopy (Solver pro SPM) respectively. XPS measurements were performed on an ESCA apparatus (Make SPECS GmbH) with an Al-K_α (1486.6 eV) X-ray Source. The binding energy scale for XPS was calibrated using Au-$4f_{7/2}$ line of 83.95 eV. As the films were highly insulating, the obtained spectra were corrected for the charge effect using C 1s line (284.5 eV) from adventitious aliphatic carbon as internal reference.

2.3. Gas sensing studies

Gas sensors were fabricated by thermal evaporation of gold to form interdigitated electrodes on the CZO films, using a shadow mask (5 electrodes each side) with 0.5 mm electrode width and 100 μm separation between the electrodes. The response of the sensor to various test gases (CO, NH_3, H_2, SO_2, H_2S) was recorded using a static gas sensing set-up. Briefly, the sensor was mounted on a heating stage fixed in a stainless steel chamber (volume = ~1 L). Heating stage temperature was precisely controlled by a PID programmer/controller. Prior to the sensing test, the sensor was annealed at 250 °C for 2 h in the test chamber under ambient atmosphere. The sensor resistance was stabilized at each operating temperature for about 30 min prior to test gas exposure. Using a gas tight syringe, measured quantity of commercially available diluted gas (1000 ppm in N_2) was introduced in the chamber so as to yield the desired gas concentration. The response curves were measured by applying a fixed bias across the electrodes and time dependence of current was recorded using an electrometer or Source-Measure unit. After steady-state was achieved, recovery in response was studied by exposing the sensor to fresh air. From the response curves, the sensitivity (S) was calculated using the relation:

$$\text{Sensitivity (S)} = ((R_a - R_g)/R_a) \times 100$$

where, R_a and R_g are resistances in air and test gas, respectively.

3. Results and discussion

3.1. Structural and morphological studies

The typical XRD patterns of undoped and doped ($Zn_{1-x}O$: Cu_x) films with x = 0.01, 0.02 and 0.05 are shown in Fig. 1. Both films (undoped and doped) are polycrystalline with a structure that belongs to the ZnO hexagonal wurtzite type. Since Cu has similar ionic radius and electronic shell structure as Zn, Cu ions can replace either substitutional or interstitial Zn atoms in the ZnO lattice. In Fig. 1, no extra peaks corresponding to Cu, oxides of Cu or Cu related secondary phases are seen, which may be attributed to the substitution of Cu ions into the Zn lattice site rather than interstitial ones. While ZnO powder contains crystals in random directions with multiple peaks, sputtered ZnO films contain nanograins which are oriented normal to substrate surface, indicating a preferential orientation along the c-axis [23]. It is seen from Fig. 1 that the shift in (002) peak position with Cu doping is very small, indicating that the Cu^{2+} ions have substituted Zn sites without affecting the crystal structure of ZnO much. Similar small shift in (002) peak position has been observed in previous studies on Cu doped ZnO [23–25].

Average crystallite size of the as grown films is calculated from the diffraction line width of (002) peak based on Debye Scherrer relation [26]:

$$D = 0.9\lambda/\beta \cos\theta$$

where D is the average particle size, λ is the wavelength of X-rays, β is the angular peak width at half maximum in radian along (002) plane, and θ is Bragg's diffraction angle. The peak positions, FWHM