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CdO:ZnO nanocomposite thin films for oxygen gas sensing at low temperature

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ABSTRACT

CdO:ZnO nanocomposite were synthesized via sol-gel technique and optimized for oxygen sensing. The transport properties of the CdO:ZnO thin films were analyzed for enhancing the gas sensing properties at low operating temperatures. CdO:ZnO (1:3) nanostructure was obtained that has a 25 nm grain size with a 4.870 Å lattice constant. A highly transparent thin film of CdO:ZnO (3:1) with hollow sphere morphology and band gap of 2.4 eV was found to be less resistive. The sensing parameters such as sensor response, response time, recovery time, selectivity and stability of sensor were analyzed for different operating temperatures based on resistivity measurements. CdO:ZnO thin films of volume ratio 3:1 has the best sensitivity of 98.96 at an operating temperature of 150 °C. The present studies are encouraging for the realization of CdO:ZnO nanocomposite based sensor for efficient oxygen sensing properties at low temperatures fabricated with a low cost simple spin coating technique.

1. Introduction

The oxygen gas detectors are used in several applications such as for, automotive application [1] to measure the internal combustion engines, industrial heating (detector) [2], purification of waste water [2], in underground mines to monitor the environment [3] for the presence of enough oxygen which will help for the breathing of the workers and also in various medical applications [4]. Oxygen gas has been one of the most extensively studied gases due to the above issues. Nanostructured metal oxides such as ZnO, WO_3, SnO_2, ZrO_2, TiO_2, CdO and carbonic structures have shown high sensitivity [5–14].These materials have become promising candidates for gas sensing with high sensitivity, fast response time, and small size. ZnO is sensitive to many gases of interest such as hydrocarbons, H_2, benzene-toluene-xylene (BTX), O_2, H_2O_2, etc. and has a good stability for sensing applications [15–20].

ZnO, a direct wide band gap (3.37 eV) semiconductor with high exciton binding energy (60 meV) has stimulated great research interest due to its unique optical and electrical properties that are useful for solar cells, piezoelectric nanogenerators, nanolasers, gas sensors, etc. [21,22]. CdO is also a well-known group II–VI n-type semiconductor that has interesting properties for optoelectronic applications due to its large bandgap, low electrical resistivity and high optical transmittance in the visible region of the solar spectrum. CdO has a rocksalt crystal structure with a direct bandgap of 2.2–2.5 eV and indirect bandgap of 1.98 eV, which makes it useful for a wide range of applications such as solar cells, photodiodes, transparent electrodes and sensors [8,9]. CdO-ZnO nanocomposites offer interesting properties, due to various defects e.g., vacancies (V_o) and interstitials (O_i) oxygen atoms and vacancies (V_{Zn}) and interstitials (Z_{in}) zinc atoms, which increase the sensing properties due to their defect crystal structure. Plenty of nanostructures have been reported by previous researchers including nanowires, nanorods, nanobelts and nanosheets [23–28], because of their size or morphology dependent properties or device performances. High surface to volume ratio are required for gas sensing applications. The gas sensing mechanism involves chemisorption of oxygen on the oxide surface followed by charge transfer during the reaction between chemisorbed oxygen reducing and target gas molecule, leading to a change in surface resistance of the sensor element [29]. In order to be suitable for gas sensing applications, ordered formed nanostructures by closed interior pores should occur having a high specific surface area for reaction with gas molecules. Different types of gas sensors such as based on photoluminescence, refractive index, holographic, infrared, ultrasonic and resistivity have been reported by previous researchers [20–34]. Resistivity based gas sensors have importance due to easy detection and high sensitivity. Gas sensing properties for non-toxic O_2, He, H_2 and Ar

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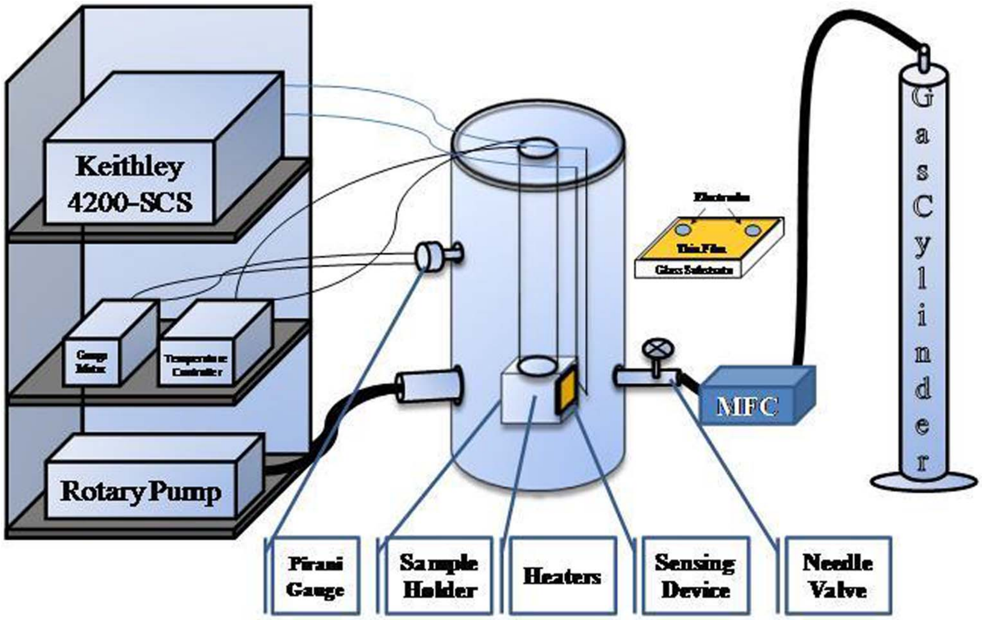

Fig. 1. Complete schematic diagram of gas sensing measurement (pictures are not in relative ratio).

gases are also attracting researcher attention in recent years.

Oxygen gas is an invisible, odourless, flammable gas but support combustion and most important it is a gas of life importance. ZnO based oxygen sensors are sensitive in the range of higher temperatures in the range 400–500 °C [35]. Therefore, it is most important to develop oxygen sensors that are able to be sensing at lower temperatures or close to room temperature with a high sensor response as well [36]. Oxygen sensors are used to control the combustion process (air to fuel ratio) in automobile engines exhaust gases and in industrial heating furnaces, to monitor environments as underground mines, oil fields, and to prevent gas poisoning. Among several synthesis techniques sol-gel spin coating method is an attractive method to obtain thin films of different materials and this is well known for its simplicity, reproducibility and possibility of producing cheap large-area films [37]. In most of the cases, the devices show a slow time response and need a higher working temperature (more than 200 °C). In the present paper the transport properties of spin coated CdO-ZnO thin films and their gas sensing characteristics to oxygen gas have been reported. It is an attempt to design a resistivity based oxygen sensor at low temperature by a low cost spin coating technique. Based on the literature survey and to the best of our knowledge, oxygen sensing by CdO-ZnO nanocomposite thin film has not been carried out at this stage.

2. Materials and methods

CdO-ZnO thin films synthesized by sol–gel spin coating techniques were deposited on glass substrates without a pre depositing contacting pad. The sensing material for precursors solution were zinc acetate dihydrate [$Zn(Ac)_2$, Alfa Aesar] and cadmium acetate dihydrate [$Cd(Ac)_2$, Sigma Aldrich] as source of zinc (Zn) and cadmium (Cd) respectively, while 2-methoxyethanol ($C_3H_8O_2$, Alfa Aesar) and monoethanolamine (C_2H_7NO, MEA, Alfa Aesar) were used as a solvent and stabilizer, respectively. Firstly, ZnO and CdO precursor solutions of 0.5 M molarity were prepared via sol-gel method subsequently they were mixed in 1:3 (CdO:ZnO) and 3:1 (CdO:ZnO) volume ratio. To prepare CdO/ZnO precursor solution, $Cd(Ac)_2/Zn(Ac)_2$ was dissolved in 2-methoxyethanol followed by addition of MEA as a precursor solution stabilizer. Molar ratio of MEA to cadmium acetate was kept at 1.0 M. The prepared mixture was stirred with the help of a magnetic stirrer at 60 °C for 1 h to yield a homogeneous, colourless and transparent solution. The solution was kept for ageing for 24 h prior to film deposition. CdO:ZnO solutions of ratio 1:3 and 3:1 were prepared by adding the required amount of CdO and ZnO volume and stirred with the help of a magnetic stirrer at room temperature for 1 h. The films were deposited on cleaned glass substrates with a spin coater at the rotating speed of 3000 rpm for 30 s. After each coating, the as deposited films were dried at 200 °C in air for 10 min to evaporate the organics residual. The procedures from coating to drying were repeated for ten times to get the desired thickness. Finally, films obtained were annealed for 1 h at 450 °C in a microprocessor controlled furnace. The thin film were named here after R_1, R_2, R_3 and R_4 corresponding to CdO:ZnO ratios of 4:0, 3:1, 1:3 and 0:4 respectively.

Before the sensing characterization the physical properties of thin films were characterized. X-ray diffraction (XRD) measurements were made using a Bruker D8 advance diffractometer with Cu K_α radiation (wavelength 0.15418 nm) to investigate the structural properties. The morphology of the samples was examined using scanning electron microscopy (SEM) with an EVO-40 ZEISS operated at an acceleration voltage of 20.0 kV. The energy dispersive X-ray (EDX) spectrum was carried out with the same machine to identify the chemical elements. The optical transmittance spectra were collected using a UV–Vis-IR UV-3600 spectrophotometer (Shimadzu). The photoluminescence (PL) data was recorded using a 325 nm He-Cd laser based system. The current–voltage (I-V) measurement was carried out using a Keithley 4200-SCS. Relative humidity (RH%) was measured by humidity sensor [Evirotech Instrument Private Limited]. A DektakXT, Bruker ellipsometer was used for thin film thickness measurements and was found to be approximately 200 nm.

The sensors were fabricated after an initial analysis of the thin films by the above characterization techniques. After avoiding contacting pad technique, the silver electrodes were built on the same surface of the thin films as shown in Fig. 1.The gas sensing performance of the CdO:ZnO thin films were studied in a specially designed gas sensor test rig (GSTR) having a sealed stainless steel cylindrical test chamber. The sensor was kept on a sample holder in the chamber and the temperature of platform was varied from 32 to 200 °C. The temperature of the sensor was monitored by using a thermocouple placed in contact with the sensor and controlled by an automatic computerised thermometer. The target gas was allowed to flow through a gas needle valve with gas flow meter in the chamber from a gas cylinder. The volume of the test chamber was taken to be 2.6 L and a pirani gauge with a rotary pump was used to measure the gas pressure in the test chamber. Vacuum of