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Heterocontact type CuO-modified SnO_2 sensor for the detection of a ppm level H_2S gas at room temperature

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Abstract

Thick films of SnO_2 were prepared by screen printing technique. The films were modified with Cu^{2+} by dipping them into an aqueous solution of copper chloride for different intervals of time and fired at 550 °C for 24 h. The copper chloride would be transformed upon firing into copper oxide. The p-type CuO grains around n-type SnO_2 grains would form n-SnO_2/p-CuO heterojunctions. Upon exposure to H_2S gas, the barrier height of n-SnO_2/p-CuO heterojunctions decreases markedly due to the chemical transformation of p-CuO into well conducting Cu_2S, leading to a drastic change in resistance. These sensors were observed to be operated at room temperature. An exceptional sensitivity was found to low concentrations (below threshold limit value = 10 ppm) of H_2S gas at room temperature, and no cross sensitivity was observed even to high concentrations of other hazardous and polluting gases. The efforts have, therefore, been made to develop the heterocontact type gas sensor based on tin oxide surface-modified with cupric oxide. The effects of microstructure and surfactant concentration on the sensitivity, selectivity, response and recovery of the sensor in the presence of H_2S gas were studied and discussed.

Keywords: SnO_2; CuO; Heterojunctions; High sensitivity; Thick film; Room temperature gas sensor; Selectivity; Response time; Recovery time

1. Introduction

Fuels are widely consumed for transport services all over the world. During combustion, various polluting and toxic gases are released in the environment, resulting in crucial pollution. It can cause serious health hazards. Upon burning, toxic hydrogen sulfide [1] gas is oxidized to sulfur dioxide by atomic oxygen, molecular oxygen or ozone. Combustions of petroleum and coal [2] are the predominant sources of the gases containing sulfur. The gases containing sulfur can result in undesirable disastrous deformations such as infection to respiratory track and lung cancer [2,3]. Infection to respiratory track causes difficult breathing or breathing under pressure. Therefore, monitoring of traces of such gases has become extremely important. Materials like ZnO, SnO_2, Fe_2O_3, Ga_2O_3, etc. [4–19] have been known to detect inflammable and toxic gases. The gas sensing characteristics of the materials can be improved by incorporating some additives [20–22] into the oxide films. Catalysts like Pt, Pd, Ag, Ru and CuO are often added [21,22] to the base material to improve the gas sensitivity and selectivity. Among various additives tested, CuO is an outstanding promoter in enhancing the catalytic activity and gas sensing properties of SnO_2 for H_2S detection [4–8].

The most general adsorption–desorption gas sensing mechanism [23–26] of semiconductor gas sensors is the simple resistivity change, due to the desorption of surface oxygen adsorbates via reactions with reducing gases such as H_2S, CO and H_2. The p–n heterocontact concept is used in the present investigation, instead of adsorption–desorption mechanism, which was introduced in 1979 and has been applied as humidity sensors, liquid sensors and gas sensors [27–34]. The heterocontact concept was found to be very effective for the H_2S gas sensing at room temperature. Room temperature gas detection offers advantages of low power drain and reduced tendency to provide a source of ignition [27]. The heterocontact type sensors have an intrinsic difference in behavior from those based on catalytic oxidation/reduction of gas molecules. The heterocontact type works on the principle of a barrier mechanism, which needs no adsorption and desorption of oxygen for the detection of H_2S gas. Some well-known materials for H_2S gas sensing are

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SnO_2–CuO [4–9], CuO–SnO_2–ZnO [14], SnO_2–Pd [19], modified $BaTiO_3$ [35], SnO_2–Al_2O_3 [36], SnO_2–CuO-SnO_2 [37] and $ZnSb_2O_6$ [38].

In the present article, the surfaces of thick films are modified by dipping them into a Cu precursor for a particular time interval, followed by firing. Firing converts $CuCl_2$ into CuO. This process of modification of surface using CuO is referred to as CuO modified SnO_2. In the surface modification process, the p-type CuO material could be dispersed on the surface of n-type SnO_2 base material to form the n-SnO_2/p-CuO heterojunctions. The dipping technique adds a dimension to the usefulness of surfaces by allowing one to customize their properties.

Known H_2S gas (20–1200 ppm) sensors [4–14] showed relatively lower response ($\sim 10^3$) at higher temperatures (150–250 °C). However, it is inadequate to operate the sensors at higher temperatures. The efforts have, therefore, been made to develop the sensors, which could detect a ppm level of H_2S gas at room temperature.

2. Experimental procedure

2.1. Powder and paste preparation

Pure (99.9%) AR grade tin oxide powder was ground in an agate pastle mortor to ensure sufficiently fine particle size. The fine powder was calcined at 1100 °C for 24 h, in air and re-ground. The thixotropic paste was formulated by mixing the resulting SnO_2 fine powder with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste was then used to prepare thick films.

2.2. Thick film preparation

The thixotropic paste was screen printed on a glass substrate in desired patterns [39–40]. The films prepared were fired at 550 °C for 24 h. These films were surface modified by dipping them into a 0.01 M aqueous solution of cupric chloride for different intervals of time and were dried at 80 °C followed by firing at 550 °C for 24 h in air ambient. The $CuCl_2$ dispersed on the films was oxidized in firing process, and sensor elements with different mass% of CuO were obtained. Silver contacts were made by vacuum evaporation for electrical measurements.

2.3. Characterization

The crystalline structure of the films was analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using Cu K_α radiation with a wavelength 1.5418 Å. The microstructure and chemical composition of the films were analyzed using a scanning electron microscope (JOEL JED 2300) coupled with an energy dispersive spectrometer (6360 LA). Thickness measurements were carried out using a Taylor-Hobson (Talystep, UK) system. Electrical and gas sensing characteristics were measured using a static gas sensing system.

2.4. Details of the gas sensing system

The sensing performance of the sensors was examined using 'static gas sensing system'. There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON (240 s) and OFF (60 s) time intervals. A 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 test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and current was measured by a digital picoammeter. Air was allowed to pass into the glass dome after every H_2S gas exposure cycle.

3. Materials characterization

3.1. XRD of CuO-modified films

Fig. 1 shows the X-ray diffractogram of the CuO-modified film, which was most sensitive to H_2S gas at room temperature. The observed peaks are matching well with ASTM reported data of SnO_2. The sharp peaks of the XRD pattern correspond to SnO_2 material and are observed to be microcrystalline in nature. No peaks corresponding to CuO may be due to its very small mass% dispersed on the surface of SnO_2. The average grain size was determined using Scherrer formula and was estimated to be of 170 nm. The crystals show anisotropy because different directions within the repeating pattern interact differently with incident radiations.

3.2. Microstructure SEM

Fig. 2(a–c) depict the SEM of unmodified (pure), most sensitive CuO-modified film (15 min) and a film CuO-modified for largest interval of time (60 min), respectively. Unmodified SnO_2 film (Fig. 2(a)) consists of randomly distributed grains with larger size and shape distribution. Fig. 2(b) depicts the

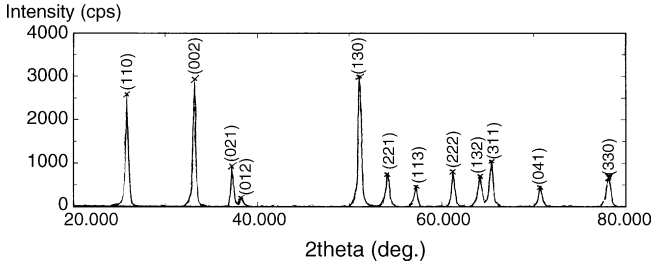

Fig. 1. XRD of CuO-modified (for 15 min) SnO_2 fired at 550 °C for 24 h.