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Nanocrystalline samarium oxide coated fiber optic gas sensor

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ABSTRACT

Nanocrystalline Sm_2O_3 coated fiber optic sensor is proposed for detecting toxic gases such as ammonia, methanol and ethanol vapors. Sm_2O_3 in the as prepared form as well as annealed form have been used as gas sensing materials, by making them as cladding of a PMMA fiber. The spectral characteristics of the Sm_2O_3 gas sensor are presented for ammonia, methanol and ethanol gases with different concentrations ranging from 0 to 500 ppm. The sensor exhibits a linear variation in the output light intensity with the concentration. The enhanced gas sensitivity and selectivity of the sensor for ethanol is discussed briefly.

1. Introduction

Resistive type metal-oxides sensors are traditionally used for gas sensing applications however their gas sensitivity is poor at room temperature and lot of research is going on to improve their gas sensitivity [1–4]. Metal-oxides also exhibit high dielectric constant and wide band gap. The optical properties of these materials have been used for gas sensing applications at room temperature by using them as thin films [5–8]. The use of nanocrystalline Sm_2O_3 as the cladding material on a fiber optic probe has been demonstrated in this paper since fiber optic sensors have many advantages such as high sensitivity, small size and low cost. The developed probe is basically an intrinsic intensity modulated fiber optic sensor based on evanescent wave. This cladding modification methodology is very attractive because of its large dynamic range and high sensitivity. When exposed to chemical vapors, the refractive index of the cladding material varies due to chemical reactions. This leads to light loss through evanescent waves, and hence light intensity modulation is achieved at the fiber output end [9–11]. Clad-modified fiber optic gas sensors based on metal-oxides such as ZnO [12] and SnO_2 [13] have also been reported.

Samarium oxide (Sm_2O_3) is an important rare earth oxide material which exhibits properties similar to metal oxides. It has been used in resistive type of gas sensors [14–17]. The influence of doping SnO_2 thin film with Sm_2O_3 nanoparticles by different amounts on the gas sensitivity and selectivity has been studied [18]. The study on samarium (Sm) doping in ceria films showed enhancement of electrical conductivity compared to pure ceria films [19]. It was observed that the doping enhanced adsorption of oxygen. The 6% of Sm doping on Ceria was found to show highest conductivity. This phenomenon has been used for oxygen gas sensing applications. The SnO_2 doped with 5% weight of Sm_2O_3 exhibited higher response to CO and ethanol in the presence of methane [20].

Sm_2O_3 exhibits high refractive index (1.93) and a wide band gap of 4.33 eV. The samarium oxide exhibits high optical transmission (about 80%) similar to metal oxides. However its optical properties were not explored for gas sensing. In this paper, a study is made on the gas sensing characteristics of samarium oxide clad-modified fiber optic sensor. The studies have been conducted on ammonia, methanol and ethanol gases. The time response of the sensor is also reported.

2. Experimental procedure

The experimental setup is shown in Fig. 1. The fiber optic sensor uses a white light source (Model SL1, Stellar Net Inc., USA) with wavelength ranging from 200 to 2000 nm and a miniature fiber optic spectrometer (EPP-2000, Stellar Net Inc., USA) having spectral range of 200–1100 nm. The heart of the sensor is the multimode step index optical fiber having length 42 cm and diameter 750 μm with the sensing region of about 3 cm at the center of the fiber. This fiber made up of poly methyl methacrylate (PMMA) is cleaved at both ends to have flat edges and is then integrated with the light source and the spectrometer. The refractive index of the core is

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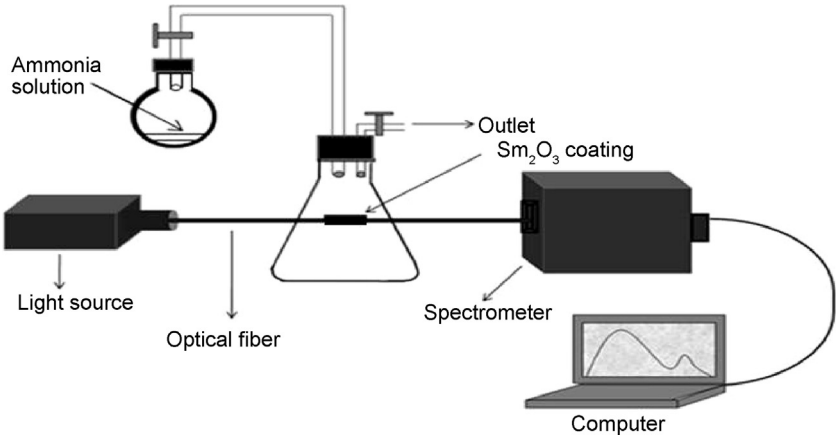

Fig. 1. Schematic diagram of a fiber optic gas sensor.

1.492 and cladding is 1.402. The gas sensing region was obtained by completely removing the clad part with the careful use of a razor without affecting the core of the fiber. The clad removed surface should be smooth and hence its uniformity was monitored by an optical microscope.

Nanocrystalline Sm_2O_3 was mixed with isopropyl alcohol to form a paste and coated on the sensing region by dip coating method. The thickness of the coating was around 30 microns. This Sm_2O_3 is now the modified cladding of the fiber. After the coating was dried at room temperature, the sensing region of the optical fiber was inserted into the gas chamber. Various concentrations of the ammonia, methanol and ethanol gases (0–500 ppm) prepared through serial dilution factor method were passed into the chamber. White light was passed through the fiber at one end and the spectrum of the output light at the other end was recorded using the spectrometer interfaced with a personal computer. The response time required for the sensor to stabilize to its final value was studied for each concentration and measurements were done after this for the accurate assessment of the concentration of ammonia, methanol and ethanol. Measurements were carried out at room temperature (24 °C). The adhesion between nanoparticles and fiber surface was found to be good. Experiment was carried out many times with sensing fiber at different intervals. The results were consistent. Absorption characteristics of as-prepared and annealed (500 °C and 1200 °C) Sm_2O_3 were studied using spectrophotometer (Model UV-1700, Shimadzu, Japan).

3. Synthesis of nanocrystalline samarium oxide

The sample was prepared by chemical synthesis method. Initially, 0.1 M solution of samarium chloride was taken in a flask and hydrolyzed. Then, appropriate amount of ammonia solution was added to it and precipitates were obtained. The precipitates were washed well with water and finally samarium oxide powders were obtained. Some of the powders were annealed at 500 and 1200 °C for 1 h in air. As-prepared and annealed powders were characterized by X-ray diffraction for phase analysis and grain size estimation. The morphology was studied using a scanning electron microscope.

4. Results and discussion

4.1. XRD and SEM analysis of synthesized samples

Fig. 2 shows the powder diffraction pattern of the as-prepared and annealed samarium oxide. The peaks correspond to cubic phase

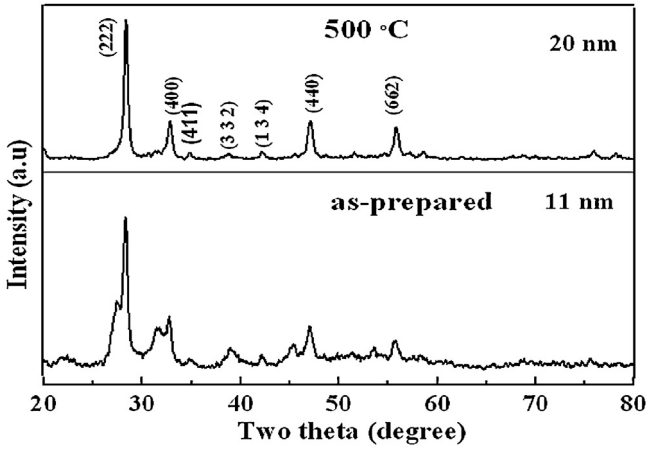

Fig. 2. XRD patterns of the as-prepared and annealed samples of Sm_2O_3 nanoparticles.

of the samarium oxide. As-prepared sample have additional peaks compare to annealed sample and it may be due to impurity of $Sm(OH)_3$. The grain size and crystallinity of the samples increased with annealing temperature. The grain size of the samples were estimated with Scherrer's formula [12] and were found to be 11, 20 and 28 nm for as-prepared, 500 and 1200 °C annealed samples, respectively.

Fig. 3(a) and (b) shows surface morphology of as-prepared and annealed samples of samarium oxide. It shows the aggregation of many primary particles. Spherical like morphology is observed for as-prepared sample and rod like morphology for sample annealed at 500 and 1200 °C. The rod shape is obtained due to the catalytic effect of Sm_2O_3 at higher temperature. Fig. 4(a) and (b) shows SEM picture of the coating made on the optical fiber for as-prepared and annealed (500 °C) sample.

4.2. Gas sensing characteristics

Figs. 5(a–c), 6(a–c) and 7(a–c) show the output spectral characteristics of as-prepared and annealed (500 °C and 1200 °C) Sm_2O_3 samples, respectively, in different gas environments for various concentrations. The spectra exhibit three peaks around 690, 767 and 949 nm which is characteristics of the PMMA fiber. It is observed that the peak remains same, however, the spectral intensity changes with the change in the concentration of gas. It is found that the intensity increases for all samples (as prepared, annealed