Study of Screen Printed MoO_3 Thick Films as NH_3 Sensor

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ABSTRACT

In this paper, gas sensing property of a MoO_3 was studied. Thick films of MoO_3 were prepared on alumina substrate by screen printing method and fired at 600^0C.The structural behavior, surface morphology was studied by XRD, SEM and EDAX techniques respectively. From XRD the crystallite size was calculated using Scherer's formula and observed as 19.97nm. From SEM the particle size was observed as 45nm to 156nm.EDAX analysis shows non- stoichiometric behavior of the films. Gas sensing behavior of the films was tested in static gas sensing system. Current flowing through the films was measured in air and then in different gases atmosphere at different temperatures. Films were exposed to different gases as LPG.NH_3, NO_2, Ethanol vapour and CO. At 200^0C, MoO_3 films showed good sensing for NH_3. The gas sensitivity was determined as 67.3% for 1000 ppm of NH_3. The films showed good response and recovery time.

Keywords: MoO_3; XRD; SEM; Sensitivity; Selectivity.

INTRODUCTION:

Transition metal oxides like TiO_2, WO_3, and MoO_3 are very promising materials in the field of sensors, catalysts, display devices, high density memory devices and optical smart windows [1-6]. Solid-state semiconducting gas sensors have been extensively investigated because of their wide range of applications. MoO3 is a wide band gap (Egap ~3.1 eV) n-type semiconductor. Recently semiconducting MoO_3 films have shown potential as new gas sensing element. In this study, MoO_3 films were prepared by screen printing method. Screen printing method was employed for film preparation since the method is relatively easy and low cost. [7].The NH_3 gas sensing behavior of MoO_3 films is studied.

EXPERIMENTAL WORK:

The MoO_3 powder (AR grade, 99.99 %) was weighed and calcinated in air at 400^0C for 2 hrs. The calcinated MoO_3 powder was crushed and mixed thoroughly with glass frit as permanent binder and ethyl cellulose as a temporary binder. The mixture was then mixed with butyl carbitol acetate as a vehicle to make the paste. The paste was used to prepare thick films on alumina substrate by using standard screen printing technique using screen of 40s, mesh no. 355 [7]. After screen printing, the films were dried under IR-lamp for 45 minutes and then fired at temperatures of 600^0C for 1 hour. Structural and Morphological Studies using X-ray diffraction (Miniflex Model, Rigaku, Japan) analysis from 20-80^0, 2θ was carried out to examine the final compositions of the MoO_3 thick films samples. The average grain sizes of MoO_3 thick film samples were calculated by using the Scherer formula [7]:

$$D = \frac{0.9\lambda}{\beta Cos\theta}$$

Where D is the average grain size, λ =0.1542 nm (X-ray wavelength), and β is the peak FWHM in radiation and θ is diffraction peak position. The surface morphology and chemical composition of the films were analyzed using a scanning electron microscope [SEM model JEOL 6300 (LA) Germany] coupled with an energy dispersive spectrometer (EDS JEOL, JED-2300, Germany). The gas sensing studies were carried out on a static gas sensing system under normal laboratory conditions. The NH_3 gas response of MoO_3 thick films was studied in test assembly. The electrical resistances of MoO_3 films in air (Ra) and in the presence of MoO_3 gas (Rg) were measured to evaluate the gas response (S) given by the relation[8]

$$Sensitivity(S) = \left| \frac{R_a - R_g}{R_a} \right| \times 100$$

Where Ra is the resistance of the MoO_3 thick film sample in air and Rg is the resistance of the MoO_3 thick film sample in NH_3 gas atmosphere.

RESULT AND DISCUSSION:

XRD:

Figure.1 shows the X-ray diffractometer plot for MoO_3 thick films. Plot shows 3 major peaks. The peaks were compared with JCPDS card no. (05-0508 & 21-0569). This comparison confirmed the presence of MoO_3 in considerable pure form. The permanent binder also melted away quite nicely. [2 1 0] was found to be the most preferred plane among the planes. From XRD the crystallite size was calculated using Scherer's formula and observed as 19.97nm.

SEM:

Figure 1 shows SEM image of MoO_3 thick films. It shows cylindrical (rod-like) structure with prominent voids in between. The microstructure is with significant porosity. It also shows that the binders have been properly melted due to the firing. From SEM the particle size was observed as 45nm to 156nm.

Fig.1 XRD Pattern of MoO_3 films

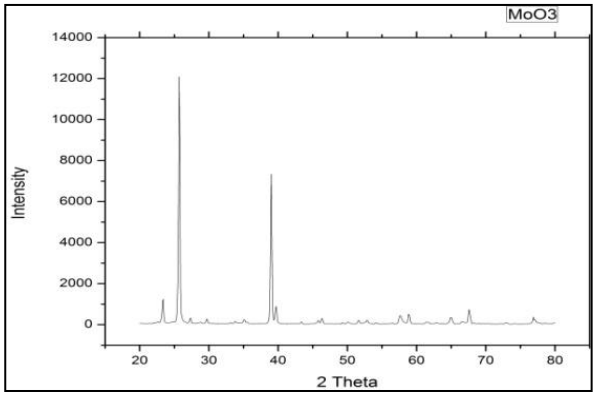
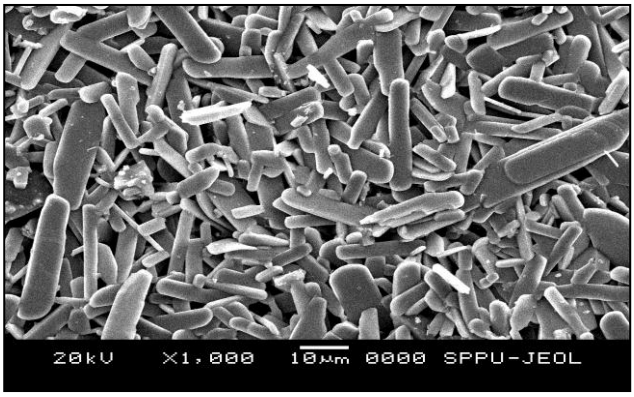


Fig. 2 SEM image of MoO_3 thick films



Gas sensing:

Figure 3 shows variation of sensitivity of MoO_3 thick films for different gases with operating temperatures. The films showed highest sensitivity that of 67.3% to NH_3 vapors at 200^0C than for other gases. **Figure 4** shows histograms indicating the selectivity of MoO_3 thick films for different gases against NH_3. Selectivity or specificity is defined as the ability of a sensor response to a certain (target) gas in the presence of other gases.
Figure 5 shows the variation of sensitivity of MoO_3 thick films with NH_3 concentrations (in ppm) at 200^oC temperature. The response and recovery times of MoO_3 thick films are represented in **Figure 6**. The response was quick (~ 16 sec) to 1000 ppm of NH_3 while the recovery was slow (~ 30 sec).

Figure 3: Variation of sensitivity with tempearture for diff. gases

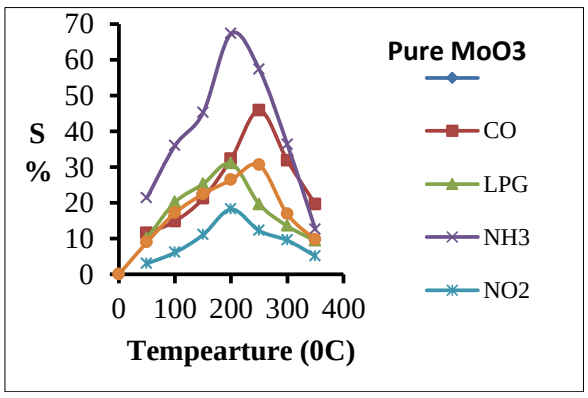


Figure 4: Selectivity of Pure MoO_3 film for different gases

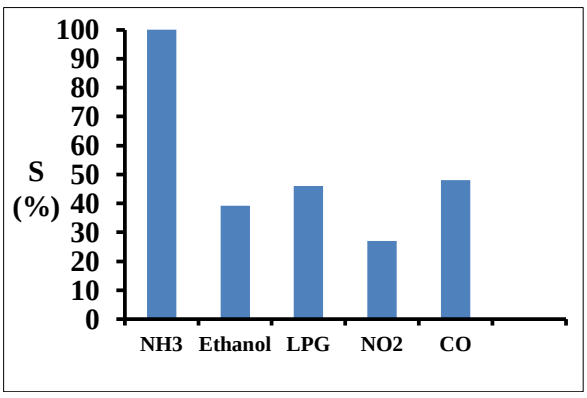


Figure 5: Variation of sensitivity with concentration of NH_3

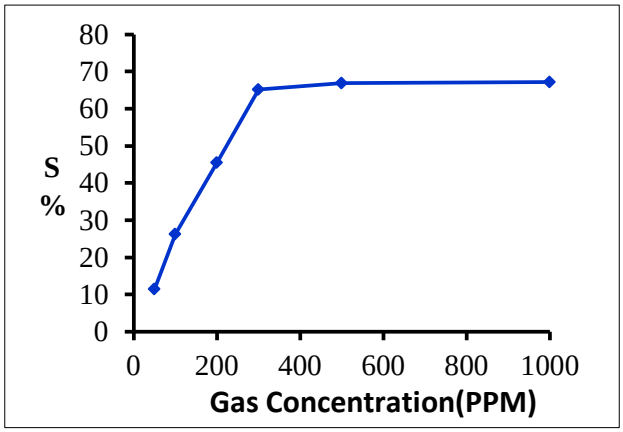
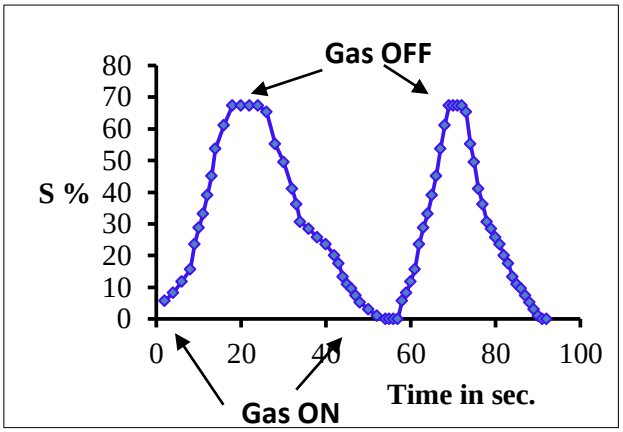


Figure 6: Response and recovery time of MoO_3 film for NH_3



The electrical conductivity of MoO_3 thick film is due to oxygen vacancies. In the absence of reducing gases, oxygen species are chemisorbed on sensor surface resulting in lower free carrier concentration due to which the conductivity reduces. In the presence of small amount of reducing gases, a gas molecule react with adsorbed oxygen species, release electrons in the bulk and therefore increases the film conductance [9].

It is obvious from the **Figure 3** that operating temperature is very crucial in the response of the film. Actually, there exists an optimum operating temperature of a film to get the maximum response to a gas of interest, i.e. the mechanism of dissociation and further chemisorptions of a gas on the particular film surface; the higher response may be attributed to the some misfits to react with the gas. The response could be attributed to the adsorption–desorption type of sensing mechanism. It produces a reversible variation in the resistivity with the exchange of charges between ethanol vapors and the MoO_3 surface leading to changes in the depletion length [10].

The quick response may be due to faster oxidation of gas.

CONCLUSIONS:

From the results obtained, following conclusions can be made for the sensing performance of MoO3 thick films.

(1) It has become possible to fabricate thick film MoO_3 sensors using screen printing technique,
(2) MoO_3 thick films showed highest response to NH_3 at 200^0C.
(3) The sensitivity increases in proportion to the test gas concentration up to 300 ppm and then increase is slow.
(4) The sensor has good selectivity to NH_3 against LPG, Ethanol, CO_2 and NO_2 at 200^0C.
(5) The sensor showed very rapid response and slower recovery to NH_3.

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