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# Ethanol vapour sensing properties of screen printed $WO_3$ thick films

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**Abstract.** **This paper presents ethanol vapour sensing properties of $WO_3$ thick films. In this work, the $WO_3$ thick films were prepared by standard screen-printing method. These films were characterized by X-ray diffraction (XRD) measurements and scanning electron microscopy (SEM). The ethanol vapour sensing properties of these thick films were investigated at different operating temperatures and ethanol vapour concentrations. The $WO_3$ thick films exhibit excellent ethanol vapour sensing properties with a maximum sensitivity of ~1424·6% at 400°C in air atmosphere with fast response and recovery time.**

**Keywords.** **$WO_3$ thick film; screen printing; ethanol vapour.**

## 1. Introduction

Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxide semiconductors have been used extensively for the detection of toxic, pollutant gases, combustible gases and organic vapours. It is reported that tungsten oxide ($WO_3$) films have promising electrical and optical properties, in combination with their wide band gap, abundance in nature, and absence of toxicity. These properties render $WO_3$ as a liable material for a variety of applications. Various techniques have been used to prepare doped or undoped $WO_3$ thin and thick films.

In recent years, $WO_3$ thick films have been considered to be the most promising materials for detecting gases like $NO_2$, $CH_4$, $NH_3$, $H_2S$, CO and $CO_2$ (Tomchenko 2000; Berger *et al* 2004; Ionescu *et al* 2005; Stankova *et al* 2006). The screen printing is a feasible and economical method to prepare thick films of various materials which have been used to develop varistors, sensors and actuators (Prudenziati 1994). The thick film gas sensors based on semiconductor oxides prepared by using screen printing method have certain advantages such as low cost, simple in construction, small size and excellent sensing properties (White and Burner 1997; Ryeol *et al* 2000).

Detection of ethanol vapour is an important feature of the breath alcohol checker devices used to monitor ethanol vapour in human breath or even to detect leaks in industrial distribution lines. It has not been one of the extensively studied gases in the thick film gas sensors. The detection of ethanol vapour based on thin film of $SnO_2$ (Mishra *et al* 2002) and $WO_3$ semiconductor material has been reported (Wang *et al* 2001). In 2006, Jie *et al* reported ethanol and acetone sensing properties of $SnO_2$ thin films deposited by dip coating. Also, the sensing properties of $SnO_2$ thin films deposited by thermal deposition technique for five organic vapours i.e. ethanol, methanol, acetone, isopropanol and acetic acid, have been reported (Gong *et al* 1999).

The aim of the present study is to prepare $WO_3$ thick films by using screen printing method onto alumina substrates and to investigate their sensing properties for ethanol vapour.

## 2. Experimental

The $WO_3$ powder (purity, ~99·99%) was mechanically milled in an acetone medium using Fisher type electric agate pestle and mortar for 24 h. After drying at 200°C for 20 min, the powder (99·5 wt.%) was thoroughly mixed with a permanent binder (lead boro-silicate glass frit with composition, 70 wt% PbO, 18 wt% $Al_2O_3$, 9 wt% $SiO_2$ and 3 wt% $B_2O_3$). The organic vehicles such as butyl carbitol acetate (BCA) and ethyl cellulose were added to this mixture to achieve proper thixotropic properties of the paste. The paste thus formed was screen printed onto an alumina substrate. The films were allowed to stabilize at room temperature for 24 h and then the films were cured at 800°C for 1 h. During this process the glass frit melts and the functional material gets sintered. The thickness of $WO_3$ thick film was found to be ~15 μm.

The structural properties of $WO_3$ thick films were investigated using X-ray diffraction (XRD) technique. The X-ray diffraction patterns were recorded with a Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having $CuK_\alpha$ ($\lambda$ = 0·1542 nm) radiation. The scanning electron microscopy (SEM) was employed to characterize the surface morphology with a Leica Cambridge 440 Micro-

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scope (UK). The thickness of $WO_3$ thick film was measured by a light section microscope (Nikon Optical Microscope, M44).

The gas sensing studies were carried out using a static gas chamber to sense ethanol vapour in air ambient. The $WO_3$ thick films were used as the sensing elements. The sensing element was kept directly on a heater in the gas chamber and the temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensing element. The known volume of the ethanol vapour was introduced into the gas chamber pre-filled with air and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured by a simple two-probe configuration, before and after exposure to ethanol vapour using a sensitive digital multi meter (METRAVI 603). The electrical contact leads were fixed 1cm apart on the surface of the film. The sensitivity ($S$) of the sensing element is defined as

$$S(\%) = \frac{R_a}{R_g} \times 100,$$

where $R_a$ and $R_g$ denote the values of resistance of the sensor element before and after exposure to ethanol vapour.

## 3. Results and discussion

The XRD pattern of $WO_3$ thick film is shown in figure 1. It indicates the diffraction peaks at $2\theta$ values of 23·6°, 24·2°, 27·2°, 28·2°, 33·8°, 42·2°, 48·8°, 50·8°, 54·0°, 54·6°, 55·2°, 56·4°, 61·6° and 62·6°, which reveals the formation of the triclinic phase of $WO_3$ (JCPDS Data card 83-0948).

The surface morphology of the screen printed $WO_3$ thick film deposited onto the alumina substrate is as shown in figure 2(a). It clearly shows that the surface of $WO_3$ films is porous and forms channels with bundles of grains. Therefore, the screen printed $WO_3$ film can adsorb more atmospheric oxygen due to more exposed surface area of the film. The grains observed on the surface have laminate structure (Ivanov *et al* 2004). The channel formation on thick film occurs due to the softening of the glass frit as a permanent binder. The EDX analysis (figure 2(b)) indicates that the matrix contains only W and O with atomic % of 57·87% and 42·13%, respectively. This suggests that the screen printed $WO_3$ thick film is non-stoichiometric.

The dependence of sensitivity of $WO_3$ thick film towards 50 ppm ethanol vapour on the operating temperature is shown in figure 3. It is observed that the sensitivity of $WO_3$ thick film to 50 ppm ethanol vapour slowly increases as the operating temperature is raised from 250–350°C. Beyond 350°C, the sensitivity suddenly increases and it is found to be ~1424·6% at 400°C. With further increase in the operating temperature, the sensitivity significantly decreases and it is observed to be ~221·56% at 450°C. Therefore, the sensitivity to 50 ppm ethanol vapour is maximum at 400°C and it is found to be ~1424·6%. The response time of $WO_3$ thick film to ethanol vapour was nearly 10 s and the recovery time was found to be nearly 45 s.

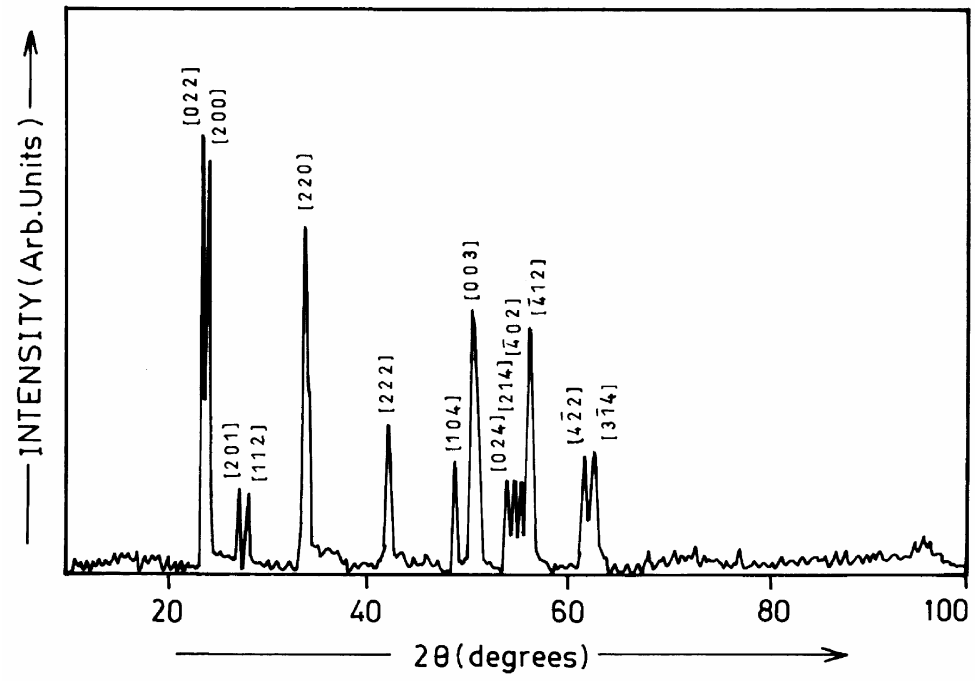


**Figure 1.** The X-ray diffraction pattern of $WO_3$ thick film.

The ethanol vapour sensing mechanism is a complex process. It is based on the changes in resistance of $WO_3$ thick film, which is controlled by ethanol vapour species and the amount of the chemisorbed oxygen on the surface. As mentioned earlier, the screen printed $WO_3$ thick film is porous and non-stoichiometric in nature. Therefore, the oxygen chemisorption centres viz. oxygen vacancies, localized donor and acceptor states and other defects, are formed on the surface during synthesis. These centres are filled by adsorbing oxygen from air. The $WO_3$ film interacts with oxygen by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as $O_2^-$ or $O^-$. The reaction kinematics may be explained by the following reactions (Dyshel 2001; Mishra *et al* 2002; Arshak and Gaidan 2005; Mbarek *et al* 2006):

$$O_2 \text{ (gas)} \Leftrightarrow O_2 \text{ (absorbed)},$$

$$O_2 \text{ (absorbed)} + e^- \Leftrightarrow O_2^-,$$

$$O_2^- + e^- \Leftrightarrow 2O^-.$$

The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease in the electron concentration in the film. As a consequence, an increase in the resistance of $WO_3$ film is observed.

In ethanol vapour molecules the reducing hydrogen species are bound to carbon, therefore, the ethanol vapour dissociates less easily into the reactive reducing components on the $WO_3$ film surface. When the screen printed $WO_3$ thick film is exposed to reducing gas like ethanol vapour, the ethanol vapour reacts with the chemisorbed oxygen thereby releasing an electron back to the conduction band which decreases the resistance of $WO_3$ film. The overall reaction of ethanol vapour with the chemisorbed oxygen may take place by two different ways as shown below:

$$C_2H_5OH \text{ (gas)} + O^- \Leftrightarrow CH_3CHO + H_2O + e^-$$

$$C_2H_5OH \text{ (gas)} \Leftrightarrow H + C_2H_5O \text{ (surface)}$$

$$C_2H_5O \rightarrow H + CH_3CHO$$

$$CH_3CHO + O \text{ (bulk)} \rightarrow CH_3COOH + O \text{ (vacancies)}$$

When the screen printed $WO_3$ thick film is heated at a temperature of 250–350°C, the reaction products do not desorb from the film surface. Nevertheless, they cover the sensing sites on the surface of the film which prevents further reaction of ethanol vapour with chemisorbed oxygen. Subsequently, no appreciable change in resistance of the film is observed.

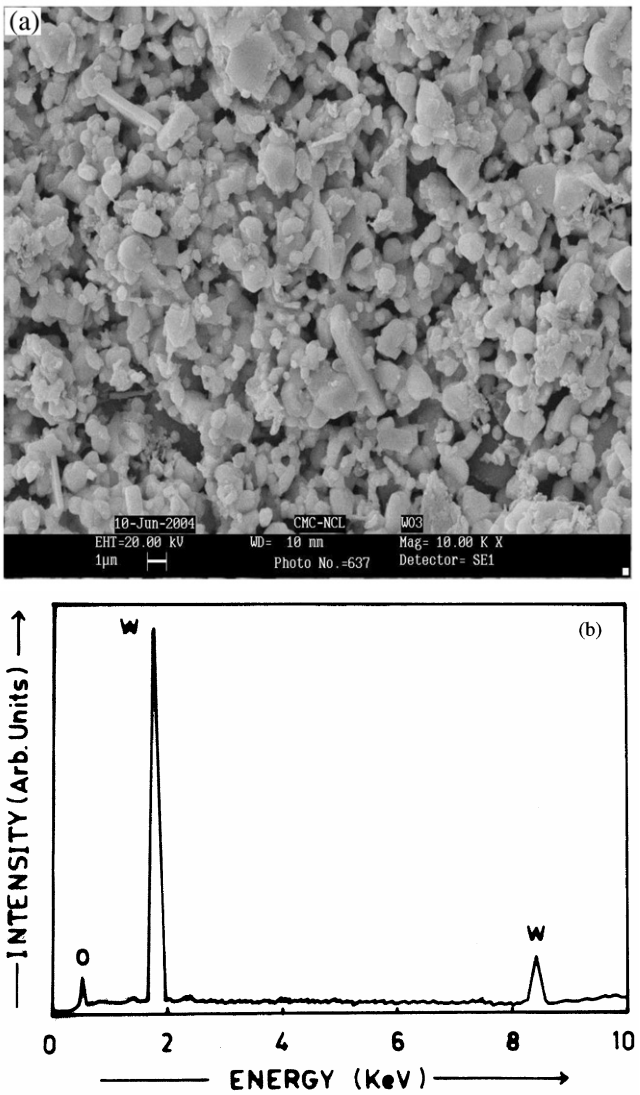


**Figure 2.** (**a**) SEM image of the screen printed $WO_3$ thick film on the alumina substrate and (**b**) EDX spectrum of $WO_3$ thick film on the alumina substrate.

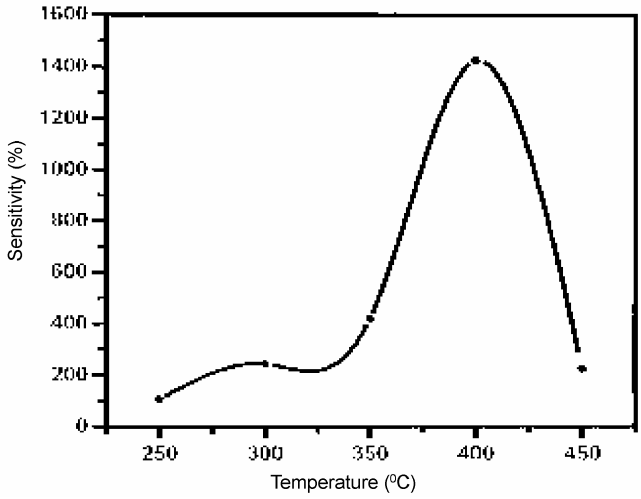


**Figure 3.** Relationship between operating temperature and sensitivity of screen printed $WO_3$ thick film for 50 ppm ethanol vapour in air.

At high operating temperature such as 400°C, the reaction products may get desorbed immediately after their formation providing the opportunity for new gas species to react with the sensing sites on the film surface. Wang *et al* (2001) reported possible process of reactions of ethanol vapour with $WO_3$ sensor at high temperatures (250–400°C). Ethanol is adsorbed and reacts with W ion to produce $O–CH_2–CH_3$ and adsorbed $OH^-$ group form ethylene through dehydration. This reaction releases electrons to the $WO_3$ film. The reaction rate increases with temperature (Wang *et al* 2001). Also the ethylene molecules may react with adsorbed oxygen at such high operating temperature to produce ethylene oxide releasing additional free electron to the $WO_3$ film. Thus, the ethanol vapour reacts most effectively with $WO_3$ film surface at such a particular temperature, which results in the significant decrease in the resistance of the film. Therefore, the maximum sensitivity of the $WO_3$ thick film towards ethanol vapour is expected at such a particular temperature.

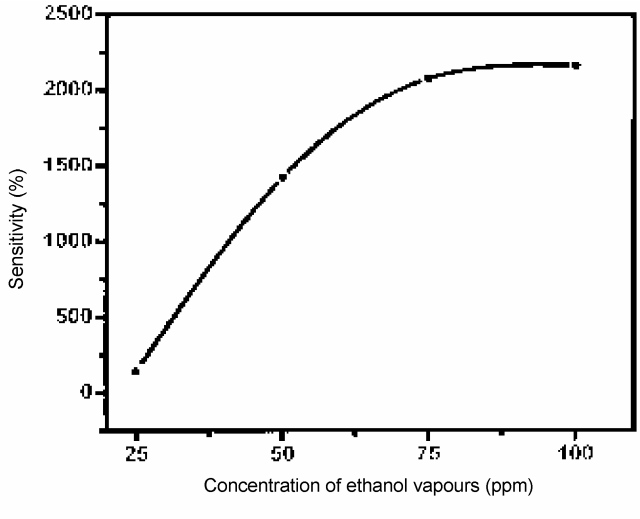


**Figure 4.** Dependence of sensitivity on ethanol vapour concentration of the screen printed $WO_3$ thick film.

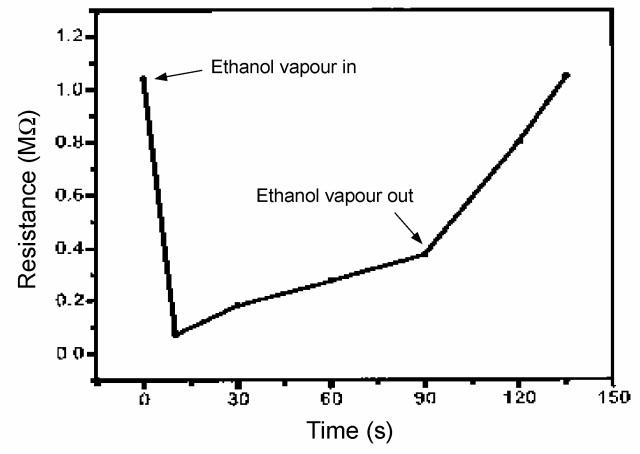


**Figure 5.** Response of screen printed $WO_3$ thick film operated at 400°C to 50 ppm ethanol vapour in air.

At higher temperatures (> 400°C), the amount of adsorbed oxygen ion species are insufficient to react with ethanol vapour molecules. Therefore, the probability of the reduction reaction of ethanol vapour with chemisorbed oxygen is less, which results in a very small change in resistance of the film at higher temperatures. Therefore, the screen printed $WO_3$ thick film operates as a sensing element to the ethanol vapour only within a specific temperature window. In the present case, the optimum operating temperature for $WO_3$ thick films is 400°C at which the sensor sensitivity attains its maximum value.

The relationship between the sensitivity of $WO_3$ thick film and ethanol vapour concentration for an operating temperature of 400°C is shown in figure 4. It is observed that the sensitivity increases linearly up to 75 ppm of ethanol vapour concentration and after that it saturates. The linear relationship between sensitivity and ethanol vapour concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the ethanol vapour. The low gas concentration implies a lower surface coverage of gas molecules, resulting in a lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in gas concentration increases the surface reaction due to a large surface coverage. Further increase in the surface reaction will be gradual when saturation of the surface coverage of gas molecules is reached. Thus, maximum sensitivity was obtained at an operating temperature of 400°C after exposure to 75 ppm of ethanol vapour. It is obvious from figure 4 that not only temperature but also ethanol vapour concentration plays a role in determining the sensitivity of $WO_3$ thick film. The $WO_3$ thick film is able to detect up to 25 ppm ethanol vapour with reasonable sensitivity at an operating temperature of 400°C. The linearity of sensitivity in the low ethanol vapour concentration range (25–75 ppm) suggests that the screen printed $WO_3$ thick films can be reliably used to monitor the concentration of ethanol vapour over this range.

Figure 5 shows response of the screen printed $WO_3$ thick film operated at 400°C for the exposure and removal of 50 ppm ethanol vapour. It indicates that $WO_3$ thick film operating at 400°C temperature shows a response within ~10 s after exposure to 50 ppm ethanol vapour and recovers back within ~45 s after removal of the vapour.

## 4. Conclusions

In this work, $WO_3$ thick films were prepared by using screen printing method. These thick films were characterized by using XRD and SEM coupled with EDX. The ethanol vapour sensing properties were investigated at different operating temperatures and gas concentrations.

The $WO_3$ thick films exhibit excellent ethanol vapour sensing properties with maximum sensitivity, ~1424·6% at 400°C, with fast response and recovery time. Further, it was shown that the screen printed $WO_3$ thick films can be reliably used to monitor the concentration of vapour over the range 25–75 ppm. The response and recovery characteristics of $WO_3$ thick films are almost reproducible and quick. Thus, this study demonstrates the possibility of utilizing $WO_3$ thick films as a sensor element for the detection of ethanol vapour.

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